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Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
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SUMMARY

The purpose of this exploratory study, conducted by Pacific Northwest Laboratory for Westinghouse Hanford Company, was to determine the effect of applying advanced chemical separations technologies to the processing and disposal of high-level wastes (HLW) stored in underground tanks. The major goals of this study were to determine 1) if the wastes can be partitioned into a small volume of HLW plus a large volume of low-level waste (LLW), and 2) if the activity in the LLW can be lowered enough to meet NRC Class A LLW criteria.

This report presents the results obtained in a brief scouting study of various processes for separating radionuclides from Hanford complexant concentrate (CC) waste. This type of waste was chosen for study because of its complexity and the demands that it would impose on chemical separations technology. Also, CC waste is the most voluminous of the Hanford double-shell tank wastes currently considered to require pretreatment. Implementation of advanced separation processes would allow the bulk of the waste to be disposed of as Class A LLW, an option much less costly than geologic disposal of HLW.

This report presents the following conclusions:

- Complete dissolution of CC waste solids (in nitric acid-based solutions) will probably be achievable.
- Methods to separate Cs and Pu from alkaline CC waste supernate are available (these involve sorption processes).
- The separation of Tc from either alkaline or acidic solution can be achieved by extraction with tetraalkylammonium compounds.
- Technologies for the removal of Sr and Am from alkaline CC waste supernate require development.
- Technologies for the removal of Cs from acidic solution require development.
- All advanced separation methods, even those identified as promising, require further research to develop practical processes that will meet Class A LLW criteria and result in a minimum quantity of HLW.

- To minimize waste volumes, the best approach to the pretreatment of CC waste involves separation of the sludge and supernate, dissolution of the sludge, and separate processing of the dissolved sludge solution and the alkaline supernate. However, unless suitable methods are developed to separate ^{241}Am and ^{90}Sr from alkaline CC supernate, direct acidification of the entire CC waste followed by TRUEX and SREX processing will be necessary to separate these radionuclides.

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ACRONYMS

ANL	Argonne National Laboratory
CC	complexant concentrate
CMPO	carbamoylmethylphosphine oxide
DF	decontamination factor
DST	double-shell tank
EDTA	ethylenediaminetetraacetate
HDDNS	didodecylnaphthalenesulfonic acid
HDNNS	dinonylnaphthalenesulfonic acid
HEDTA	hydroxyethylenediaminetriacetate
HLW	high-level waste
LLW	low-level waste
MONC	4-(1-methyl-1-octylnonyl) catechol
NCA	neocarboxylic acid
NPH	normal paraffin hydrocarbon
NRC	U.S. Nuclear Regulatory Commission
NTA	nitrilotriacetate
PNL	Pacific Northwest Laboratory
SREX	strontium extraction process
TBAH	tetra-n-butylammonium hydroxide
TBAN	tetra-n-butylammonium nitrate
TBP	tributylphosphate
TC	total carbon
TCMA	tricaprylmonomethyl ammonium nitrate
TOAB	tetra-n-octylammonium bromide
TOC	total organic carbon
TRU	transuranic waste
TRUEX	transuranic extraction process
WHC	Westinghouse Hanford Company

CONTENTS

FIGURES

TABLES

1.0 INTRODUCTION

For over 40 years, one of the primary missions of the Hanford Site was to produce ^{239}Pu. During the course of this effort, various high-level wastes (HLW) and transuranic wastes (TRU) were generated and stored in underground carbon-steel tanks. Today cleanup and closure of these tanks is a major mission of the Hanford Site. The current baseline for this activity includes retrieval of wastes from the tanks and, for selected waste types, partitioning into a relatively large volume of low-level waste (LLW) and a small volume of HLW. The LLW will be cast in grout and disposed of onsite in near-surface vaults, while the HLW will be vitrified and disposed of in a geologic repository. Because of the high costs of vitrification and geologic disposal (compared to disposal as grout), it is desirable to minimize the amount of HLW; chemical separations will play a key role in this minimization.

The purpose of this exploratory study, conducted by Pacific Northwest Laboratory (PNL)(a) for Westinghouse Hanford Company (WHC), is to determine the effects of applying advanced chemical separations technologies to the processing and disposal of HLW. While no criteria have yet been established for the LLW portion of the treated waste, for this study it was assumed that U.S. Nuclear Regulatory Commission (NRC) Class A LLW criteria would have to be met (Table 1.1).

TABLE 1.1. NRC Class A LLW Criteria

Nuclide	Maximum Concentration
^{137}Cs	1 Ci/m^3
^{90}Sr	0.04 Ci/m^3
^{99}Tc	0.3 Ci/m^3
TRU	10 nCi/g

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Of the tank wastes stored in double-shell tanks (DST) at Hanford, the waste type known as "complexant concentrate" (CC) presents the greatest challenge in terms of separation chemistry. This waste contains complexants such as ethylenediaminetetraacetate (EDTA), hydroxyethylenediaminetriacetate (HEDTA), nitrilotriacetate (NTA), and citrate; also present are degradation products of these complexants. Because of the complexants, certain ions including Fe^{3+}, Sr^{2+}, and TRUs are in solution that would have otherwise precipitated under the alkaline conditions present in this waste. The effects of these complexants on separation processes are not fully known. Because most radionuclide separation processes are driven by complexation phenomena, it is expected that the presence of complexants hinders rather than enhances separations. For this reason, CC waste was chosen as the subject of this exploratory processing study. Many of the chemical separation processes that are successfully used for CC waste will likely be applicable to other Hanford tank wastes.

Figure 1.1 summarizes possible scenarios for the pretreatment of CC waste. Three routes are considered. The first step in Option I is the destruction of the complexants under alkaline conditions, which would result in the precipitation of the TRUs and ^{90}Sr. After removal of ^{99}Tc and ^{137}Cs, the supernatant solution might qualify as Class A LLW. The precipitated solids and the solids originally present are dissolved and the various radionuclides (TRUs, ^{90}Sr, ^{137}Cs, and ^{99}Tc) are separated. Toxic metals such as chromium might also be removed from the LLW stream before nitrate separation/destruction. Option II involves the separation of the CC supernate from the solids. The alkaline supernate is treated to remove TRUs, ^{90}Sr, ^{137}Cs, and ^{99}Tc. The complexants are then destroyed and nitrate ion removed or destroyed. The solids are dissolved and treated much the same as those in Option I. Option III involves direct acidification of the CC supernate/solids mixture to dissolve the solids. TRUs, ^{90}Sr, ^{137}Cs, ^{99}Tc, and possibly toxic metals are removed, then the complexants are destroyed and nitrate is removed or destroyed.

Possible technologies for each required separation appear in Figure 1.1. This information is not exhaustive, but serves as a guideline to identify

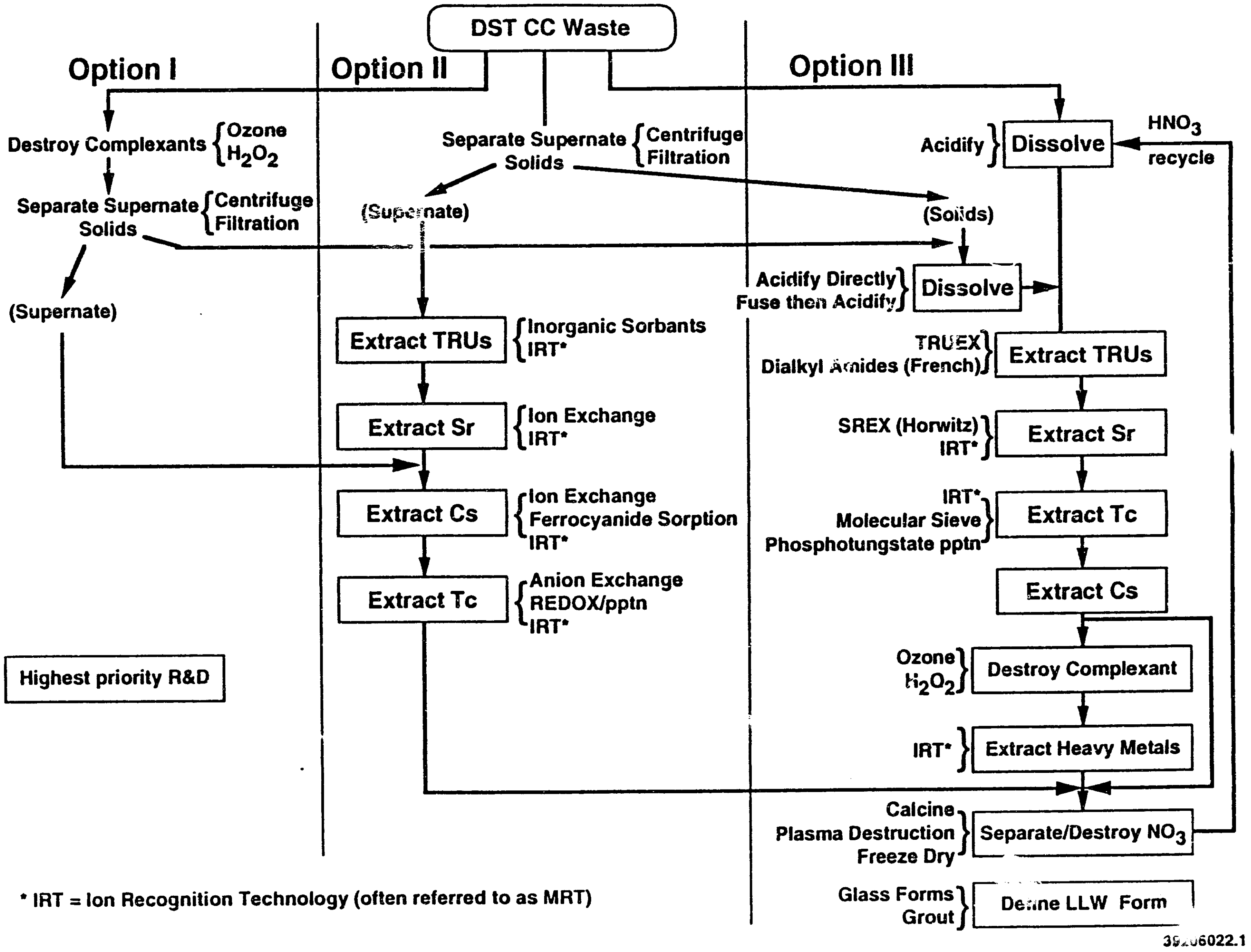

FIGURE 1.1. Options for the Pretreatment of CC Waste

those areas where established separation methods are not available. These areas are identified by bold boxes in Figure 1.1. This work has focused on five separation problems: separation of 1) Cs from acid solution, 2) Tc from acid solution, 3) TRUs from alkaline solution, 4) Sr from alkaline solution, and 5) Tc from alkaline solution. In addition to these separation problems, the problem of dissolution of CC waste solids was also addressed in this study.

2.0 METHODS AND MATERIALS

The following is a brief description of materials and sources: dicyclohexano-18-crown-6 (DC18C6), 4-t-butylcatechol, 3,5-di-t-butylcatechol, and 1-octanol were obtained from Aldrich Chemical Co. (Milwaukee, Wisconsin). Dinonylnaphthalenesulfonic acid (HDNNS), tetra-n-butylammonium hydroxide (TBAH) (55% aqueous solution), and tetra-n-octylammonium bromide (TOAB) were purchased from Alfa Products (Ward Hill, Massachusetts). The TBAH was converted to tetra-n-butylammonium nitrate (TBAN) by neutralization with NHO_3. Di-t-butylbenzo-21-crown-7 was donated by Prof. Richard Bartsch of Texas Tech University. Neocarboxylic acid (NCA) was obtained from ETRAC, Inc. (Knoxville, Tennessee). A proprietary experimental Cs-selective chromatographic material consisting of a macrocycle bound to silica gel was provided by IBC Technologies, Inc. (Provo, Utah). This material will hereafter be referred to as "Si-L." The TRUEX[a] process solvent [0.2 M octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) + 1.4 M tributylphosphate (TBP) in normal paraffin hydrocarbon (NPH)] was obtained from WHC. The TRUEX solvent was washed successively with sodium carbonate solution and water before use. Resorcinol-formaldehyde organic ion exchange resin (BSC-187) was obtained from Boulder Scientific Co. (Boulder, Colorado). Phenol-formaldehyde cation-exchange resin (Na-form) (ARC-359) and the granular phenol-formaldehyde condensation polymer (H-form) (CS-100) were purchased from Diamond Shamrock Co. (Cleveland, Ohio). Sodium aluminosilicate zeolite (chabazite structure) with (TIE-96) and without (IE-96) 5 wt% TiO_2 were supplied by UOP (Tarrytown, New York). Tricaprylmonomethylammonium chloride was obtained from General Mills Chemical Division.

4-(1-Methyl-1-octylnonyl)catechol (MONC) was syntheiszed from n-octanol, methyl acetate, and catechol. The three step synthesis involved: 1) conversion of n-octanol to n-bromooctane by reaction with sulfuric acid and sodium bromide; 2) reaction of n-bromooctane with Mg to give the $Mg[(CH_2)_7CH_3]_2$, which was then reacted with methyl acetate to give 9-methyl-9-heptadecanol; and 3) alkylation of catechol with 9-methyl-9-heptadecanol. The last step was

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[a] Transuranic extraction process.

performed by heating at reflux a mixture of 9-methyl-9-heptadecanol (10 g), catechol (4.5 g), and toluenesulfonic acid (1.4 g) in 100 mL benzene. The reaction flask was equipped with a Dean Stark trap to remove water from the reaction mixture; removal of water was necessary to drive the reaction to completion. The MONC was purified by liquid chromatography using pentane and methylene chloride as eluents.

2.1 CC SOLIDS DISSOLUTION

The sample of actual CC waste used in this project was received by PNL in July 1983; the sample was taken from Tank 102-AZ. The sample had a total volume of ~32 mL with ~9 mL of this volume occupied by settled solids. The volume of solids had not increased since the sample was last examined 7 years previously.

The CC waste sample was homogenized by stirring, the slurry (5 mL) was transferred to a separate vial for dissolution experiments, and 5 mL of water was added to the slurry. The mixture was stirred for 1.5 h and allowed to stand overnight. Next the solids were filtered, washed with three 5-mL portions of water and then transferred to a vial for dissolution. The filtrate was used for batch tests of various solid sorbents. The solids were slurried with 15 mL of water, and 0.1 mL concentrated HNO_3 was added to give $[HNO_3] = 0.1\ \underline{M}$. After this solution was stirred for 2 h at ambient temperature, it was sampled for analysis. The HNO_3 concentration was adjusted to 1.8 $\underline{M}$ by addition of 1.8 mL concentrated HNO_3. The solution was stirred for 2 h at ambient temperature, then for 2 h at 100°C. This treatment resulted in dissolution of all solids.

2.2 PREPARATION OF SYNTHETIC CC WASTE

The synthetic CC waste was prepared according to a procedure described in Lokken et al. (1991). The various components were added in the sequence as numbered in Table 2.1. The procedure was carried out at ambient temperature. After the first addition of sodium carbonate, the pH was adjusted to 7.7 with sodium hydroxide, then sodium carbonate was added a second time. The mixture

TABLE 2.1. Composition of the Synthetic CC Waste Supernate

	Component	Amount Added	Target Concentration, M	Concentration Found, M
1	water	600 mL		
2	HNO_3, concentrated	330 mL		
3	$Al(NO_3)_3 \cdot 9H_2O$	15.56 g	0.024	0.022
4	$Fe(NO_3)_3 \cdot 9H_2O$	30.70 g	0.038	0.00003
5	$Ca(NO_3)_2 \cdot 4H_2O$	11.80 g	0.025	0.024
6	KNO_3	9.30 g	0.046	0.042
7	$La(NO_3)_3 \cdot 6H_2O$	0.24 g	0.00028	0.0002
8	$Nd(NO_3)_3 \cdot 5H_2O$	0.80 g	0.00095	0.0004
9	$Mg(NO_3)_2 \cdot 6H_2O$	5.64 g	0.011	
10	$Mn(NO_3)_2$, 50% solution	5.16 g	0.0072	
11	$Ni(NO_3)_2 \cdot 6H_2O$	4.66 g	0.0080	0.007
12	Na_2HPO_4	6.24 g	0.022	0.020
13	NaCl	4.80 g	0.041	
14	$Na_2B_4O_7 \cdot 10H_2O$	16.02 g	0.021	0.022
15	$Cu(NO_3)_2 \cdot 3H_2O$	0.20 g	0.00041	0.0004
16	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	1.58 g	0.00064	0.00063
17	0.1 M $CsNO_3$	15 mL	0.00075	0.00087
18	0.1 M $Sr(NO_3)_2$	15 mL	0.00075	0.0006
19	Na_4EDTA	23.6 g	0.034	
20	citric acid, monohydrate	26.90 g	0.064	
21	$Na_3HEDTA \cdot 2H_2O$	28.72 g	0.042	
22	Na_3NTA	37.6 g	0.13	
23	Na_2CO_3	216 g		
24	50% NaOH	160 mL		
25	Na_2CO_3	258 g	1.2	
26	50% NaOH	32 mL		
27	$NaNO_2$	110.4 g	0.80	
28	50% NaOH	20 mL		

was diluted to 2 L with water, and the final pH was adjusted to 12.5 by adding sodium hydroxide. The resulting mixture consisted of a pale blue solution and a rust colored precipitate.

2.3 ACIDIFICATION OF CC WASTE

To assess the various acid-side separation processes, samples of both the synthetic CC waste and the actual CC waste were acidified with HNO_3. The CC waste (solids and supernate) was homogenized by stirring and concentrated HNO_3 was added carefully until the pH 1 was reached. It was assumed that all of the hydrolyzable ions had been protonated at pH 1. Concentrated HNO_3 was then added to give $[HNO_3] = 1$ M. The total acid concentration was determined by titration with standard NaOH. The total acid concentration (titrated to pH 7) was 1.1 M for the acidified synthetic waste and 1.4 M for the acidified actual CC waste. The reason that the measured total acid concentrations of these solutions were above 1.0 M was likely because hydrolyzable ions were present. The compositions of both the acidified synthetic CC waste and the actual CC waste are compared in Table 2.2. Good agreement was found between many of the waste constituents, especially Al, Fe, La, Nd, and Ni. The amount of Na in the acidified synthetic waste was somewhat higher than in the actual waste; this was also true for Cs and Sr.

2.4 SOLVENT EXTRACTION EXPERIMENTS

Solvent extraction experiments were performed by mixing an appropriate aqueous solution with the extractant solution of interest. The contacts were accomplished in small vials using a vortex mixer to mix the two phases; contact times were generally one or two minutes in duration. After centrifuging to separate the phases, each phase was sampled for analysis. For tracer experiments, concentrations of ^{241}Am, ^{85}Sr, and ^{137}Cs were determined by gamma counting; concentrations of ^{99}Tc were determined by liquid scintillation counting. For the extraction of Sr with 0.05 M DC18C6 + 0.1 M NCA in toluene, the solvent was first contacted twice with 6 mL of 0.33 M NaOH + 3.33 M $NaNO_3$. This procedure converted the neocarboxylic acid into its corresponding sodium salt. For the extraction of Tc (alkaline or acidic) with TOAB or TBAN, the

TABLE 2.2. Composition of Acidified Actual and Synthetic CC Waste

Component	Actual Waste, M	Synthetic Waste, M
Al	0.017	0.021
Cd	0.00023	
Ce	0.00080	
Cr	0.0012	
Cs	0.000043	0.00060[a]
Cu	0.00006	0.00032
Fe	0.030	0.027
K	0.0063	0.042
La	0.00013	0.0002
Mg	0.00087	
Mn	0.0062	
Mo	0.00003	0.0035
Na	2.92	4.77
Nd	0.00043	0.00065
Ni	0.0037	0.0056
P	0.0060	0.015
Pb	0.00091	
Sr	not detected	0.00053
Zn	0.00020	0.00002
Zr	0.00043	

(a) Estimated from the concentration of Cs found in the synthetic CC waste supernate.

solvents were prepared by dissolving the tetraalkylammonium compound in an appropriate diluent. Most solutions were used directly; however, in the case of tricaprylmonomethyl ammonium chloride, the extractant was dissolved in 1-octanol and was then contacted repeatedly with 1 M HNO_3 to convert from the chloride to the nitrate form. A portion of the last 1 M HNO_3 contact was tested for chloride ion by addition of silver nitrate; no chloride ion was found, which indicated complete conversion to the nitrate form. Hereafter, the nitrate form of the tricaprylmonomethly ammonium extractant will be referred to as "TCMA."

Distribution coefficients (D) were calculated as the concentration of a given component in the organic phase divided by the concentration of that component in the aqueous phase.

2.5 BATCH DISTRIBUTION EXPERIMENTS

A weighed amount of the sorbent to be tested was contacted by shaking with the test solution. In most cases, the contact period was ~72 h. As a control, a sample of the test solution was placed in a similar bottle (without the sorbent) and agitated in the same way. This feed blank represented the feed solution before contact with the solid exchanger. For tracer experiments, the synthetic CC waste supernate was diluted with two volumes of water and spiked with the appropriate radionuclide (^{137}Cs, ^{85}Sr, ^{239}Pu, ^{99}Tc, or ^{241}Am). For experiments with the actual CC waste, the supernatant solution was diluted with an equal volume of water before contact with the sorbent of interest. The samples and feed solution were filtered (0.2-μm-pore filter), and the concentration of the radionuclide of interest was determined by gamma counting (^{137}Cs and ^{85}Sr) or liquid scintillation counting (^{239}Pu, ^{99}Tc, and ^{241}Am). Batch distribution ratios, R_d, were calculated as the concentration of the radionuclide of interest in the solid sorbent (quantity/g of sorbent) divided by the concentration in solution (quantity/mL of solution).

2.6 EVALUATION OF Si-L FOR REMOVAL OF Cs

A chromatographic material (Si-L) consisting of a macrocycle bound to a silica gel support was tested for removal of Cs from acid solution. Two grams of Si-L(a) was wet-packed into a column 10.5-mm ID; the bed volume was 4 mL. The column was washed with 20 mL of 5 $\underline{M}$ HNO_3, then with 5 mL of 1.0 $\underline{M}$ HNO_3. The feed solution was 1.0 $\underline{M}$ HNO_3 spiked with ^{137}Cs (~0.1 μCi/mL). This

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(a) This particular sample of Si-L had been previously used in experiments at PNL by Camaioni et al. (1991). In that experiment, the Cs was eluted from the Si-L with 0.01 $\underline{M}$ HNO_3.

solution was passed through the column. One-milliliter fractions of the effluent were taken, and the ^{137}Cs activity in each was determined by gamma counting using a sodium iodide detector.

2.7 MACRORETICULAR SUPPORT IMPREGNATED WITH SODIUM NICKEL FERROCYANIDE (FeCN-XAD-4) FOR THE REMOVAL OF Cs

Twenty-five milliliters of 0.5 $\underline{M}$ $Na_4Fe(CN)_6$ (12.5 mmole) was added to a slurry of Amberlite® XAD-4 beads (10 g) in 25 mL of water. After the mixture was stirred for 15 min, 12.5 mL of 1.0 $\underline{M}$ $Ni(NO_3)_2$ (12.5 mmole) was added, and the mixture was stirred for another 15 min. The beads were filtered, washed with three 10-mL portions of 1.0 $\underline{M}$ HNO_3 and then with three 10-mL portions of water, and dried *in vacuo*. This sorbent material will be referred to as FeCN-XAD-4.

Batch distribution measurements were taken for FeCN-XAD-4. First, 0.1 g of FeCN-XAD-4 was shaken with 4 mL of the appropriate test solution, which had been spiked with ^{137}Cs. Then after 2 h, a sample of the solution was withdrawn for gamma counting. Two experiments were then performed to assess the efficiency of FeCN-XAD-4 in removing ^{137}Cs from acidic solution. The feed solution in one experiment was 1.0 $\underline{M}$ HNO_3, while the feed solution in the other was acidified synthetic CC waste (1.1 $\underline{M}$ H^+); both solutions were spiked with ^{137}Cs. The procedure was the same for both experiments. FeCN-XAD-4 was wet-packed into a column 10.5-mm ID; the bed volume was 4 to 7 mL. The appropriate feed solution was passed through the column, and 1-mL fractions were collected for gamma counting.

2.8 PRECIPITATION OF Cs WITH SODIUM PHOSPHOTUNGSTATE

An amount of 22 μL of 0.1 $\underline{M}$ $Na_3PW_{12}O_{40}$ was added to 8 mL of acidified (1.1 $\underline{M}$ H^+) synthetic CC waste spiked with tracer ^{137}Cs. After the mixture was stirred for ~16 h, the amount of Cs remaining in solution was determined by gamma counting. An additional 20 μL of 0.1 $\underline{M}$ $Na_3PW_{12}O_{40}$ was added. This solution was then stirred for an additional 16 h. The Cs remaining in solution was again determined by gamma counting.

Eight milliliters of acidified (1.4 M H^+) actual CC waste was treated with $Na_3PW_{12}O_{40}$ in the following successive steps: 1) 20 μL 0.1 M $Na_3PW_{12}O_{40}$, contact time 16 h; 2) 20 μL 0.1 M $Na_3PW_{12}O_{40}$, contact time 2 h; 3) 200 μL 0.1 M $Na_3PW_{12}O_{40}$, contact time 24 h; 4) 200 μL 0.1 M $Na_3PW_{12}O_{40}$, contact time 1 h. The concentration of ^{137}Cs remaining in solution after each step was determined by gamma energy analysis.

3.0 RESULTS AND DISCUSSION

3.1 CHARACTERIZATION OF CC WASTE SAMPLES

The supernatant solutions from the synthetic CC waste and the actual CC waste samples were analyzed for metal cations, total organic carbon (TOC), and total carbon (TC). The compositions of synthetic and actual CC supernates are compared in Table 3.1. This table presents the difficulties encountered in CC waste simulation. Iron is a major component of the actual CC waste supernate, but when the synthetic CC waste was prepared, most of the Fe precipitated, as evidenced by the rust-colored precipitate formed and the low Fe concentration in the supernate (2×10^{-5} M). The TOC content of the synthetic waste was much less than in the actual CC waste solution. This may account for the precipitation of most of the Fe. The concentrations of other components in the synthetic CC waste deviated considerably from those found in the actual waste; however, the recipe used to prepare the synthetic CC waste was based on the analysis of a different CC waste sample (from Tank 107-AN) (Lokken et al. 1991). Certain components (e.g., Cr, Cd, and Pb) were omitted from the synthetic CC waste to allow easier disposal of the material upon completion of the project.

The current composition data for the actual waste were generally similar to the 1983 data from the same sample, especially for components present at ≥0.01 M. Exceptions were Al and Mn because only 67% and 47%, respectively, were found in the current data compared to the 1983 data.

The radionuclide content of the actual CC waste supernate is summarized in Table 3.2. The TRU content of 1000 nCi/g (solution density is 1.36 g/mL) is 10 times the NRC Class C LLW criterion and 100 times the Class A LLW limit. The ^{137}Cs content is 260 times the Class A LLW limit of 1 µCi/mL. The contents reported here for ^{241}Am, ^{60}Co, ^{137}Cs, and ^{154,155}Eu agree closely (when corrected for decay) with those measured in this sample in 1983. However, the current Pu value is ~60% higher than that reported earlier; it is not known whether this difference indicates some changing chemistry within the sample.

TABLE 3.1. Composition of Actual and Synthetic CC Waste Supernates

Component	Actual Waste, mol/L This Work	Actual Waste, mol/L 1983 Data	Synthetic Waste, mol/L
Al	0.012	0.018	0.022
As	0.00023		
B	0.0011		0.089
Ba	0.00012	0.00009	
Ca	0.015	0.016	0.024
Cd	0.00034		
Ce	0.00067		
Cr	0.0030	0.0028	
Cu	0.00056		0.00039
Fe	0.077	0.069	0.00002
K	0.020	0.017	0.042
La	0.00040	0.00031	0.00017
Mg	0.0010	0.0014	
Mn	0.017	0.036	
Mo	0.00014	0.00011	0.0044
Na	7.6	7.6	6
Nd	0.0013	0.00056	0.0004
Ni	0.010	0.010	0.0071
P	0.015		0.020
Pb	0.0026		
Re	0.0029		
Ru	0.00031		
Si	0.00082		
Sr	0.00006	0.00006	0.00060
Th	0.00024		
U	0.0010		
Zn	0.00072	0.0017	0.00002
Zr	0.0014	0.0011	
TC	6.2		2.03
TOC	5.2		1.07
TIC	1		0.96

TABLE 3.2. Radionuclide Content of CC Waste Supernate

	nCi/mL	
Radionuclide	This Work	1983
Total alpha	1360	not reported
$^{239,240}Pu$	160	103
^{238}Pu + ^{241}Am	1130	1,080
$^{243,244}Cm$	60	not reported
^{242}Cm	7	not reported
^{60}Co	510	470(a)
^{137}Cs	260,000	224,000(a)
^{154}Eu	3,230	4,080(a)
^{155}Eu	3810	not reported
^{241}Am (gamma)	1590	not reported

(a) Corrected for decay.

3.2 CC SOLIDS DISSOLUTION

When a slurry of the actual CC waste was diluted with an equal volume of water (and stirred for 1.5 h), the concentrations of the major components in the resulting supernatant solution were as expected for a one-to-one dilution; this indicates that the amounts of such components that had dissolved from the solids were minimal at most. However, the concentrations of certain minor components in the supernatant solution were greater than expected for a one-to-one dilution. These components are listed in Table 3.3 along with their respective concentrations. In the cases of As, Ti, and V, dilution with one volume of water resulted in complete dissolution; none of these components were observed in the solid material remaining. Significant amounts of Mg and Sr remained in the solid material. No TRU elements were dissolved upon addition of water.

The CC solids were separated from the supernate by filtration and were washed with water. Analysis of the wash solution revealed that additional quantities of Al and Sr had been dissolved by washing the solids with water.

TABLE 3.3. Components of Actual CC Solids That Dissolved by Dilution with Water

Component	Concentrations Supernate, $\underline{M}$	Expected for 1-to-1 Dilution, $\underline{M}$	Found After 1-to-1 Dilution, $\underline{M}$
As	0.00023	0.00012	0.00028
Mg	0.0010	0.0005	0.0007
Sr	0.00006	0.00003	0.00017
Ti	0.0	0.0	0.00063
V	0.0	0.0	0.0047

The ratios of grams of Al or Sr to grams of Na in the wash solution (g Al/g Na = 0.0044, g Sr/g Na = 0.00068) were significantly greater than in the filtered supernate solution (g Al/g Na = 0.0018, g Sr/g Na = 0.00016). For all other components, the ratio of g component/g Na was the same in the wash solution and the filtered supernate.

The washed solids were treated successively with 0.1 $\underline{M}$ HNO_3, 1.8 $\underline{M}$ HNO_3 at ambient temperature, and 1.8 $\underline{M}$ HNO_3 at 100°C. After the final treatment, all solids had dissolved. The percentage of each component in the solids found in solution during the various dissolution steps are listed in Table 3.4. For most of the components, greater than 80% dissolution was obtained in 0.1 $\underline{M}$ HNO_3; exceptions to this were Fe, Mn, and Pb. Upon raising the HNO_3 concentration to 1.8 $\underline{M}$, all of the components except Pb dissolved to 95% or greater. Heating at 100°C dissolved the remaining Pb.

Listed in Table 3.5 are the amounts of each actual CC waste component found in a) the supernatant solution after one-to-one dilution with water, b) the solution obtained from washing of the solids, and c) the final dissolved sludge solution. Also listed are the grams of each element per gram of CC waste (slurried), and the percentage of each element found in the washed solid portion of the waste. As expected, the quantity of Na in this waste

TABLE 3.4. Summary of Actual CC Solids Dissolution

Component	Percentage 0.1 M HNO_3	 1.8 M HNO_3 (ambient temperature)	 1.8 M HNO_3 (100°C)
Al	87	96	100
Ca	90	98	100
Cr	88	100	100
Fe	15	95	100
Mg	90	97	100
Mn	49	100	100
Na	95	96	100
Pb	0	0	100
Sr	97	100	100

dwarfs the amount of other elements,[a] with Na accounting for 15% of the total mass of the CC waste. The next most abundant elements are Fe (0.4%) and Al (0.2%). The most abundant elements found in the washed solid portion of the waste are Al and Na.

These results suggest that CC solids readily dissolve in dilute HNO_3. However, it must be stressed that the CC solids used in this study may differ considerably from CC sludge stored in underground tanks at Hanford. The solids present in the CC waste sample used in this study are believed to have formed after the liquid sample had been removed from Tank 102-AZ; the solids presumably precipitated as the sample cooled (or aged). Thus, further investigations regarding the dissolution of CC sludge need to be performed using solids actually removed from the tanks.

(a) Only the elements determined by inductively coupled plasma-atomic emission spectroscopy are considered, i.e., elements such as carbon also contribute greatly to the mass of the CC waste, but are not included in Table 3.5.

TABLE 3.5. Quantities of Actual CC Waste Components

Elements	Amount of Waste Components, g Diluted Supernate	Wash Solution	Dissolved Sludge Solution	Per Gram CC Waste	Washed CC Solids, %
Al	0.00164	0.00046	0.0126	0.00216	86
As	0.00021	0	0	0.00003	0
B	0.00006	0	0	0.00001	0
Ba	0.00009	0.00001	0.00001	0.00002	11
Ca	0.00355	0.00040	0.00022	0.00061	5
Cd	0.00020	0	0	0.00003	0
Ce	0.00042	0	0	0.00006	0
Cr	0.00081	0.00009	0.00006	0.00014	7
Cu	0.00018	0.00002	0	0.00003	0
Fe	0.02253	0.00248	0.00167	0.00392	6
K	0.00391	0	0	0.00057	0
La	0.00028	0	0	0.00004	0
Mg	0.00016	0.00003	0.00016	0.00005	47
Mn	0.00479	0.00050	0.00002	0.00078	0
Mo	0.00007	0	0	0.00001	0
Na	0.915	0.105	0.0135	0.152	1
Nd	0.00098	0	0	0.00014	0
Ni	0.00314	0.00033	0	0.00051	0
P	0.00248	0	0	0.00036	0
Pb	0.00240	0.00026	0.0011	0.00055	28
Re	0.00278	0.00026	0	0.00045	0
Ru	0.00020	0	0	0.00003	0
Si	0.00011	0	0	0.00002	0
Sr	0.00014	0.00007	0.00018	0.00006	45
Th	0.00023	0	0	0.00003	0
Ti	0.00030	0	0	0.00004	0
U	0.00119	0	0	0.00017	0
V	0.00241	0	0	0.00036	0
Zn	0.00026	0	0	0.00004	0
Zr	0.00023	0	0	0.00003	0

3.3 SEPARATIONS FROM ACIDIC SOLUTION

Various methods were evaluated for the separation of ^{137}Cs, ^{99}Tc, and ^{90}Sr from HNO_3 solutions. Three methods showed promise for the separation of ^{137}Cs: 1) extraction with di-t-butylbenzo-21-crown-7 (DtBB21C7) + HDNNS, 2) sorption on FeCN-XAD-4, and 3) precipitation with phosphotungstate. Extraction of ^{137}Cs with DtBB21C7 + HDNNS and sorption of ^{137}Cs on FeCN-XAD-4 were sensitive to high Na concentrations; thus, these methods would be useful only in a case where a washed sludge was dissolved for processing. Precipitation with phosphotungstate can be performed in the presence of large amounts of Na, but a batch precipitation process such as this would not be as favorable as a continuous process for Cs removal. Extraction of Tc with tetraalkylammonium salts showed great promise, but a suitable method of stripping the Tc from the solvent needs to be developed. A screening of the SREX process for extraction of Sr from acidified CC waste indicated this method is suitable for removal of Sr from CC waste.

3.3.1 Separation of Cs from Acidic Solution

Si-L. The ability of Si-L to remove trace quantities of Cs from acidic solution was evaluated. A feed solution consisting of 1.0 $\underline{M}$ HNO_3 spiked with ^{137}Cs was passed through a column containing the Si-L. The amount of ^{137}Cs in the effluent was monitored by gamma-counting techniques. The concentration of ^{137}Cs in the effluent began to rise sharply after 1.5 bed volumes of feed had been passed through the column (Figure 3.1). These data suggest that the Si-L used in this experiment is not suitable for removal of trace quantities of Cs from 1.0 $\underline{M}$ HNO_3 solution.(a)

FeCN-XAD-4. Ferrocyanide salts have been sorbed onto macroreticular supports, and such materials have demonstrated an affinity for Cs (Hendrickson and Riel 1975). A sample of Amberlite® XAD-4 was impregnated with sodium nickel ferrocyanide. The affinity of this material (FeCN-XAD-4) for Cs was

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(a) The Si-L used in this experiment was not virgin material; it had been used in a previous experiment carried out at PNL by Camaioni et al. (1991). It is possible that the properties of this material were altered in this previous experiment, decreasing its affinity for Cs. It might be worthwhile to repeat this test with virgin Si-L.

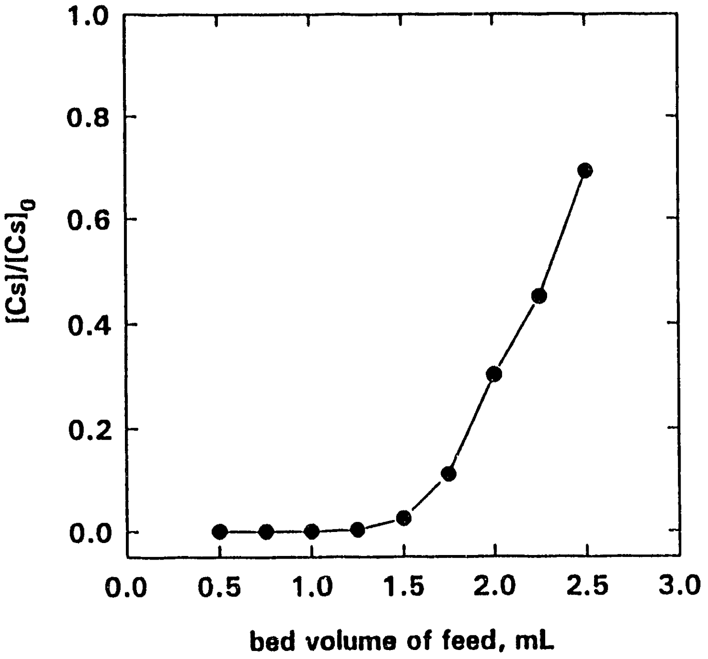

FIGURE 3.1. Breakthrough Curve for Sorption of Cs on Si-L

evaluated by batch distribution methods at ambient temperature. The affinity for Cs from 1.0 M HNO_3 solution was initially very high (R_d = 8500 $mL \cdot g^{-1}$), but decreased as the sorbent was aged under dry conditions (R_d = 240 $mL \cdot g^{-1}$ after 4 weeks). Two columns were prepared with FeCN-XAD-4. Through one of these columns was passed a 1.0 M HNO_3 solution spiked with ^{137}Cs; through the other, acidified (1.1 M H^+) synthetic CC waste (also spiked with ^{137}Cs). The results are summarized in Figure 3.2. In the case of the 1.0 M HNO_3 solution, 6 bed volumes of feed were passed through the column before Cs began to break through. However, breakthrough for the synthetic waste occurred after 0.5 bed volume of feed had passed through the column, suggesting the FeCN-XAD-4 would not be suitable for removal of ^{137}Cs from directly acidified CC waste.

Because the concentration of Cs in the synthetic CC waste was several orders of magnitude greater than in the spiked 1.0 M HNO_3 solution, the breakthrough data (Figure 3.2) for these two solutions could not be compared directly; that is, the early breakthrough for the synthetic CC waste might have occurred because the column was saturated with Cs. However, interference

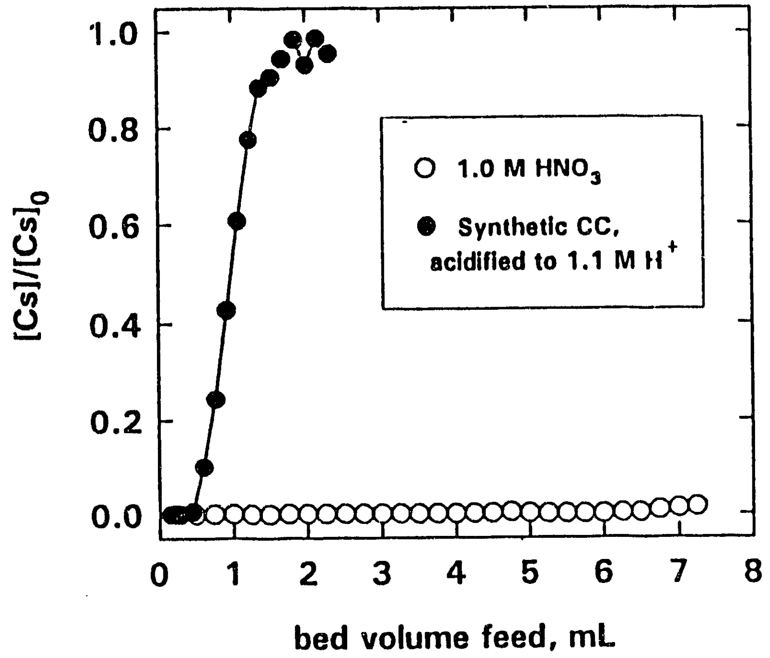

FIGURE 3.2. Breakthrough Curve for the Sorption of Cs on FeCN-XAD-4

by sodium ion was thought to be a more plausible explanation. To assess whether large amounts of Na contributed to the poor performance of FeCN-XAD-4 for the synthetic CC waste, the affinity of FeCN-XAD-4 for Cs from 1.0 M HNO$_3$ solution in the presence (3.5 M NaNO$_3$) and absence of Na was evaluated by batch distribution measurements. When 3.5 M Na was present, the R_d for Cs was 72 mL·g^{-1}, whereas when no Na was present a much higher R_d (240 mL·g^{-1}) was observed. Thus, the presence of large quantities of Na suppressed the removal of Cs by FeCN-XAD-4.

The results presented here suggest that a sorbent consisting of sodium nickel ferrocyanide on a macroreticular support would not be suitable for removal of ^{137}Cs from directly acidified CC waste (Option III, Figure 1.1) because of the high sodium ion concentration that would be present. However, if the CC supernate is separated from the sludge, and the sludge is washed before dissolution, the concentration of Na in the dissolved sludge solution is expected to be quite low. If the amount of ^{137}Cs remaining in the sludge is enough to require removal, a sorbent such as FeCN-XAD-4 might be suitable.

Extraction of Cs with DtBB21C7 and HDNNS. McDowell et al. (1986) have reported the synergistic extraction of Cs from acidic solutions with dibenzo-21-crown-7 (DB21C7) and didodecylnaphthalenesulfonic acid (HDDNS). The possibility of using such a system to extract Cs from acidified CC waste was explored. This study employed DtBB21C7 in place of DB21C7 (because DtBB21C7 has better solubility characteristics), and HDNNS instead of HDDNS.(a) The results are summarized in Figure 3.3 and Table 3.6. These data indicate that the extraction is highly dependent on the diluent; higher Cs distribution coefficients are obtained when toluene rather than 1-octanol is used as diluent. Because of its low flash point, toluene is not a desirable diluent for a large scale process. However, the Cs distribution coefficients obtained with an extractant consisting of 0.05 M DtBB21C7 + 0.05 M HDNNS in toluene are

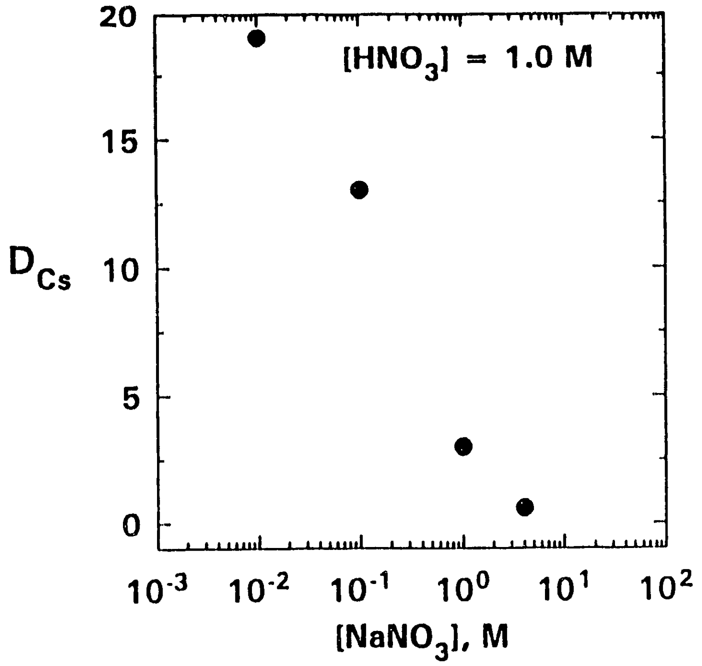

FIGURE 3.3. Extraction of Cs with 0.05 M DtBB21C7 and 0.05 M HDNNS in Toluene. Distribution coefficient for Cs as a function of $NaNO_3$ concentration.

(a) The properties of HDNNS are very similar to those of HDDNS. Because of the availability of HDNNS, this extractant was chosen for this study.

TABLE 3.6. Extraction of Cs with DtBB21C7 and HDNNS

Aqueous Phase (spiked with ^{137}Cs)	Organic Phase			
	[DtBB21C7]	[HDNNS]	Diluent	D_{Cs}
1.0 $\underline{M}$ HNO_3	0.1	0.0	1-octanol	0.21
1.0 $\underline{M}$ HNO_3	0.075	0.075	1-octanol	0.25
1.0 $\underline{M}$ HNO_3 + 5 $\underline{M}$ $NaNO_3$	0.075	0.075	1-octanol	0.17
0.1 $\underline{M}$ HNO_3	0.075	0.075	1-octanol	2
0.01 $\underline{M}$ HNO_3	0.075	0.075	1-octanol	18
1.0 $\underline{M}$ HNO_3	0.05	0.05	toluene	14
Acidified (1.1 $\underline{M}$ HNO_3)	0.05	0.05	toluene	0.3
1.0 $\underline{M}$ HNO_3 + 0.01 $\underline{M}$ $NaNO_3$	0.05	0.05	toluene	19
1.0 $\underline{M}$ HNO_3 + 0.1 $\underline{M}$ $NaNO_3$	0.05	0.05	toluene	13
1.0 $\underline{M}$ HNO_3 + 1 $\underline{M}$ $NaNO_3$	0.05	0.05	toluene	3
1.0 $\underline{M}$ HNO_3 + 4 $\underline{M}$ $NaNO_3$	0.05	0.05	toluene	0.6

among the highest reported for 1.0 $\underline{M}$ HNO_3 (when $[Na^+]$ is low). Thus, further investigation of this type of system is warranted; identification of a suitable diluent is required.

The data presented in Figure 3.3 indicate that the extraction of Cs with DtBB21C7 and HDNNS is suppressed by high concentrations of sodium. Removal of the bulk Na by sludge washing before acid dissolution would be required if such extractants are to be used to separate ^{137}Cs from acidified CC waste (assuming removal of ^{137}Cs is required after sludge washing).

<u>Precipitation of Cs with Sodium Phosphotungstate</u>. As part of this study, precipitation with phosphotungstate was investigated as a means of removing Cs from acidified CC waste. When a solution of ^{137}Cs-spiked acidified synthetic CC waste (1.1 $\underline{M}$ H^+; 5.5 x 10^{-6} mole Cs) was treated with $Na_3PW_{12}O_{40}$ (2.2 x 10^{-6} mole), 98.87% of the Cs present precipitated giving a DF[(a)] of 88.7. A second strike with 2.0 x 10^{-6} mole $Na_3PW_{12}O_{40}$ resulted in

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(a) Decontamination factor (DF) is the concentration of a given component in the feed divided by the concentration after a given process has been performed.

the removal of an additional 1.05% of the original amount of Cs present (99.92% Cs removed overall), yielding a Cs DF of 1300.

3.3.2 Separation of Tc from Acidic Solution

The results of tests on the solvent extraction of Tc (as pertechnetate ion) from acidic solution are summarized in Figure 3.4 and Table 3.7. The distribution coefficients for Tc obtained with TRUEX solvent and dilute HNO_3 solutions are approximately three-fold higher than those reported by others, which were measured at a higher temperature of 40°C (Horwitz et al. 1985). The presence of $NaNO_3$ had a large effect on the distribution of Tc in the TRUEX process. When the 0.5 M HNO_3 solution was increased to 5 M in $NaNO_3$, the D_{Tc} decreased from 8.8 to 1.4.

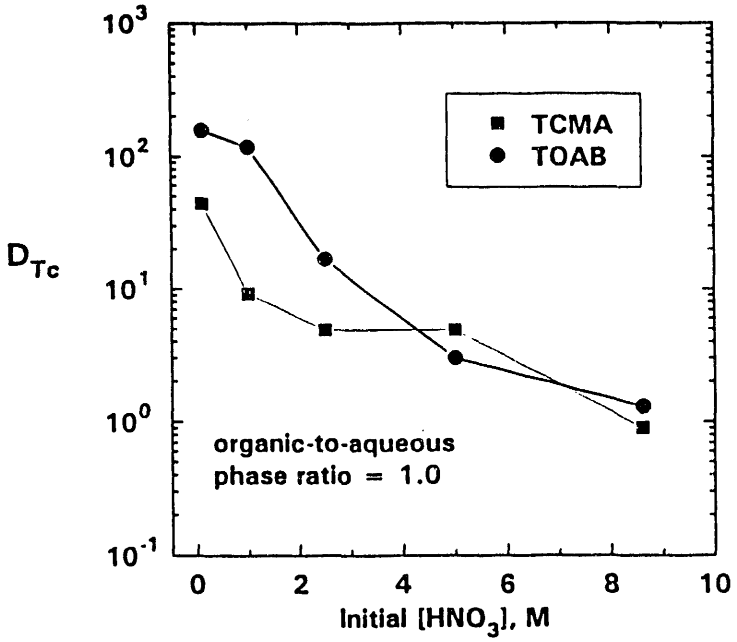

FIGURE 3.4. Extraction of Tc with 0.1 M TOAB in Cyclohexanone and 0.2 M TCMA in 1-Octanol as a Function of HNO_3 Concentration

TABLE 3.7. Extraction of Tc from Acidic Solution

Aqueous Phase	Organic Phase	D_{Tc}
0.5 M HNO_3	TRUEX	8.8
0.5 M HNO_3	0.1 M TBAN in cyclohexanone	126
0.5 M HNO_3	0.1 M TOAB in cyclohexanone	205
0.5 M HNO_3	0.1 M TOAB in 1-octanol	12
1.0 M HNO_3	TRUEX	7.9
1.0 M HNO_3	0.1 M TBAN in cyclohexanone	62
1.0 M HNO_3	0.1 M TOAB in cyclohexanone	76
1.0 M HNO_3	0.1 M TOAB in 1-octanol	7.9
0.5 M HNO_3 + 5 M $NaNO_3$	TRUEX	1.4
0.5 M HNO_3 + 5 M $NaNO_3$	0.1 M TBAN in cyclohexanone	23
0.5 M HNO_3 + 5 M $NaNO_3$	0.1 M TOAB in cyclohexanone	17
Simulated CC (0.5 M HNO_3)	TRUEX	2.2
Simulated CC (0.5 M HNO_3)	0.1 M TBAN in cyclohexanone	12
Simulated CC (0.5 M HNO_3)	0.1 M TOAB in cyclohexanone	11
Simulated CC (0.5 M HNO_3)	0.1 M TOAB in 1-octanol	1.6

Technetium was strongly extracted by solutions of tetraalkylammonium salts in cyclohexanone. The distribution coefficients for the extraction of Tc from 0.5 M HNO_3 with 0.1 M TBAN or 0.1 M TOAB in cyclohexanone were 126 and 205, respectively. The extraction of Tc by 0.1 M TOAB in cyclohexanone as a function of HNO_3 concentration is summarized in Figure 3.4. The distribution coefficient for Tc decreased with increasing $[HNO_3]$ but very high HNO_3 or $NaNO_3$ concentrations would be needed to strip Tc from this solvent. A strip procedure involving the reduction of pertechnetate ion might prove more effective, however, such a method has not yet been developed (see Section 3.4.2).

As was observed with the TRUEX process solvent, the presence of $NaNO_3$ suppressed the extraction of Tc with TOAB or TBAN in cyclohexanone. However, the distribution coefficients for Tc remained high enough for a workable process. Extraction of Tc from the acidified synthetic CC waste (0.5 M H^+) with 0.1 M TBAN or 0.1 M TOAB in cyclohexanone yielded D_{Tc} of 12 and 11, respectively.

Because of its low flash point (46°C), it is unlikely that cyclohexanone would be used in a large-scale process. Alternative diluents for the TOAB extractant were investigated in this study. TOAB was insoluble in NPH, but it did dissolve satisfactorily in 1-octanol. The distribution coefficients for the extraction of Tc by 0.1 M TOAB in 1-octanol were much lower than those obtained when cyclohexanone was the diluent. In the presence of high $NaNO_3$ concentration, the suppression of the Tc extraction by TOAB was great enough that a viable process using 1-octanol as the diluent is unlikely to be developed (at 0.1 M TOAB).

The utility of using TCMA as an extractant for Tc was investigated. This tetraalkylammonium chloride compound was insoluble in NPH, but soluble in 1-octanol. TCMA was converted to the nitrate salt because of the undesirability of the presence of chloride ion in nuclear waste processing. The extraction of Tc with 0.2 M TCMA as a function of HNO_3 concentration is shown in Figure 3.4. The behavior of this extractant was similar to that of TOAB in cyclohexanone. The potential utility of TCMA in extracting Tc from acid solution is high, but a suitable method for stripping Tc will need to be developed.

3.3.3 Separation of Sr from Acidic Solution

One of the most effective methods of separating Sr from acidic solution is the SREX process currently under investigation at Argonne National Laboratory (ANL) (Horwitz et al. 1991). This solvent extraction process uses a solvent consisting of 0.2 M di-t-butylcyclohexano-18-crown-6 (DtBC18C6) in 1-octanol. An experiment was carried out to assess the suitability of this method for removal of ^{90}Sr from acidic CC waste solutions. A sample of acidified synthetic CC waste ($[H^+]$ = 1.1 M) spiked with ^{85}Sr was contacted successively with three portions of 0.2 M DtBC18C6 in 1-octanol (organic-to-aqueous phase ratio of 0.33 for each contact). The distribution coefficients for Sr were 7.4, 5.8, and 6.4 for the three contacts, respectively. These values were slightly lower than the D_{Sr} of 10 (1.0 M HNO_3) reported by Horwitz et al. (1991), but this is not surprising considering variations observed with different lots of DtBC18C6 at ANL. Also, the values reported by ANL were recorded at 40°C, while these reported here were measured at ambient temperature. The Na content of the feed solution used in the ANL study (0.15 M) was also much less than that used here (4.8 M).

The DF obtained using the SREX procedure was 40, which is probably not sufficient to lower the ^{90}Sr levels in CC waste to below the Class A LLW criterion. Higher acid concentrations in the feed and an increased organic-to-aqueous phase ratio (or more contact stages) would result in improved Sr removal. While a more careful assessment is required to determine if SREX can adequately lower Sr levels to meet Class A LLW requirements, these initial results are considered promising.

3.4 SEPARATIONS FROM ALKALINE SOLUTION

Sorption and solvent extraction methods were evaluated for the removal of radionuclides from alkaline CC waste supernate. The organic ion exchange resin BSC-187 and the inorganic sorbent TIE-96 showed promise for the separation of Cs and Pu. When treated with TCMA, TIE-96 also adsorbed Tc. Tetraalkylammonium compounds showed promise for the extraction of Tc from alkaline CC waste supernate, but stripping of Tc continues to be a problem. Efficient methods of extracting Am and Sr from alkaline CC waste supernate remain to be developed.

3.4.1 Sorption Processes

A series of solid sorbents was investigated for the removal of Sr, Cs, Am, Pu, and Tc from alkaline solution. The affinity of each sorbent for the various elements of interest was determined using batch distribution measurements. For these measurements, the synthetic CC supernate was diluted with two volumes of water, spiked with an appropriate tracer (^{85}Sr, ^{137}Cs, ^{241}Am, ^{239}Pu, or ^{99}Tc), and contacted with the solid sorbent of interest. The results are summarized in Table 3.8.

The most promising sorbents investigated here were BSC-187 (resorcinol-formaldehyde resin) (Bray et al. 1990; Bibler et al. 1990) and TIE-96 (Bray and Hara 1991). Both of these materials displayed high affinity for Pu and

TABLE 3.8. Batch Distribution Ratios for Sr, Cs, Am, Pu, and Tc

Exchanger	Batch Distribution Ratio, Rd				
	Sr	Cs	Am	Pu	Tc
BSC-187	0.3	826	42	1325	5
CS-100	0.8	58	38	189	10
ARC-359	<0.1	25	47	931	11
IE-96	<0.1	199	17	24	1.6
TIE-96[a]	12	167	44	1327	<1
TIE-96A[b]	(c)	(c)	(c)	(c)	473
Charcoal	(c)	(c)	(c)	(c)	70

(a) IE-96 contained 5 wt% TiO_2.
(b) TIE-96 contained 9.8 wt% TCMA.
(c) Not measured.

Cs; BSC-187 had an exceptionally high affinity for Cs (14 times that of CS-100). However, the affinities of these materials for the other of interest were generally low. When treated with TCMA, the affinity of TIE-96 for Tc increased dramatically. Efficient sorbents for the separation of Sr and Am from alkaline CC waste have not been identified. BSC-187 and TIE-96 do have some affinity for Am, but whether or not adequate DFs for Am could be achieved with these materials is questionable. The addition of Ti to IE-96 (5 wt% TiO_2 = TIE-96) resulted in a batch distribution ratio of 12 for Sr. These promising results warrant further investigation in this area.[a]

3.4.2 Solvent Extraction Methods

Strontium-90. The extraction of Sr from alkaline solutions with dicyclohexano-18-crown-6 (DC18C6) plus a high molecular weight neocarboxylic acid (NCA) was performed by McDowell et al. (1986). The utility of this

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[a] The sorption of Sr on sodium titanate was not investigated in this work because the literature suggested that the presence of organic complexants such as EDTA suppresses the sorption of Sr from highly alkaline media (Heinonen et al. 1981).

method for the extraction of Sr from alkaline CC waste supernate was investigated in this study (Table 3.9). An extractant consisting of 0.05 M DC18C6 + 0.1 M NCA in toluene, which had been preequilibrated with a sodium hydroxide/$NaNO_3$ solution, successfully extracted Sr from the alkaline solution. However, the presence of complexants suppressed the extraction. For example, when a 0.45 M Na_2CO_3 + 0.45 M NaOH solution spiked with ^{85}Sr (~100 nCi ^{85}Sr/mL) was contacted with 0.05 M DC18C6 + 0.1 M NCA in toluene, the distribution coefficient for Sr was 149. D_{Sr} decreased to 0.12 when the aqueous phase also contained 0.009 M EDTA. Likewise, the D_{Sr} obtained in the extraction of Sr from synthetic CC waste supernate was 0.05. Thus, this method showed little promise for the extraction of Sr from alkaline CC waste.

Technetium-99. The extraction of Tc from alkaline solution with cyclohexanone and tetraalkylammonium salts was investigated (Table 3.10). As had been previously reported, Tc is extracted from alkaline solutions with cyclohexanone (Boyd and Larson 1960; Schulz 1980). The extraction by cyclohexanone is increased by adding tetraalkylammonium salts to the solvent. High extraction of Tc from the simulated CC waste supernate was achieved with 0.1 M solutions of TBAN or TOAB in cyclohexanone (D_{Tc} = 33 and 49, respectively).

As mentioned in Section 3.3.2, the use of cyclohexanone on a large scale would be undesirable due to its low flash point. Thus, the use of 1-octanol as diluent was explored. Tc was well extracted from 1 M Na_2CO_3 by 0.1 M TOAB in 1-octanol (D_{Tc} = 110), but from more complicated matrices the distribution coefficient for Tc dropped dramatically (D_{Tc} = 4.3 from the synthetic CC waste supernate), probably due to competition between pertechnetate ion and nitrate ion. Thus, a suitable diluent remains to be identified.

TABLE 3.9. Extraction of Sr with 0.05 M DC18C6 + 0.1 M NCA in Toluene

Aqueous Phase (Spiked with ^{85}Sr)	D_{Sr}
0.5 M Na_2CO_3 + 0.5 M NaOH	131
0.45 M Na_2CO_3 + 0.45 M NaOH	149
0.45 M Na_2CO_3 + 0.45 M NaOH + 0.009 M EDTA	0.12
synthetic CC supernate	0.05

TABLE 3.10. Extraction of Tc from Alkaline Solution

Aqueous Phase	Organic Phase	D_{Tc}
1 $\underline{M}$ Na_2CO_3	cyclohexanone	10
1 $\underline{M}$ Na_2CO_3	0.1 $\underline{M}$ TBAN in cyclohexanone	78
1 $\underline{M}$ Na_2CO_3	0.1 $\underline{M}$ TOAB in cyclohexanone	285
1 $\underline{M}$ Na_2CO_3	0.1 $\underline{M}$ TOAB in 1-octanol	110
1 $\underline{M}$ Na_2CO_3 + 5 $\underline{M}$ $NaNO_3$	cyclohexanone	4.7
1 $\underline{M}$ Na_2CO_3 + 5 $\underline{M}$ $NaNO_3$	0.1 $\underline{M}$ TBAN in cyclohexanone	102
1 $\underline{M}$ Na_2CO_3 + 5 $\underline{M}$ $NaNO_3$	0.1 $\underline{M}$ TOAB in cyclohexanone	49
1 $\underline{M}$ Na_2CO_3 + 5 $\underline{M}$ $NaNO_3$	0.1 $\underline{M}$ TOAB in 1-octanol	2.7
synthetic CC waste supernate	cyclohexanone	7.0
synthetic CC waste supernate	0.1 $\underline{M}$ TBAN in cyclohexanone	33
synthetic CC waste supernate	0.1 $\underline{M}$ TOAB in cyclohexanone	49
synthetic CC waste supernate	0.1 $\underline{M}$ TOAB in 1-octanol	4.3
0.1 $\underline{M}$ NaOH + 2 $\underline{M}$ $NaNO_3$	0.2 $\underline{M}$ TCMA in 1-octanol	5.2
synthetic CC waste supernate	0.2 $\underline{M}$ TCMA in 1-octanol	5.6

TCMA was observed to extract Tc from alkaline solution. When a solution of 0.2 $\underline{M}$ TCMA in 1-octanol was used as extractant, the distribution coefficients for Tc were 5.2 and 5.6 for extraction from 0.1 $\underline{M}$ NaOH + 2 $\underline{M}$ $NaNO_3$ and the synthetic CC waste supernate, respectively.

Attempts to strip Tc from cyclohexanone/tetraalkylammonium salt solutions under reductive conditions were unsuccessful. Several experiments were performed in which an organic phase containing Tc was contacted with a strip solution containing Sn^{2+} and EDTA (Table 3.11). It was expected that the TcO_4^- ion would be reduced by Sn^{2+}, and the resulting Tc cation (oxidation state unknown) would be complexed by EDTA in the aqueous phase. The distribution coefficients for Tc decreased as $[Sn^{2+}]$ increased, but they remained too high for efficient stripping even at 0.01 $\underline{M}$ Sn^{2+}. Thus, an effective method to strip Tc remains to be developed.

The effect of pH on the extraction of Tc with 0.1 $\underline{M}$ TOAB in 1-octanol was explored (Table 3.12). The extraction of Tc is independent of pH in the range pH 1 to 13, suggesting that hydronium ion is not involved in the

TABLE 3.11. Reductive Stripping of Tc

Extractant	Diluent	$[Sn^{2+}]$, M	D_{Tc}
--	cyclohexanone	0.01	34
TOAB	cyclohexanone	0.001	77
TOAB	cyclohexanone	0.01	34
TOAB	1-octanol	0.001	14
TOAB	1-octanol	0.01	1.5

TABLE 3.12. Extraction of Tc from 5 M $NaNO_3$ Solution with 0.1 TOAB in 1-Octanol as a Function of pH

Initial pH	Equilibrium pH	D_{Tc}
0.65	0.73	4.1
2.81	2.92	4.5
7.18	5.41	4.4
8.07	5.85	4.1
8.12	5.72	4.3
10.25	6.70	4.3
12.70	12.79	4.2

extraction mechanism. In most cases where the initial solution was alkaline, the pH dropped upon contact with 0.1 M TOAB in 1-octanol. This was probably due to extraction of hydroxide ion by TOAB.

Americium. Research has been conducted by Myasoedov et al. (1980) and Karalova et al. (1984) on the extraction of Am from alkaline solution by alkylated catechol derivatives. Presumably, Am was present as one or more types of carbonate complexants in the aqueous phase. The possibility of applying this technique to the separation of Am from the alkaline CC waste supernate was investigated in this study. Three compounds were explored as possible extractants for Am: 4-t-butylcatechol (tBC), 3,5-di-t-butylcatechol (DtBC), and 4-(1-methyl-1-octylnonyl)catechol (MONC). (The compound MONC was used in the studies conducted in 1980 and 1984.) The results are summarized in Table 3.13. The alkylated catechols were found to extract Am from alkaline

TABLE 3.13. Extraction of Am from Alkaline Solution with Alkylated Catechols

Aqueous Phase	Organic Phase	D_{Am}
0.5 $\underline{M}$ Na_2CO_3 + 0.5 $\underline{M}$ NaOH	0.2 $\underline{M}$ DtBC in 1-octanol	41
0.5 $\underline{M}$ Na_2CO_3 + 0.5 $\underline{M}$ NaOH	0.2 $\underline{M}$ DtBC in NPH	420
0.5 $\underline{M}$ Na_2CO_3 + 0.5 $\underline{M}$ NaOH	0.2 $\underline{M}$ tBC in 1-octanol	11
0.45 $\underline{M}$ Na_2CO_3 + 0.45 $\underline{M}$ NaOH	0.2 $\underline{M}$ tBC in 1-octanol	11
0.45 $\underline{M}$ Na_2CO_3 + 0.45 $\underline{M}$ NaOH + 0.009 $\underline{M}$ EDTA	0.2 $\underline{M}$ tBC in 1-octanol	0.8
synthetic CC supernate	0.2 $\underline{M}$ DtBC in NPH	0.1
synthetic CC supernate	0.2 $\underline{M}$ DtBC in 1-octanol	0.01
0.5 $\underline{M}$ Na_2CO_3 + 0.5 $\underline{M}$ NaOH	0.1 $\underline{M}$ MONC in NPH	>5000[a]
synthetic CC supernate	0.1 $\underline{M}$ MONC in NPH	0.01

(a) Severe interfacial crud information.

solutions, but the presence of complexants suppressed the extraction. Thus, D_{Am} decreased from 11 for the extraction of Am from 0.45 $\underline{M}$ Na_2CO_3 + 0.45 $\underline{M}$ NaOH with 0.2 $\underline{M}$ tBC in 1-octanol, to 0.8 for extraction from a similar aqueous phase that also contained 0.009 $\underline{M}$ EDTA. Likewise, with 0.1 $\underline{M}$ MONC in NPH, quantitative extraction of Am (organic-to-aqueous phase ratio = 1) was obtained from a 0.5 $\underline{M}$ Na_2CO_3 + 0.5 $\underline{M}$ NaOH solution; yet from the simulated CC supernate D_{Am} was only 0.01. Thus, this method is unsuitable for the removal of Am from alkaline CC waste supernate.

3.5 TESTS WITH ACTUAL CC WASTE

Several of the separation techniques described above were tested on actual CC waste. The results of these experiments are presented in this section. Experiments were performed using either diluted CC waste supernate or acidified CC waste supernate plus solids. The concentrations of the major components in the feed solutions used for these experiments are listed in Table 3.14.

TABLE 3.14. Composition of Feed Solutions Used in Tests on Actual CC Waste

Element	Alkaline Solution, M	Acid Solution, M
Al	0.0059	0.017
Ca	0.0081	not detected
Cs	0.000058	0.000043
Fe	0.040	0.030
K	0.011	0.0063
Mn	0.0088	0.0062
Na	3.99	2.92
Ni	0.0054	0.0037
P	0.0076	0.0060
Sr	0.000031	not detected
^{137}Cs	125 μCi/mL	84.4 μCi/mL
^{90}Sr	110	89.0
^{99}Tc	0.009	0.009
^{239,240}Pu	0.088	0.049
^{238}Pu/^{241}Am	0.546	0.470

3.5.1 Precipitation of Cs with Sodium Phosphotungstate

Experiments on the precipitation of Cs from acidified synthetic CC waste suggested that high DFs for Cs can be achieved. Therefore, this method was evaluated on a sample of actual CC waste. A sample of the acidified real CC waste (1.4 M H^+) containing 3.4×10^{-7} mole Cs was treated with two successive strikes of $Na_3PW_{12}O_{40}$ (2.0×10^{-6} mole, then 2.0×10^{-5} mole). This treatment resulted in a decrease in the ^{137}Cs concentration from 84.4 μCi/mL to 2.37 μCi/mL, giving a DF of 36 for Cs. Additional strikes with $Na_3PW_{12}O_{40}$ would presumably lower the ^{137}Cs concentration to below the Class A LLW criterion (which is 1 Ci/m^3 or 1 μCi/mL). Note that a large excess of $Na_3PW_{12}O_{40}$ was required to precipitate the Cs, in contrast to earlier studies and the results obtained with synthetic waste in this study (Section 3.3.1).

3.5.2 TRUEX: Behavior of TRUs and Tc

A portion of the acidified actual CC waste that had been treated with phosphotungstate was contacted three successive times with TRUEX solvent (organic-to-aqueous phase ratio = 0.33 for all contacts, Table 3.15). Interfacial crud formed during each contact. Although, when a portion of the acidified CC waste that had not been treated with phosphotungstate was contacted with TRUEX solvent, no interfacial crud formed (contact 5). Therefore, if Cs were to be removed by phosphotungstate precipitation, this process must be carried out after the TRUEX and SREX processes (see below), because interfacial crud forms when phosphotungstate is present.

TRUEX is a suitable process for the separation of TRUs from acidified CC waste solutions. The TRU content of the feed solution was 520 nCi/mL, which decreased to 0.6 nCi/mL in the raffinate from contact 3, giving a DF of 870. The extraction behavior of the TRUs (and Tc) in contact 5 was similar to that in contact 1; thus, even though interfacial crud formed in contacts 1 through 3, the results obtained can be assumed to be similar to what would have been obtained if three successive contacts were performed with the feed not treated with phosphotungstate.

TABLE 3.15. TRUEX Experiment with Actual CC Waste[(a)]

Contact	Aqueous Phase	Organic Phase
1[(b)]	Acidified CC waste (after Cs ppt)	TRUEX
2[(b)]	Aqueous from 1	TRUEX
3[(b)]	Aqueous from 2	TRUEX
4	0.2 M HEDPA[(c)]	Organic from 1
5	Acidified CC waste (before Cs ppt)	TRUEX

(a) Organic-to-aqueous phase ratio = 0.33 for all contacts.
(b) Interfacial crud formed during contact.
(c) 1-Hydroxyethane-1,1-diphosphonic acid.

The TRUEX process was unsuitable for the extraction of Tc from acidified CC waste. The ^{99}Tc content was 8.8 nCi/mL in the feed solution, and 6.2 nCi/mL after contact 2.[a] The D_{Tc} for both contacts 1 and 2 was 0.6. The lack of extraction of Tc by the TRUEX process was most likely due to the high nitrate concentration of the feed solution. (The effects of high $NaNO_3$ concentration on the distribution of Tc in TRUEX was discussed in Section 3.3.2.) However, another possibility is that the Tc was present in a reduced state and is complexed by the organics. Such a situation would greatly complicate Tc separation processes. This possibility cannot be dismissed at present.

The concentration of Tc present in this sample of CC supernate (≈20 nCi/mL) is already below the Class A LLW criterion (0.3 Ci/m^3 or 300 nCi/mL). If this holds true for all CC wastes, then removal of Tc will not be required.

3.5.3 SREX: Behavior of Sr and Tc

A portion of the acidified actual CC waste that had been treated with phosphotungstate was contacted three successive times with SREX solvent (organic-to-aqueous phase ratio = 0.33 for contacts 6 through 8, Table 3.16). As was the case with TRUEX, interfacial crud formed in each contact. Strontium-90 was removed from the aqueous solution with a DF of 99 (8.91 x 10^4 nCi ^{90}Sr/mL in the feed; 8.96 x 10^2 nCi ^{90}Sr/mL in the raffinate from contact 8). In order to achieve a Class A LLW, the DF for ^{90}Sr from this actual waste solution must be 2.2 x 10^3 (from an initial concentration of 8.9 x 10^4 nCi/mL to a final concentration below 40 nCi/mL); an increased DF should easily be achievable by increasing the number of stages or the organic-to-aqueous flow ratio.

As was observed with the TRUEX process, Tc was not extracted by the SREX process. The distribution coefficients for Tc in contacts 6 and 7 were 0.5. The possible reasons for the lack of Tc extraction are the same as those discussed above for the TRUEX process.

(a) The raffinate from contact 3 was not analyzed for ^{99}Tc.

TABLE 3.16. SREX Experiment with Actual CC Waste[a]

Contact #	Aqueous Phase	Organic Phase
6[b]	Acidified CC waste (after Cs ppt)	SREX
7[b]	Aqueous from 6	SREX
8[b]	Aqueous from 7	SREX
9	0.01 M HNO_3	Organic from 6

(a) Organic-to-aqueous phase ratio = 0.33 for all contacts, except 9 where o/a = 0.1.
(b) Interfacial crud formed during contact.

3.5.4 Solid Sorbents

The ability of various solid sorbents to remove ^{90}Sr, ^{137}Cs, ^{241}Am, ^{239}Pu, and ^{99}Tc from alkaline CC waste supernate was assessed by batch contact methods (Table 3.17). As expected from tracer experim[illegible], the batch distribution measurements indicate that a workable Cs removal process could be developed (BSC-187, IE-96, TIE-96). On the other hand, the R_ds for Pu were

TABLE 3.17. Batch Distribution Ratios for Sr, Cs, Am, Pu, and Tc, Obtained with Actual CC Waste

	Batch Distribution Ratio, R_d			
Exchanger	Sr	Cs	Pu	Tc
BSC-187	8.2	270	34.2	415
CS-100	7.4	29	25.4	175
ARC-359	4.9	11.4	19.2	239
IE-96	3.5	120	15.2	222
TIE-96[a]	6.7	99.8	22.9	94.4
TIE-96A[b]	4.5	91.3	14.4	181
Charcoal	8.2	4.1	14.8	256

(a) IE-96 contained 5 wt% Ti02.
(b) TIE-96 contained 9.8 wt% TCMA.

much lower than expected (based on results with synthetic waste, Table 3.8), and those for Tc were much higher than expected. The reasons for these results are unclear at present. Further work must be performed to confirm these unexpected results for actual CC waste.

4.0 CONCEPTUAL FLOWSHEETS

A conceptual flowsheet based on the work performed in this study is shown in Figure 4.1. The first step on the flowsheet is separation of the solids and liquids. Then, the process splits: the processes on the left side of the flowsheet are performed on alkaline supernate; the processes on the right side, on acidified waste. There are two advantages in splitting these processes. First, direct acidification of the CC waste to dissolve the solids (option III, Figure 1.1) would greatly increase the volume of the LLW remaining after the separation of the radionuclides and reneutralization (for

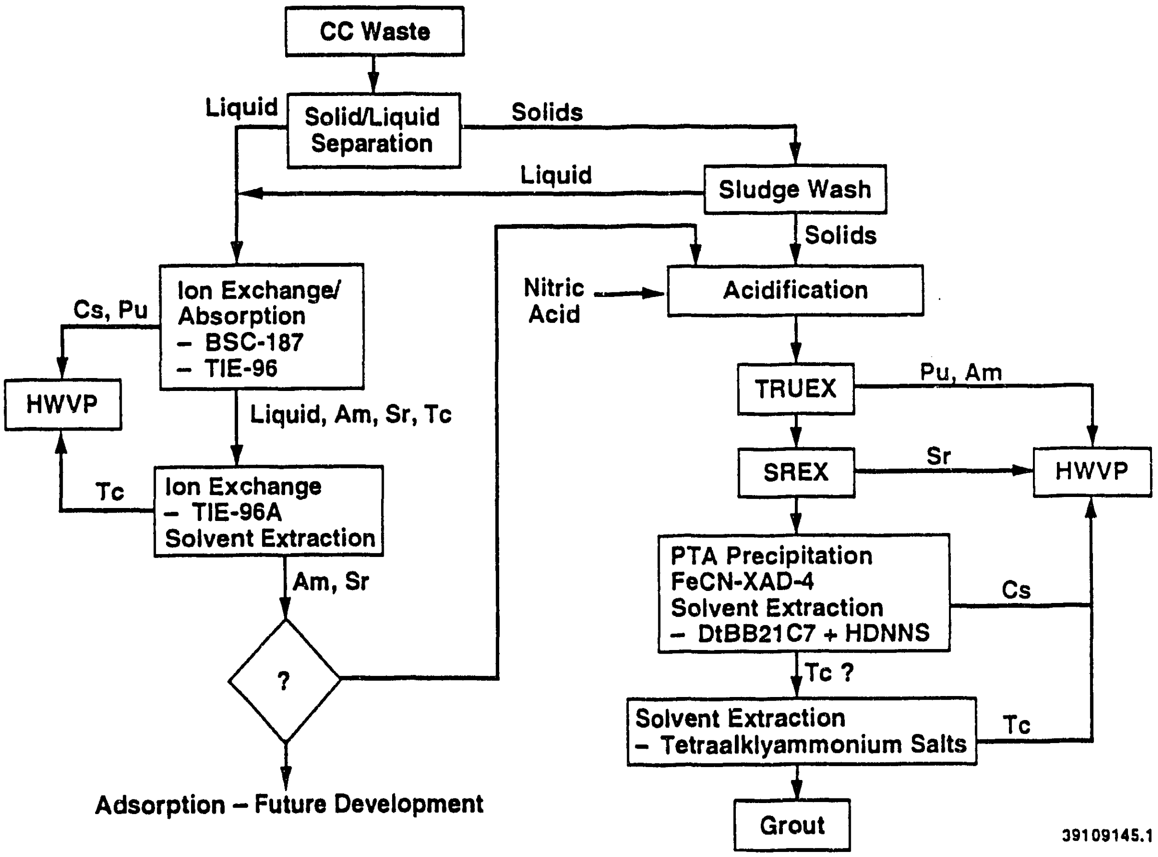

FIGURE 4.1. Conceptual Processing Flowsheet--CC Waste

interim storage in carbon steel tanks).[a] Second, the large quantities of Na present in the supernate interfere with the radionuclide removal efficiency of some of the acid-side separation processes.

As illustrated on the left side of the flowsheet, methods were identified for removing Cs, Pu, and Tc from the alkaline wastes. Two materials, one an organic (resorcinol-formaldehyde) resin (BSC-187) and the other a titanium-loaded zeolite (TIE-96), provide for removal of the Cs and Pu from the supernate. These materials could be vitrified directly. Essentially, the organic resins could be burned in the melter, although modifications to the construction and operation of the melter would be required. The loaded zeolite could more readily be vitrified with the existing design, but might result in a significant number of glass canisters being produced. Technetium could be removed from the alkaline liquid either with zeolite loaded with TCMA (TIE-96A) or by solvent extraction methods. Technetium tends to volatilize during vitrification, but a recycle stream from the off gas back to the feed would allow the concentration of Tc to build up in the feed stream so that it can be satisfactorily loaded in the glass. Methods have not been identified to remove complexed Am or Sr from alkaline liquids.

An alternative processing sequence (Figure 4.2) for the ion exchange materials loaded during alkaline waste processing would involve elution of the Cs and possibly Pu from the BSC-187. Cesium is readily eluted from the BSC-187 using formic acid (Bibler et al. 1990), but the elution behavior of Pu is unknown. The Tc and remaining Pu could be loaded on TIE-96A and vitrified.

Promising methods were identified for removing all of the radionuclides of interest from the acidic dissolved sludge solution (right side of Figure 4.1). The TRUEX and the SREX solvent extraction processes are suitable for removing Pu, Am (TRUEX), and Sr (SREX), although SREX might not remove ^{90}Sr to a level acceptable for Class A LLW criteria. These processes have the potential to remove Tc, but results obtained in this study with actual CC

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[a] The effects of direct acidification upon the LLW volume could be minimized if an acid recovery step is included in the process.

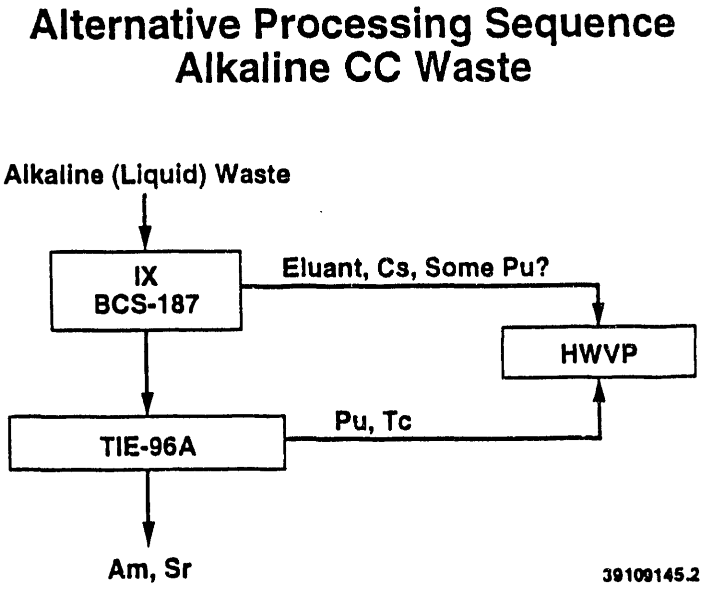

FIGURE 4.2. Alternative Processing Sequence Alkaline CC Waste

waste indicate that Tc is not extracted by TRUEX or SREX. Removal of Tc, if necessary, could be achieved by solvent extraction using tetraalkylammonium salts or possibly tertiary amine extractants. Cesium can be removed by precipitation with phosphotungstate or sorbed onto Amberlite® XAD-4 impregnated with FeCN-XAD-4 (providing adequate removal of Na by sludge washing has been achieved). It may also be possible to remove Cs by solvent extraction using DtBB21C7 and HDNNS in a suitable diluent.

Given the lack of suitable technologies for removal of complexed Am and Sr from alkaline solution, the best approach at present for removal of these radionuclides appears to be acidification of the entire CC waste followed by the use of the TRUEX and SREX processes.

5.0 DIRECTIONS FOR FUTURE RESEARCH

A number of promising techniques for removing radionuclides from Hanford CC waste have been identified in this study. Each method should be further examined to fully assess its utility for treating CC waste. Other methods investigated in this study gave disappointing results, however, these results served to identify gaps in radionuclide separations technology. Recommendations for future research are made in this section.

5.1 CC SOLIDS DISSOLUTION

Acid dissolution of actual CC solids was investigated as part of this study (Section 3.2). The results suggested that CC solids dissolve readily in HNO_3. However, the solids in the actual CC waste sample used for this study might not be representative of the sludge that currently exists in Hanford tanks containing CC waste. For this reason, it will be necessary to perform dissolution testing of CC solids actually removed from the tanks.

5.2 SEPARATION OF Cs FROM ACIDIC SOLUTION

An efficient method of separating Cs from acidic solution has not been demonstrated. Three of the methods investigated in this study showed some promise for the removal of Cs from acidic media, but all three had serious shortcomings (Table 5.1). Another method, which was not investigated in this work, is the extraction of Cs with cobalt dicarbollide (Afonin et al. 1990). Although this method has been demonstrated to efficiently extract Cs from HNO_3 solution, the ability to strip the Cs from the solvent remains in question. Also, the method only works well when nitrobenzene is used as diluent. The use of such a highly toxic diluent in a large-scale operation is undesirable. Thus, much work remains to develop an acid-side process for Cs separation.

Research in the area of acid-side Cs separation should include efforts to: 1) search for suitable diluents for the DtBB21C7/HDNNS and the cobalt dicarbollide extraction methods, 2) develop methods of stripping Cs from the

TABLE 5.1. Disadvantages of Acid-Side Cs Separations

Method	Disadvantage
Extraction with DtBB21C7 + HDNNS	• Requires removal of Na by sludge washing • Requires strong acid solution to strip Cs • Undesirable diluent (toluene)
Sorption on FeCN-XAD-4	• Requires removal of Na by sludge washing • No method to elute Cs, requires disposal of Cs-loaded sorbent • Affinity for Cs decreased upon storage
Phosphotungstate Precipitation	• Batch process • Presence of PTA interferes with solvent extraction processes, method must follow TRUEX, SREX, etc.

DtBB21C7/HDNNS and the cobalt dicarbollide solvents, 3) develop new, more selective Cs extractants, and 4) investigate inorganic ion exchangers, especially ammonium molybdophosphate (Faubel and Ali 1986). Testing of Si-L with virgin material should also be performed.

5.3 SEPARATION OF Tc

Extraction of Tc from acidic or alkaline solution with tetraalkylammonium compounds shows great promise. The following areas of research are identified in order to develop a practical process:

- choice of extractant, e.g., TOAB or TCMA (availability, cost, and performance should be taken into account)
- effect of extractant concentration
- effect of diluent
- development of efficient method to strip Tc.

The question as to whether removal of Tc from DST wastes is necessary to meet Class A LLW criterion must also be addressed.

5.4 SORPTION OF TRUs, Sr, Cs, AND Tc

BSC-187 and TIE-96 show great promise for the removal of ^{137}Cs and Pu from alkaline CC waste supernate. Issues that must be resolved to develop a practical process include:

- use of real CC waste to confirm sorption processes for the various radionuclides on the solid sorbents
- capacity of the sorbents for the targeted radionuclides
- kinetics of adsorption
- elution of the targeted radionuclides from the sorbent
- disposal of spent sorbent, e.g., vitrification or grouting
- modification of sorbent to remove other radionuclides, e.g., TIE-96A for Tc
- assessment of whether adequate DFs for Am could also be attained using these sorbents.

5.5 REMOVAL OF ^{90}Sr AND Am FROM ALKALINE CC WASTE SUPERNATE

Efficient methods for removing ^{90}Sr and Am from alkaline CC waste supernate need to be developed. Technologies to achieve such separations do not appear to be near at hand. Fundamental understanding of the coordination chemistry of Sr(II) and Am(III) ions may be necessary for the development of suitable separation technologies.

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