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Experimental Data Developed to Support the Selection of a Treatment Process for West Valley Alkaline Supernatant

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Prepared for
West Valley Nuclear Services Co., Inc.
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EXPERIMENTAL DATA DEVELOPED TO SUPPORT THE SELECTION OF A TREATMENT PROCESS FOR WEST VALLEY ALKALINE SUPERNATANT

L. A. Bray
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SUMMARY AND CONCLUSIONS

At the request of West Valley Nuclear Services Co., Inc., the Pacific Northwest Laboratory (PNL) has studied alternative treatment processes for the alkaline PUREX waste presently being stored in Tank 8D2 at West Valley, New York. Five tasks were completed during FY 1983:

1. simulation and characterization of the alkaline supernatant and sludge from the tank. The radiochemical and chemical distributions between the aqueous and solid phase were determined, and the efficiency of washing sludge with water to remove ions such as Na^+ and $SO_4^=$ was investigated.
2. evaluation of a sodium tetraphenylboron (Na-TPB) precipitation process to recover cesium (Cs) and a sodium titanate (Na-TiA) sorption process to recover strontium (Sr) and plutonium (Pu) from the West Valley alkaline supernatant. These processes were previously developed and tested at the U.S. Department of Energy's Savannah River Plant.
3. evaluation of an organic cation-exchange resin (Duolite® CS-100) to recover Cs and Pu from the alkaline supernatant followed by an organic macroreticular cation exchange resin (Amberlite® IRC-718) to recover Sr.
4. evaluation of an inorganic ion exchanger (Linde Ionsiv® IE-95) to recover Cs, Sr, and Pu from the alkaline supernatant.
5. evaluation of Dowex®-1,X8 organic anion exchange resin to recover technetium (Tc) from alkaline supernatant.

The findings of these tasks are related below.

West Valley alkaline waste was simulated to determine the distribution of key radionuclide species between the supernatant and sludge phases prior to sludge washing. Raising the pH of the alkaline PUREX waste from 10 to 13 decreased the solubility of Pu 100-fold; of neptunium (Np), 10-fold; and of americium (Am) and rare earths (RE), 4-fold. The solubilities of Cs, Sr, and

Tc were not significantly affected by the change in pH, and were about as expected at 99, 0.005, and 90% in solution, respectively.

The current process for treatment of Tank 8D2 sludge involves separation of the sludge and supernatant and washing of the resultant sludge to remove soluble salts. After four washes, the $SO_4^=$ level in the sludge phase was reduced to 1 wt% equivalent of Na_2SO_4 in the waste glass (equivalent to 4 wt% of the original $SO_4^=$ in Tank 8D2). Levels of Na^+ were reduced to an equivalent loading of <7 wt% Na_2O in the waste glass; and 4 and 9 wt% of Cs and Tc, respectively, remained in the sludge.

The Na-TPB precipitation recovery of Cs from alkaline supernatant was independent of pH in the range of 10.4 to 12.8, and independent of temperatures in the range of 25 to 50°C. The recovery of Cs was dependent on the mole ratio of Na-TPB/Cs + K + Rb. To achieve a Cs decontamination factor (DF) of >10,000, this ratio must be at least 1.4:1. The complex processing of the resulting organic precipitate, the loss of Na-TPB to the decontaminated supernatant, and the impact that this process would have on the vitrification system and the low-level waste treatment facility (LLWTF) were not addressed.

The Na-TiA process for recovery of Sr and Pu from alkaline supernatant was enhanced at a pH of 13.7 compared to 10.4, and at a temperature of 50 compared to 25°C. Recovery of Sr was independent of Sr concentration, indicating that the Sr concentration is not the controlling factor of recovery. To achieve DFs of 225 for Sr and >6 for Pu, the weight of Na-TiA required to process Tank 8D2 supernatant was estimated to be 1.2×10^5 kg. While no adverse effects were noted when Na-TPB and Na-TiA were combined in the experiments, the precipitant chemicals should only be added to supernatant separated from the sludge.

To select ion-exchange materials for the recovery of Cs, Sr, Pu, and Tc from alkaline supernatant, a batch sorption screening test was completed. The results show that the organic ion-exchange resins CS-100 and IRC-718, and an inorganic ion exchanger such as IE-95, are viable candidates for the removal of Cs, Sr, and Pu from alkaline waste. Removal of Tc using an anion resin such as Dowex-1,X8 also appears feasible.

The removal of Cs by Duolite CS-100 was dependent upon the resin particle size, temperature, and feed pH. Higher Cs loadings were achieved at smaller resin size classifications. Cesium loadings improved by a factor of 1.3 as the feed temperature was lowered from 50 to 6°C. When the alkaline supernatant feed pH was increased from 10.4 to 13.6, the cesium loading capacity at 0.5 C/Co increased by a factory of 3.3. At a feed pH of 13.8, the highest Cs decontamination factor achieved by the CS-100 ion-exchange resin was about 1600. No Pu decontamination was found. Elution was achieved using 0.1 M formic acid.

Amberlite IRC-718 recovery of Sr was dependent upon feed pH. Strontium DFs of 100 and 1000 were achieved after 10 cv of feed were loaded at alkaline supernatant pH values of 10.8 and 13.3, respectively. Elution was achieved using 2 M formic acid.

Linde Ionsiv IE-95 removal of radionuclides from West Valley alkaline supernatant was dependent on temperature, flow rate, Na/Cs feed ratio, and pH. Loadings for Cs improved by a factor of 1.6 as the temperature was lowered from 50 to 6°C at 0.5 C/Co. Cesium loadings increased by a factor of 1.6 as the feed pH decreased from 13.8 to 10.4 (the West Valley supernatant at pH 10 is more compatible with IE-95 than the SRP waste at pH 13.8). Decontamination factors of $>10^4$ for Cs, 10^3 for Sr, and 10 for Pu were achieved under the following column conditions: 0.6 cv/h, pH 10.4, 8 cv, and 25°C. The Cs loading capacity on IE-95 (pH 10.4) was greater by a factor of 3.6 than on CS-100 (pH 13.8).

CONTENTS

SUMMARY AND CONCLUSIONS iii

INTRODUCTION 1

EXPERIMENTAL PROCEDURES 5

SIMULATED SUPERNATANT AND SLUDGE PREPARATION 5

ION-EXCHANGE MATERIALS 6

Description of Inorganic Cation Exchangers 7

Description of Organic Cation Exchangers 8

Description of Organic Anion Exchangers 10

Pretreatment of Ion-Exchange Materials 10

Procedures for Dynamic Ion-Exchange Loading Tests 11

EXPERIMENTAL RESULTS 15

CHARACTERIZATION OF ALKALINE SUPERNATANT 15

Feed Preparation 17

Chemical and Physical Analysis 17

Distribution of Radionuclides Between Supernatant and Sludge ... 18

LABORATORY SLUDGE WASHING STUDIES 19

Chemical Species 24

Radiochemical Species 26

PRECIPITATION AND SORPTION PROCESSES 26

Cesium Precipitation Using Na-TPB 35

Strontium and Plutonium Adsorption Using Na-TiA 39

ION-EXCHANGE PROCESS 44

Batch Sorption 46

Organic Ion Exchange 48

Inorganic Ion Exchange 59

Technetium Organic Anion Exchange 68

ASSESSMENT OF ION-EXCHANGE CANDIDATES FOR CESIUM RECOVERY 71

pH 74

Temperature 77

Cesium Loading Capacity 77

REFERENCES 83

APPENDIX A - PREPARATION OF WEST VALLEY SIMULATED ALKALINE WASTE A.1

APPENDIX B - WASHING PROCEDURES FOR WEST VALLEY ALKALINE WASTE SLUDGE B.1

APPENDIX C - PROCEDURE TO TEST ADDITIVES THAT PRECIPITATE RADIONUCLIDES FROM ALKALINE SUPERNATANT C.1

APPENDIX D - PROCEDURE TO MEASURE BATCH SORPTION RATIOS FOR ION-EXCHANGE MATERIALS USING RADIONUCLIDE TRACER TECHNIQUES D.1

FIGURES

1 Ion-Exchange Columns with a 100 mL Capacity 12

2 Sample Fraction Collector 13

3 Settled Volume of Synthetic West Valley Sludge as a Function of Time and pH 16

4 Percent of Total Cs^+ in Sludge as a Function of the Number of Wash Steps 25

5 Percent of Total Na^+ in Sludge as a Function of the Number of Wash Steps 27

6 Percent of Total NO_2^- in Sludge as a Function of the Number of Wash Steps 28

7 Percent of Total NO_3^- in Sludge as a Function of the Number of Wash Steps 29

8 Percent of Total $SO_4^=$ in Sludge as a Function of the Number of Wash Steps 30

9 Precipitation Process 34

10 Cesium Precipitation from Simulated West Valley Alkaline Supernatant as a Function of Na-TPB/Cs+K+Rb Mole Ratio, 4 M Na+ 37

11 Cesium Precipitation from Simulated West Valley Alkaline Supernatant as a Function of Na-TPB/Cs+K+Rb Mole Ratio, 7 M Na+ 38

12 Adsorption of Strontium from Simulated West Valley Alkaline Supernatant Using Na-TiA 41

13 Adsorption of Plutonium from Simulated West Valley Alkaline Supernatant Using Na-TiA 42

14 Organic Ion-Exchange Process 49

15 Cesium Breakthrough as a Function of Mesh Size for Organic Exchanger CS-100 51

16 Cesium Breakthrough as a Function of Temperature for Organic Exchanger CS-100..... 52

17 Cesium Breakthrough as a Function of the Influent Cesium Feed Concentration for Organic Exchanger CS-100 53

18 Cesium, Plutonium and Strontium Breakthrough for Organic Exchanger CS-100 at pH 10.4 55

19 Cesium Breakthrough for Loading and Elution Cycle of Organic Exchanger CS-100 56

20 Strontium and Plutonium Breakthrough as a Function of Column Volumes Loaded for Organic Exchanger IRC-718 at pH 10.8 57

21 Strontium and Plutonium Breakthrough for Loading and Elution Cycle of Organic Exchanger IRC-718 at pH 13.3 58

22 Inorganic Ion-Exchange Process 60

23 Cesium in Solution as a Function of Added Powdered Zeolite Exchanger IE-95 62

24 Cesium Breakthrough as a Function of Temperature for the Zeolite Exchanger IE-95 at pH 10.4 63

25 Cesium Breakthrough as a Function of Temperature for the Zeolite Exchanger IE-95 at pH 13.6 64

26 Cesium Breakthrough as a Function of Flow Rate for Zeolite Exchanger IE-95 at pH 10.4 66

27 Cesium Breakthrough as a Function of the Influent Cesium Concentration for the Zeolite Exchanger IE-95 67

28 Plutonium Breakthrough as a Function of Temperature for Zeolite Exchanger IE-95 69

29 Strontium Breakthrough as a Function of Temperature for Zeolite Exchanger IE-95 70

30 Elution of the Zeolite Exchanger IE-95 Using 1M HNO_3 72

31 Elution of the Zeolite Exchanger IE-95 Using 4M HNO_3 73

32 Technetium Breakthrough for Organic Anion Resin Dowex-1,X8 75

33 Technetium Breakthrough for Loading and Elution Cycles of Organic Anion Resin Dowex-1,X8 76

34 Cesium Breakthrough as a Function of Exchanger and Feed pH 78

35 Cesium Loading Capacity as a Function of Temperature 80

36 Cesium Loading Capacity as a Function of Na/Cs Mole Ratio 82

TABLES

1 Average Composition of West Valley, Hanford, and SRP Alkaline Supernatant 6

2 Particle Size Distribution of Wet-Sieved Exchangers 11

3 Analysis of Synthetic Alkaline Supernatant 18

4 Distributions and Concentrations of Radiochemical Species in West Valley Alkaline Waste 20

5 Cesium Tracer Tests in Alkaline Supernatant 21

6 Strontium Tracer Tests in Alkaline Supernatant 21

7 Europium Tracer Tests in Alkaline Supernatant 21

8 Technetium Tracer Tests in Alkaline Supernatant 22

9 Plutonium Tracer Tests in Alkaline Supernatant 22

10 Neptunium Tracer Tests in Alkaline Supernatant 23

11 Americium Tracer Tests in Alkaline Supernatant 23

12 Radiochemical Species Washing Data 26

13 Percent of Total Sr and Pu in Final Washed Supernatant 27

14 Chemical Species Washing Data, pH 10 31

15 Chemical Species Washing Data, pH 10 + Na-TiA 31

16 Chemical Species Washing Data, pH 13 32

17 Chemical Species Washing Data, pH 13 + Na-TiA 32

18 Precipitation of Cesium Using Na-TPB 35

19 Removal of Cesium from Alkaline Supernatant Using Na-TPB at Different Temperatures and Sodium Concentrations 36

20 Removal of Strontium from Alkaline Supernatant Using Na-TiA Slurry ... 40

21 Removal of Plutonium and Strontium from Alkaline Supernatant Using Na-TiA as a Function of pH and Temperature 43

22 Optimum Conditions for a Precipitation System 45

23 Batch R_d Values for Radionuclides for Different Exchanger Types 47

24 Cesium Loaded on CS-100 as a Function of Na/Cs Mole Ratio 54

25 Optimum Conditions for an Organic Ion-Exchange System 59

26 Volumes of Feed Loaded as a Function of Temperature and pH 65

27 Cesium Loaded on IE-95 as a Function of Na/Cs Mole Ratio 68

28 Breakthrough Values for IE-95 as a Function of Temperature 71

29 Batch Elution of IE-95 Using Nitric and Formic Acid 71

30 Optimum Conditions for an Inorganic Ion-Exchange System 74

31 Cesium Loading Capacity on IE-95 and CS-100 as a Function of pH for the West Valley Synthetic Alkaline Supernatant 79

32 Cesium Loading Capacity on IE-95 and CS-100 as a Function of Temperature for the West Valley Alkaline Supernatant 81

34 Cesium Loading Capacity on IE-95 and CS-100 as a Function of the Na/Cs Mole Ratio for the West Valley Alkaline Supernatant 81

INTRODUCTION

Under contract to the Department of Energy (DOE), West Valley Nuclear Services Co., Inc. (WVNS) will construct and operate facilities at West Valley, New York, to solidify existing alkaline PUREX and acidic Thorex waste presently stored in underground tanks. These wastes will be solidified in a form suitable for transportation to and disposal in a federal geologic repository in compliance with the West Valley Demonstration Project (WVDP) Act of 1980 (Public Law 96-368).

The principal focus of high-level waste (HLW) solidification at West Valley will be on the alkaline PUREX waste because of its physical and chemical characteristics and its large volume (2×10^6 L) when compared to the acidic Thorex waste (4.5×10^4 L). Based upon an early Environmental Impact Statement (DOE/EIS-0081, US DOE 1982), a record of decision was published in the Federal Register (July 16, 1982) specifying a preferred processing approach for the West Valley wastes based upon technical, environmental, and economic considerations. The preferred approach involves separating and decontaminating the alkaline PUREX waste supernatant and combining radioactive materials recovered from the supernatant with the remaining alkaline PUREX sludge and acidic Thorex wastes. These HLW streams will be converted to a stable terminal waste form such as borosilicate glass. The decontaminated supernatant will be solidified as a low-level waste (LLW) product.

WVNS has requested assistance from Pacific Northwest Laboratory (PNL) in defining and characterizing the processes to be used for waste treatment and solidification. The purpose of this study is to provide a preliminary assessment of ion exchange and precipitation processes for decontaminating the alkaline waste supernatant and to characterize the waste in the West Valley high-level waste tank 8D2.

The technology for decontamination of alkaline PUREX supernatant has been developed and demonstrated at Hanford, Washington and the Savannah River Plant (SRP), South Carolina. The processes developed for supernatant decontamination have included inorganic ion exchange, organic ion exchange, and precipitation. Using this technology as a starting point, experimental studies were conducted

at PNL to examine the performance of these processes using simulated West Valley alkaline wastes. These studies have narrowed the list of potential processes for use at West Valley to three, each capable of satisfying minimum technical requirements:

- an organic ion-exchange process which utilizes Duolite CS-100 resin for Cs and Pu recovery, and Amberlite IRC-718 resin for Sr recovery.
- an inorganic process which utilizes zeolite Ionsiv IE-95 ion exchanger for Cs, Sr, and Pu recovery. This inorganic ion exchanger can be blended with the alkaline waste sludge and converted to a glass waste form, or eluted with acid and processed as LLW.
- a precipitation process which utilizes Na-TPB to selectively precipitate cesium (Cs), potassium (K), and rubidium (Rb), combined with Na-TiA for Sr and Pu recovery.

A fourth process for removal of technetium (Tc) from the alkaline supernatant was also investigated. This organic anion-exchange process utilizes a quaternary ammonium polystyrene, strong-base anion exchange resin such as Dowex-1,X8 for Tc recovery. It would be used in conjunction with the first three processes for treatment of the alkaline supernatant.

Additional studies were completed to simulate and characterize the alkaline waste and sludge representing the HLW in West Valley tank 8D2. The chemical and radiochemical distribution between the sludge and supernatant was determined with and without precipitant chemicals. Sludge washing efficiencies for the principal chemical and radiochemical species were determined after batch washing of the sludge with water.

Laboratory tests were conducted to provide a technical data base for a preliminary conceptual engineering design, completed in 1983, for treatment of the West Valley alkaline supernatant. High level waste similar to that determined by the preliminary analysis of Tank 8D2 was simulated and characterized by caustic neutralization and precipitation of acidic PUREX waste. Chemical and radiochemical distributions were determined for the resulting sludge and supernatant phases. The sludge was then washed to determine the chemical and radiochemical distribution between the water and sludge. The efficiency of Na^+

and $SO_4^=$ ion removal from the sludge by washing was investigated. A simulated alkaline supernatant was also prepared by direct chemical mixing to test proposed precipitation and ion-exchange flowsheets.

Laboratory experiments were conducted to study the performance of a precipitation process (Na-TPB) for the recovery of Cs, and a sorption process (Na-TiA) for the recovery of Sr and Pu from simulated alkaline supernatant. The effects of temperature, pH, contact time, and quantity of precipitant chemicals were investigated.

The ability of organic and inorganic ion exchangers to decontaminate alkaline supernatant by removing Cs, Sr, Pu, and Tc was evaluated. Determining batch relative distribution (R_d) values for selected radionuclides as a function of exchanger type provided a rapid and cost-effective method for comparing a wide variety of materials for their selectivity for specific radionuclides. The batch test was used to rank the candidate exchangers and to select exchangers for further testing in flow-through columns. Column tests were then completed; and the effects of process parameters such as flow rate, pH, and temperature on selected exchangers were examined using synthetic alkaline supernatant containing ^{137}Cs, ^{85}Sr, ^{238}Pu, ^{22}Na, or ^{99}Tc radionuclide tracers. Both radionuclide loading and elution tests were completed and evaluated.

EXPERIMENTAL PROCEDURES

Data from experiments related to the waste composition of Tank 8D2 at West Valley and a general description of ion-exchange materials tested is given in this section. For a detailed presentation of the preparation of West Valley simulated alkaline waste, sludge washing procedures, and test procedures for precipitation and batch ion exchange, see the appendixes.

SIMULATED SUPERNATANT AND SLUDGE PREPARATION

Simulated supernatant and sludge for these studies were prepared based on the West Valley waste composition outlined in a presentation by WVNS personnel to Vitro Engineering, June 29, 1982 in Richland, Washington and in pertinent documents (US DOE 1978; US DOE 1982). The ions of major importance in evaluating the chemical processes include Sr^{2+}, Cs^{+}, K^{+}, Na^{+} and OH^{-}. The estimated composition of the West Valley alkaline waste and average values for the Hanford and Savannah River Plants were compared to determine similarities. During the time period in which this study was completed, the contents of Tank 8D2 were analyzed further (Table 1).

Alkaline supernatant decontamination processes developed at Savannah River (Wallace and Ferguson 1980) and further investigated at the Westinghouse R&D Center, Pittsburgh, Pennsylvania (Grant 1983) used alkaline supernatant with a pH of 13 to 14. A review of the Hanford PUREX alkaline waste (pH 10 to 11) indicated that the West Valley supernatant (Na/Cs mole ratio of 6500, pH 10.4) may more nearly resemble Hanford waste. Therefore, both pH 10 and 13 wastes were prepared for evaluation.

Two approaches have been used to simulate alkaline wastes. In the first, the wastes were prepared by neutralization of acidic PUREX wastes, forming a sludge phase and a supernatant phase. The initial acidic wastes were adjusted to contain radionuclide tracers of interest. The resulting sludge phase was used in laboratory washing studies. The alkaline supernatant prepared by this technique was used in the supernatant characterization study. The second approach involved preparation of alkaline supernatant by direct mixing of the

TABLE 1. Average Composition of West Valley, Hanford, and SRP Alkaline Supernatant

Ion	Concentration, M			
	West Valley[a]	West Valley[b]	Hanford[c]	SRP Reference[d]
Na^+	6.9 E+0	6.6 E+0	4.6 E+0	5.8 E+0
Rb^+	1.1 E-4	3.7 E-4	--	--
K^+	6.9 E-2	1.9 E-1	2.4 E-2	7.0 E-2
Cs^+	1.1 E-3	1.4 E-3	2.0 E-4	1.3 E-4
Sr^{++}	2.6 E-6	8.7 E-6	--	1.6 E-7
NO_3^-	4.4 E+0	3.5 E+0	5.8 E-1	2.2 E+0
NO_2^-	1.7 E+0	2.1 E+0	2.2 E+0	1.1 E+0
$CO_3^=$	--	3.4 E-1	7.7 E-1	3.0 E-1
OH^-	--	2.0 E-1	--	7.5 E-1
$SO_4^=$	3.0 E-1	2.5 E-1	1.0 E-1	3.0 E-1
pH	9.5 to 10[e]	10 to 11	10 to 11	13
Ratios:				
NO_3/NO_2	2.5 E+0	1.7 E+0	2.6 E-1	2.0 E+0
Na/Cs	6.3 E+3	4.8 E+3	2.3 E+3	4.4 E+4
Na/K	1.0 E+2	3.5 E+1	1.9 E+2	8.2 E+1
Na/Rb	6.3 E+4	1.8 E+4	--	--

(a) US DOE 1978; US DOE 1982.
(b) Letter, Knabenschuh, WVNS, to Hannum, DOE, 1983.
(c) Buckingham 1967.
(d) Wiley 1976a, 1976b.
(e) Based on litmus paper test on Tank 8D2 supernatant.

appropriate chemicals. This approach was used to prepare the feed for the batch and column ion-exchange tests. Both experimental approaches are detailed in Appendix A.

ION-EXCHANGE MATERIALS

One of the objectives of this study was to assess organic and inorganic ion exchange processes for decontamination of West Valley supernatant. This section provides a brief description of the selected ion exchangers, discusses

chemical pretreatment prior to use, and describes the equipment used for column ion-exchange loading tests.

Description of Inorganic Cation Exchangers

Several naturally occurring and synthetic minerals exhibit a high cation exchange capacity and specificity for Sr and Cs. Among the most important members of this class are the zeolites. Zeolites are hydrated, crystalline aluminosilicates with the molecular structure $(M,N_2)O \cdot Al_2O_3 \cdot nSiO_2 \cdot mH_2O$, where M is an alkaline earth and N an alkali metal. Zeolites have a relatively open three-dimensional framework with channels and interconnecting cavities in the aluminosilicate lattice. The zeolite lattice consists of SiO_4 and AlO_4 tetrahedra that have their oxygen atoms in common. Since aluminum is trivalent, the lattice carries a negative electric charge (one elementary charge per aluminum atom). This charge is balanced by alkali or alkaline earth cations, which do not occupy fixed positions but are free to move in the channels of the lattice framework. These ions act as counter ions and can be replaced by other cations. Specificity and exchange capacity are determined by the SiO_2/Al_2O_3 ratio and the crystalline structure. Ion exchange capacity is increased by the lower silica/alumina ratios, and greater acid stability from the higher ratios (Swift 1962; Buckingham 1967).

Synthetic zeolites are prepared by gelling sodium silicate, sodium aluminate, and sodium hydroxide in fixed ratios followed by digestion to permit crystallization to a particle size of 0.1 to 10 microns. The zeolite crystals are then mixed with a clay binder, extruded, dried, and rotary-kiln fired at about 1200°F. The synthetic zeolites have been most widely used as "molecular sieves" which, because of their very small and uniform pore structure, can sorb small molecules but completely exclude molecules larger than the pore openings. Typical pore openings range from 3 to 13 Å, depending on the zeolite type (Buckingham 1967).

Linde Ionsiv IE-95, AW-500 and A-51 are synthetic zeolites produced by the Union Carbide Corporation. IE-95 and AW-500 are alkali metal aluminosilicates primarily of the chabazite structure in the mixed ionic (Na^+, Mg^{2+}, Ca^{2+}) form. The A-51 ion exchanger is an alkali metal aluminosilicate of the Type A

crystal structure supplied in the Na^+ form. Inorganic zeolite ion exchangers have been used in large-scale nuclear operations. Some of these are summarized below:

- recovery of Cs from alkaline supernatant at the Hanford plant (Nelson and Mercer 1963; Bray and Van Tuyl 1961).
- cesium recovery in high-alkaline supernatants during use at Hanford--DFs of 10^4 were demonstrated (Buckingham 1967).
- cleanup of ~700,000 gallons of reactor containment water at Three Mile Island--DFs of 10^9 for ^{137}Cs and ^{90}Sr were achieved (Hitz et al. 1982; Barletta and Swyler 1983).

Description of Organic Cation Exchangers

Savannah River Laboratories has studied both inorganic and organic exchangers for cesium recovery (Wallace and Wiley 1975). Duolite C-3 and its analytical grade ARC-359, both produced by Diamond Shamrock Corporation, are examples of granular strong-acid cation exchangers of the phenol-formaldehyde type of sulfonic and phenolic exchange sites.

Duolite CS-100 is a granular phenol-formaldehyde condensation polymer with carboxylic acid functional groups. It has been demonstrated to be highly selective for Cs in highly alkaline systems such as those characteristic of SRP alkaline supernatant (pH 13.8). The presence of the phenolic hydroxyl group provides the selectivity of this resin for Cs in competition with Na. This very weakly acidic group is activated at pH values above 9. CS-100 was chosen for future development because of its excellent performance with SRP wastes. Summarized below are the principal factors which led to the selection of CS-100:

- It has a high loading capacity (E. I. du Pont 1980).
- Its breakthrough capacity (expressed as L feed/L resin) is very good as a result of its loading capacity and excellent kinetics (E. I. du Pont 1980; Wallace 1980).
- Elution studies indicate that Cs elutes very efficiently from CS-100.

- CS-100 is best eluted (E. I. du Pont 1980, 1981) by formic acid, which can be processed easily in the solidification facility.
- CS-100 sorbs an appreciable amount of Sr, though not enough to eliminate the need for a Sr selective resin (E. I. du Pont 1981; Wallace and Ferguson 1980).
- Experimental work with CS-100 using simulated alkaline supernatant has shown that DFs of 10^5 for Cs are possible (Baumgarten et al. 1980).
- Plutonium DFs are expected to be in the range of 100 to 200 (E. I. du Pont 1981; Chandler 1981).
- CS-100 is expected to have very good radiation stability due to its aromatic polycondensation structure (Gangwer, Goldstein, and Pillay 1978).

Amberlite IRC-50, -84, and -718 spherical organic cation resins, manufactured by Rohm and Haas Company, are examples of macroporous cation exchange resins with varying properties and selectivities. IRC-50 and -84 contain slightly ionized carboxylic acid groups and can be regenerated easily with weak acids such as formic acid. Amberlite IRC-718 is a crosslinked macroreticular chelating cation exchanger with a particular selectivity for the heavy metal cations. Summarized below are the factors which led to the selection of IRC-718:

- IRC-718 elutes effectively with HCOOH and is regenerated with NaOH (Baumgarten et al. 1980; Wallace and Ferguson 1980).
- Sr distribution coefficients are generally a factor of 10 higher than those of competing ions on IRC-718 (3000 versus 300), even in the presence of carbonate and sulfate anions (Baumgarten et al. 1980).
- IRC-718 swells only 50% upon regeneration (Baumgarten et al. 1980).
- Radiation stability of IRC-718 is expected to be good due to its polystyrene divinylbenzene structure (Gangwer, Goldstein, and Pillay 1978).

- It is expected on the basis of limited work that the DF for Sr with IRC-718 would be ~10^4 (E. I. du Pont 1981; Chandler 1981).

Description of Organic Anion Exchangers

A group of quaternary ammonium polystyrene, strong-base anion exchange resins was selected for the recovery of Tc from alkaline supernatant. These resins included Dowex-1,X8, manufactured by Dow Chemical Company; and Amberlite IRA-401, -402, and -458, manufactured by Rohm and Haas Company. IRA-458 differs from the other styrene-divinylbenzene resins in that it has an acrylic structure. All of the resins were in the chloride form.

Pretreatment of Ion-Exchange Materials

The ion-exchange materials tested in columns were washed prior to use. Because the inorganic exchangers (IE-95, A-51, and AW-500) generate heat due to hydration when first exposed to water, they were poured into two volumes of distilled water and allowed to cool to ambient temperature prior to use. The resins (IRC-718 and CS-100) and the exchangers were then batch washed with two volumes of 1M NaOH for 16 hours with stirring. Each material was then placed in a glass ion-exchange column and backwashed with distilled water until the pH of the effluent was <10. The Dowex-1,X8 anion resin (chloride form) was placed in the ion-exchange column with H_2O and converted to the nitrate form by pouring 1M HNO_3 through the column at a rate of 1 colume volume/h until the Cl^- in the effluent was no longer detectable. The resin was then backwashed with H_2O until the pH was >1.

Several of the "as-received" exchangers used in column tests were wet sieved to determine their particle size distribution (see Table 2).

The ion-exchange materials used to measure batch sorption ratios were not pretreated prior to use. However, a 1 g sample of each material tested was dried at 105 ±10°C for 24 hours and cooled in a desiccator before being reweighed to determine the weight loss due to moisture. A correction factor was applied to each weighed sample used in the batch sorption study.

TABLE 2. Particle Size Distribution of Wet-Sieved Exchangers

Exchanger	Weight Percent	Mesh Size
IE-95	83	>40 (0.425 mm)
	15	60 (0.25 mm)
	2	80 (0.18 mm)
IRC-718	25	>20 (0.85 mm)
	73	40
	2	<40
CS-100	22	>20
	75	40
	3	<40

Procedures for Dynamic Ion-Exchange Loading Tests

The performance of an ion-exchange material in a column can be defined by a breakthrough curve, where the ratio of the effluent concentration (C) to the feed concentration (Co) of the ion being removed is plotted as a function of the feed throughput in column volumes (cv). A cv is defined as the volume of the exchanger in an ion-exchange column, including the interstitial void. When the equilibrium is favorable, the ion initially on the bed is displaced and moves faster through the bed than incoming ions, producing a self-sharpening boundary between the loaded and unloaded portions of the bed. The shape of the concentration gradient reaches a steady state within a short distance and remains unchanged as it moves down the column. The breakthrough curve is therefore determined by the steady-state shape of this boundary (Buckingham 1967).

The loading data obtained in this study were plotted using logarithmic-probability graph paper to identify the breakthrough curves. The use of the probability scale for plotting the concentration ratio C/Co and the logarithmic scale for the feed throughput largely eliminates the S-shaped curve obtained with linear scales and makes it possible to plot accurately those values which are either very small or very near unity.

The ion-exchange system shown in Figures 1 and 2 consists of a 1.8-cm-dia ID glass ion-exchange column, a 27 L temperature bath used to control the

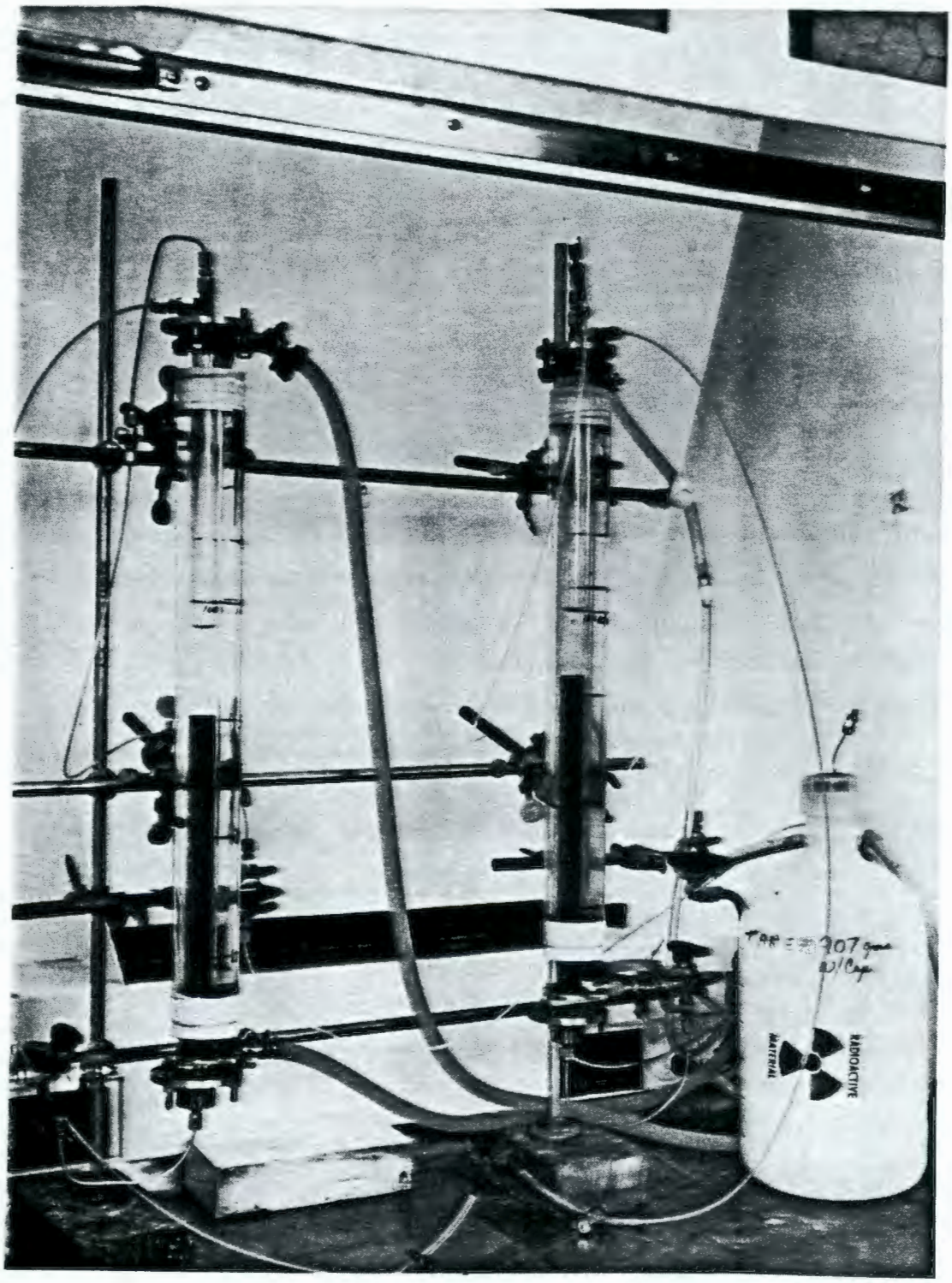


FIGURE 1. Ion-Exchange Columns with a 100 mL Capacity

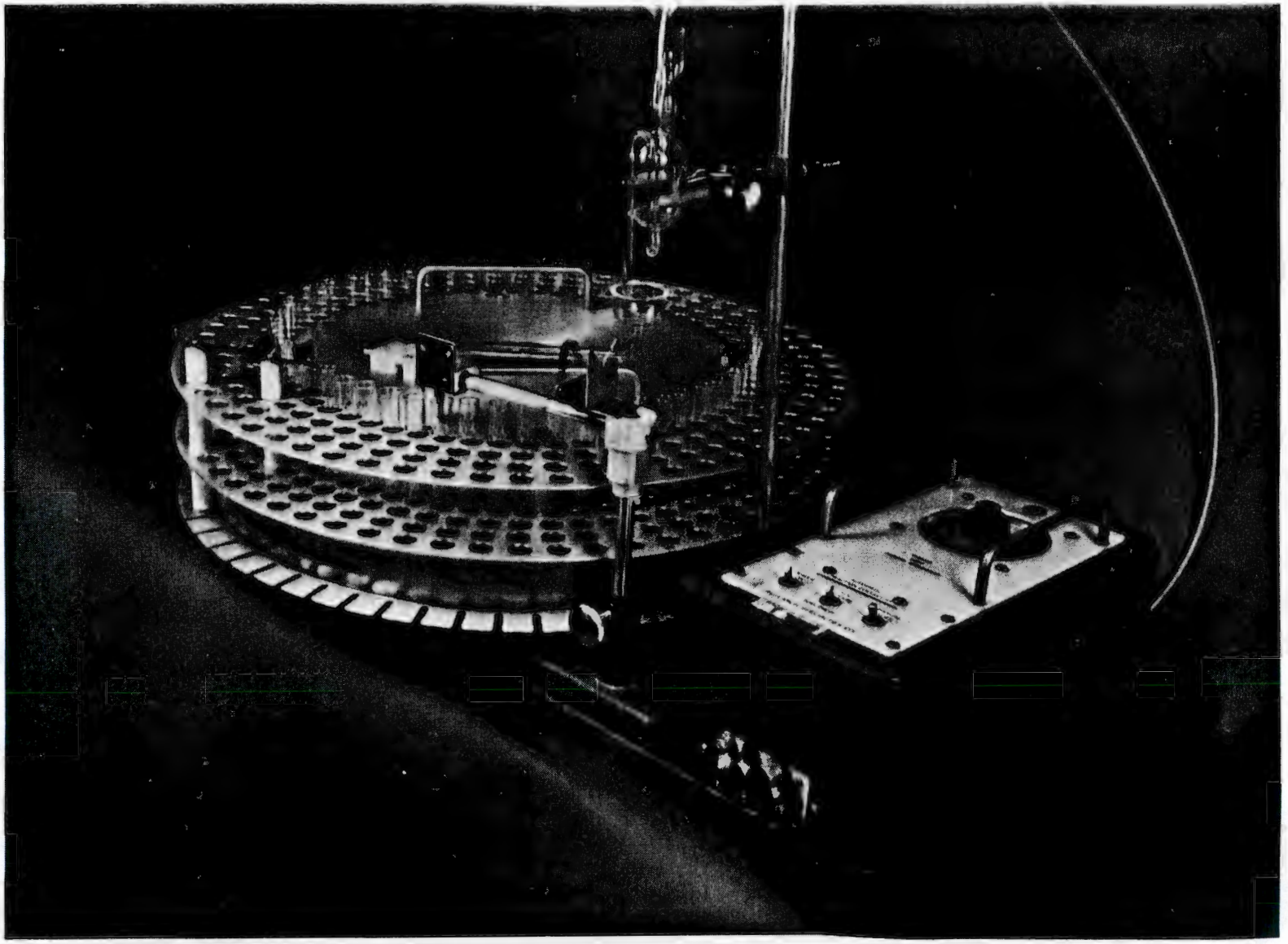


FIGURE 2. Sample Fraction Collector

column temperature within a 1°C range, a 3 psig pressurized polyethylene feed bottle, and an automatic fraction collector. The ion-exchange column was filled with 100 mL of exchanger (bed size 39 cm long x 1.8 cm dia). The column was jacketed with an outer glass column containing circulated ethylene glycol-water for temperature control. The top and bottom of the column were closed using a stainless steel plate and neoprene gasket. The feed to the column from the pressurized (3 psig) feed bottle was controlled using a needle valve. The flow rate was checked frequently during each run by counting the number of drops entering the column in a given time period. The effluent from the column was caught in a 20 mL siphon and transferred to sample tubes in the automatic fraction collector. Selected tubes were then sampled for alpha, beta, or gamma energy analysis. Experiments were completed to examine the column effects of temperature, feed pH, flow rate, and Na/Cs mole ratio in the influent feed.

EXPERIMENTAL RESULTS

A test program designed to provide the experimental data needed to support the selection of treatment processes for alkaline waste being stored at WVNS was completed in four parts: 1) feed preparation and characterization; 2) sludge washing; 3) Cs, Sr and Pu recovery from alkaline supernatant by precipitation and sorption processes; and 4) organic and inorganic ion exchange processes for the recovery of Cs, Sr, Pu and Tc. Descriptions of the four test procedures are given below.

CHARACTERIZATION OF ALKALINE SUPERNATANT

Simulated waste solutions representing the West Valley alkaline PUREX waste were prepared to determine the distribution of key radionuclide species between the supernatant and sludge phases prior to sludge washing. The radionuclides studied were Sr, Cs, Pu, Am, Np, Eu, and Tc.

The experimental procedure involved preparation of simulated acidic PUREX waste with the addition of a single radionuclide under study. The acidic PUREX waste was neutralized with excess NaOH and thoroughly digested. Upon neutralization, a solid phase formed and settled to the bottom of the test beaker. The pH of the simulated alkaline waste was adjusted to a pH of ~10 or ~13 by NaOH addition to investigate the effect of hydroxide ion concentration on the solubility of the species under study and the sludge-settling characteristics. A third waste was prepared having a pH of 13 and containing no carbonate ion to investigate the effect of carbonate on sludge-settling characteristics. Radiochemical concentrations were determined by gamma energy analysis and alpha and beta scintillation counting.

The alkaline waste at West Valley has a pH of ~10. We also studied a waste composition with a pH of ~13 because it represents an optimum condition for Cs recovery using organic ion exchange.

The sludge-settling experiments showed that pH and $CO_3^=$ concentration had little effect on settling: after 7 days the sludge volume varied from 40 to 48% of the total volume (Figure 3).

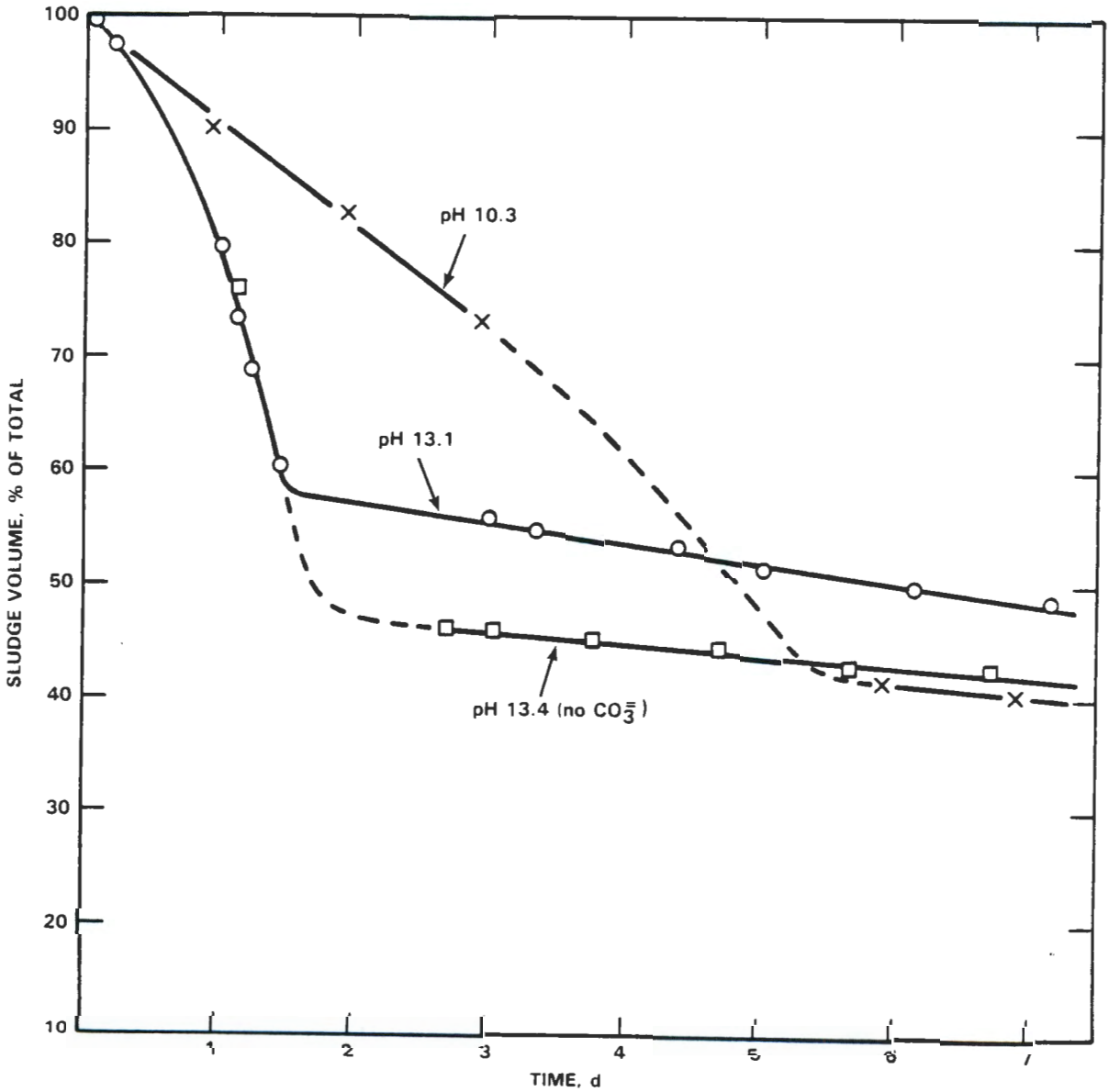


FIGURE 3. Settled Volume of Synthetic West Valley Sludge as a Function of Time and pH

Raising the supernatant pH from 10 to 13 significantly affected the solubility of the radionuclides. A 100-fold decrease in the solubility of Pu, a 10-fold decrease for Np, and a 4-fold decrease for Am and Eu were observed. Cesium, Sr, and Tc solubilities were not greatly affected by this change in pH, and were about as expected at ~99%, ~0.005% and ~90%, respectively.

If the process using organic ion exchangers is selected for West Valley, then raising the pH would increase the selectivity of the resin for Cs and aid in Pu, Np, Am, and Eu recovery by lowering their solubilities.

To simulate and characterize the alkaline waste representing West Valley HLW prepared by the neutralization and precipitation of simulated acidic PUREX waste, the test program was divided into three parts as outlined below.

Feed Preparation

The acidic stock solution containing the specific cations and anions found in the West Valley waste is given in Appendix A (Solution A). The K^+ ion concentration used for this part of the study was 0.069M. Three alkaline wastes were prepared: pH 10, pH 13 with $NaCO_3$, and pH 13 without Na_2CO_3. The carbonate was added to test its effect on the alkaline waste, since initial published West Valley waste compositions did not contain carbonate. [Hanford and Savannah River wastes contain $CO_3^=$, and more recent analysis of West Valley waste confirmed that it too contained $CO_3^=$ (0.39M).]

Chemical and Physical Analysis

Three alkaline waste solutions were prepared by adjusting an acidic stock solution to pH 10, pH 13 (with $CO_3^=$), and pH 13 (no $CO_3^=$). Each supernatant solution containing precipitated sludge was then tested to determine sludge settling rates, centrifuged solids volume, supernatant pH, and concentration of cations and anions remaining in the supernatant. The effects of time and pH on the sludge-settling experiments are shown in Figure 3. The results show that pH and $CO_3^=$ concentration have little effect on settling characteristics after 5 days, and after 7 days the sludge volume varied from 40 to 48 vol% of the total volume of supernatant and sludge. The pH 10 sludge settled more slowly than the pH 13 sludge in the first 5 days. The specific gravity for the supernatant varied from 1.32 to 1.34.

Each of the three supernatant and sludge samples was centrifuged at 1750 gravity. No clear separation was obtained during the first 30 minutes, but after 45 to 90 minutes, the sludge volume was 22, 25.2, and 24 vol% for pH 10.3, 13.1, and 13.4 (no $CO_3^=$), respectively.

The analysis of the alkaline supernatant after centrifugation is shown in Table 3. About 30% of the Cs^+ is missing from the supernatant. Other cation and anion values are as expected.

Distribution of Radionuclides Between Supernatant and Sludge

Alkaline wastes were prepared by adding tracers of Cs, Sr, Pu, Np, Eu, Am, and Tc to acidic stock solutions before precipitation. The mole concentration of nonradioactive Sr and Cs was followed by using tracers ^{85}Sr and ^{137}Cs. Technetium-99 was added, representing the molar concentration found in the West Valley alkaline waste. A $^{152-154}Eu$ tracer was added to follow all of the rare

TABLE 3. Analysis of Synthetic Alkaline Supernatant

	pH 10 Waste[a]		pH 13 Waste[b] w/$CO_3^=$		pH 13 Waste[c], No $CO_3^=$	
	g/L	M	g/L	M	Conc.	M
Na	2.2 E+2	9.3 E+0	2.0 E+2	8.7 E+0	1.9 E+2	8.3 E+0
K	3.8 E-1	1.0 E-2	4.0 E-1	1.0 E-2	4.0 E-1	1.0 E-2
Cs	9.2 E-2	6.9 E-4	1.1 E-1	7.8 E-4	9.8 E-2	7.4 E-4
Mo	4.6 E-1	5.0 E-3	5.4 E-1	6.0 E-3	5.6 E-1	6.0 E-3
Cr	2.8 E-3	5.4 E-5	3.4 E-2	6.5 E-4	8.0 E-2	1.5 E-3
Fe	1.6 E-3	2.9 E-5	2.0 E-4	3.6 E-6	3.0 E-4	5.4 E-6
P	7.0 E-1	2.3 E-2	1.9 E+0	6.1 E-2	2.0 E+0	7.1 E-2
$CO_3^=$	--	3.2 E-1	--	5.0 E-1	--	ND[d]
Si	3.0 E-4	1.0 E-4	4.6 E-1	1.6 E-2	4.2 E-1	1.5 E-2
B	8.0 E-4	7.4 E-4	3.6 E-1	3.3 E-2	2.8 E-1	2.6 E-2
OH^-	--	--	--	--	--	2.8 E-1
Cl^-	1.5 E-1	4.3 E-3	1.5 E-1	4.3 E-3	1.5 E-1	4.3 E-3
NO_3^-	1.9 E+2	3.1 E+0	1.9 E+2	3.1 E+0	1.9 E+2	3.1 E+0
NO_2^-	7.8 E+1	1.7 E+0	7.5 E+1	1.6 E+0	7.8 E+1	1.7 E+0
$SO_4^=$	2.8 E+1	2.9 E-1	2.8 E+1	2.9 E-1	2.8 E+2	2.9 E-1

(a) Actual pH 10.3.
(b) Actual pH 13.1.
(c) Actual pH 13.4.
(d) Not detectable.

earths (RE). Plutonium, Np, and Am were not added to the concentrations assumed to be in the tank, but only to a concentration sufficient to determine the solubility limit for each of the actinides. The solubility in alkaline supernatant and the percent between sludge and supernatant were determined for each tracer. The percent found in each phase does not necessarily represent actual West Valley tank conditions, and only solubility values should be applied.

Summarized in Table 4 are the distributions and solubility limits of the radiochemical species studied for the two pHs.

Tables 5, 6, and 7 summarize the data obtained for alkaline supernatant preparation using tracers of ^{137}Cs, ^{85}Sr, and ^{154}Eu. The results were obtained by counting 4 mL samples using a multichannel gamma analyzer that uses a 7.6 cm dia well NaI crystal detector.

Tables 8 through 11 summarize the data obtained for alkaline supernatant preparation using tracers of ^{99}Tc, ^{238}Pu, ^{237}Np, and ^{241}Am. The results for Pu were obtained by extracting aqueous samples into HDEHP-PCS.[a] Technetium, Am, and Np samples were mixed with PCS. All of the samples were counted using a liquid scintillation detector.

LABORATORY SLUDGE WASHING STUDIES

The current approach for treatment of the alkaline PUREX waste stored at West Valley in Tank 8D2 involves separation of the sludge and supernatant, and washing of the resultant sludge to remove soluble salts. The sludge washing procedure used is described in Appendix B. The objective of this work was to determine chemical and radiochemical distributions for the various chemical and radiochemical species between the simulated sludge and supernatant phases during the sludge-washing process. Two scenarios were investigated: 1) waste as it exists at a pH of 10 or 13, and 2) Na-TiA added to the waste to effect Pu and Sr precipitation prior to sludge separation and washing.

(a) HDEHP: di(2-ethylhexyl)phosphoric acid.
PCS: a proprietary reagent of Amersham Corp.

TABLE 4. Distributions and Concentrations of Radiochemical Species in West Valley Alkaline Waste

Radionuclide	Total Concentration[a] in West Valley Waste, M	pH ~10 Solubility Limit in Supernatant, M	pH ~10 Percent[b] in Supernatant	pH ~13 Solubility Limit in Supernatant	pH ~13 Percent[b] in Supernatant
Cs	1.0 E-3	>1.0 E-3	~1.0 E+2	>9.8 E-4	9.8 E+1
Sr	5.4 E-4[c]	2.2 E-8	4.1 E-3	2.7 E-8	5.0 E-3
Tc	6.4 E-4	5.7 E-4	8.8 E+1	5.8 E-4	9.2 E+1
RE[d]	4.4 E-3	2.1 E-5	4.7 E-1	5.2 E-6	1.2 E-1
Pu	7.4 E-5	3.3 E-10	4.5 E-4	ND[e]	--
Am	1.5 E-5	3.4 E-9	2.3 E-2	7.9 E-10	5.3 E-3
Np	6.8 E-5	8.6 E-5	1.0 E+2	8.6 E-6	1.3 E+1

(a) Supernatant + sludge.
(b) Percent calculated by dividing solubility limit by total concentration.
(c) Current value assumed for West Valley, 2.7×10^{-5}, was used in this study.
(d) Europium tracer was followed and is assumed to represent all the rare earths.
(e) ND = not detectable.

TABLE 5. Cesium Tracer Tests in Alkaline Supernatant

Parameter	pH 10.0	pH 12.8
Specific gravity, g/cm^3	1.32	1.32
Initial volume of stock A, mL[a]	120	120
Final total volume, mL[b]	216	222
Cs concentration in stock A, M	1.8 E-3	1.8 E-3
Cs concentration in supernatant, M	1.0 E-3	9.8 E-4
Initial Cs in final supernatant, %	98.1	99.5

(a) PUREX acid waste (see Appendix A).
(b) Supernatant + sludge.

TABLE 6. Strontium Tracer Tests in Alkaline Supernatant

Parameter	pH 10.1	pH 12.8
Specific gravity, g/cm^3	1.32	1.32
Initial volume of stock A, mL[a]	120	120
Final total volume, mL[b]	218	220
Sr concentration in stock A, M	4.6 E-5	4.6 E-5
Sr concentration in supernatant, M	2.2 E-8	2.7 E-8
Initial Sr in final supernatant, %	0.09	0.11

(a) PUREX acid waste (see Appendix A).
(b) Supernatant + sludge.

TABLE 7. Europium Tracer Tests in Alkaline Supernatant

Parameter	pH 9.9	pH 13.5
Specific gravity, g/cm^3	1.33	1.34
Initial volume of stock A, mL[a]	120	120
Final total volume, mL[b]	218	221
Eu concentration in stock A, M	7.3 E-3	7.3 E-3
Eu concentration in supernatant, M	2.1 E-5	5.2 E-6
Initial Eu in final supernatant, %	0.52	0.12

(a) PUREX acid waste (see Appendix A).
(b) Supernatant + sludge.

TABLE 8. Technetium Tracer Tests in Alkaline Supernatant

Parameter	pH 9.7	pH 13.1
Specific gravity, g/cm^3	1.32	1.34
Initial volume of stock A, mL[a]	120	120
Final total volume, mL[b]	214	218
Tc concentration in stock A, M	1.1 E-1	1.1 E-1
Tc concentration in supernatant, M	5.6 E-2	5.8 E-2
Initial Tc in final supernatant, %	88.4	92.7

(a) PUREX acid waste (see Appendix A).
(b) Supernatant + sludge.

TABLE 9. Plutonium Tracer Tests in Alkaline Supernatant

Parameter	pH 10.0	pH 13.1
Specific gravity, g/cm^3	1.35	1.34
Initial volume of stock A, mL[a]	120	120
Final total volume, mL[b]	214	218
Pu concentration in stock A, M	1.4 E-8	1.4 E-8
Pu concentration in supernatant, M	3.3 E-10	ND[c]
Initial Pu in final supernatant, %	4.1	ND

(a) PUREX acid waste (see Appendix A).
(b) Supernatant + sludge.
(c) ND = not detectable.

The major findings of this study are:

- Levels of $SO_4^=$ were reduced in the sludge phase to an equivalent loading of $\leq$1 wt% Na_2SO_4 in the waste glass after four water washes.
- Levels of Na were reduced in the sludge phase to an equivalent loading of <7 wt% Na_2O in the waste glass after four water washes.

TABLE 10. Neptunium Tracer Tests in Alkaline Supernatant

Parameter	pH 10.1	pH 13.3
Specific gravity, g/cm^3	1.33	1.33
Initial volume of stock A, mL[a]	120	120
Final total volume, mL[b]	218	220
Np concentration in stock A, M	5.8 E-4	5.8 E-4
Np concentration in supernatant, M	8.6 E-5	8.6 E-6
Initial Np in final supernatant, %	27	2.7

(a) PUREX acid waste (see Appendix A).
(b) Supernatant + sludge.

TABLE 11. Americium Tracer Tests in Alkaline Supernatant

Parameter	pH 9.9	pH 13.7
Specific gravity, g/cm^3	1.34	1.34
Initial volume of stock A, mL[a]	120	120
Final total volume, mL[b]	218	220
Am concentration in stock A, M	4.2 E-6	4.2 E-6
Am concentration in supernatant, M	3.4 E-9	7.9 E-10
Initial Am in final supernatant, %	0.15	0.04

(a) PUREX acid waste (see Appendix A).
(b) Supernatant + sludge.

- The pH of the four successive H_2O washes remained constant (similar to the supernatant pH).
- The addition of Na-TiA to the simulated sludge-supernatant resulted in a DF of only 6.5 for Sr and 5.1 for Pu, versus 10^3 and 400, respectively, when added to supernatant only.
- Greater than 98% of the Sr, Pu, Eu, and Am remained in the sludge after four water washes.
- Both Cs and Tc washed out of the sludge similar to Na (i.e., 3 to 9% remained in the sludge after four water washes).

- The amount of Np was split between the supernatant (39%) and the washed sludge (60%).

The West Valley sludge may not wash as efficiently as the simulated sludge because it may not be possible to remove the wash solution to the same degree as in the laboratory centrifuge study. Thus, it is expected that more than four washes will be required. From experimental data, it is concluded that the addition of Na-TiA to the combined sludge-supernatant mixture would not be effective; it should be added to the supernatant only. The results are shown in the following sections.

Figure 4 shows the percent of total Cs remaining in sludge fraction as a function of number of wash steps for two cases: pH 10 waste, and pH 10 waste with Na-TiA (see Table 12 for detailed radiochemical data). Cesium and Tc are very similar to Na in washing characteristics. Approximately 4% of the Na, Cs, and Tc remains in the sludge after four water washes. Adding Na-TiA reduces washing efficiency.

Table 13 shows the percent of the total Sr and Pu in the final supernatant after four washes, with and without Na-TiA. Note that Pu was not added to the simulated waste in the same concentration as in the actual waste. Only enough Pu was added to assure that it was present in quantities greater than its solubility limit, so the percentages of Pu in Table 13 can be used only to determine DFs, not absolute quantities. The DF for the Na-TiA addition is only 6.5 for Sr and 5.1 for Pu. This is compared to a DF of 10^3 and 400 for Sr and Pu, respectively, when Na-TiA is added to the supernatant only.

Chemical Species

Figures 5 through 8 show the effect of the washing process on the amounts of Na^+, NO_2^-, NO_3^-, and $SO_4^=$ in the simulated sludge. The graphs are presented as percent of the total quantity of a chemical species remaining in the sludge fraction as a function of the number of wash steps. Each graph has four plots, one for each of the four cases studied: pH ~10 and pH ~13, with and without Na-TiA. Quantities of Na^+, NO_2^-, NO_3^-, and $SO_4^=$ and other chemical species are presented in Tables 14 through 17.

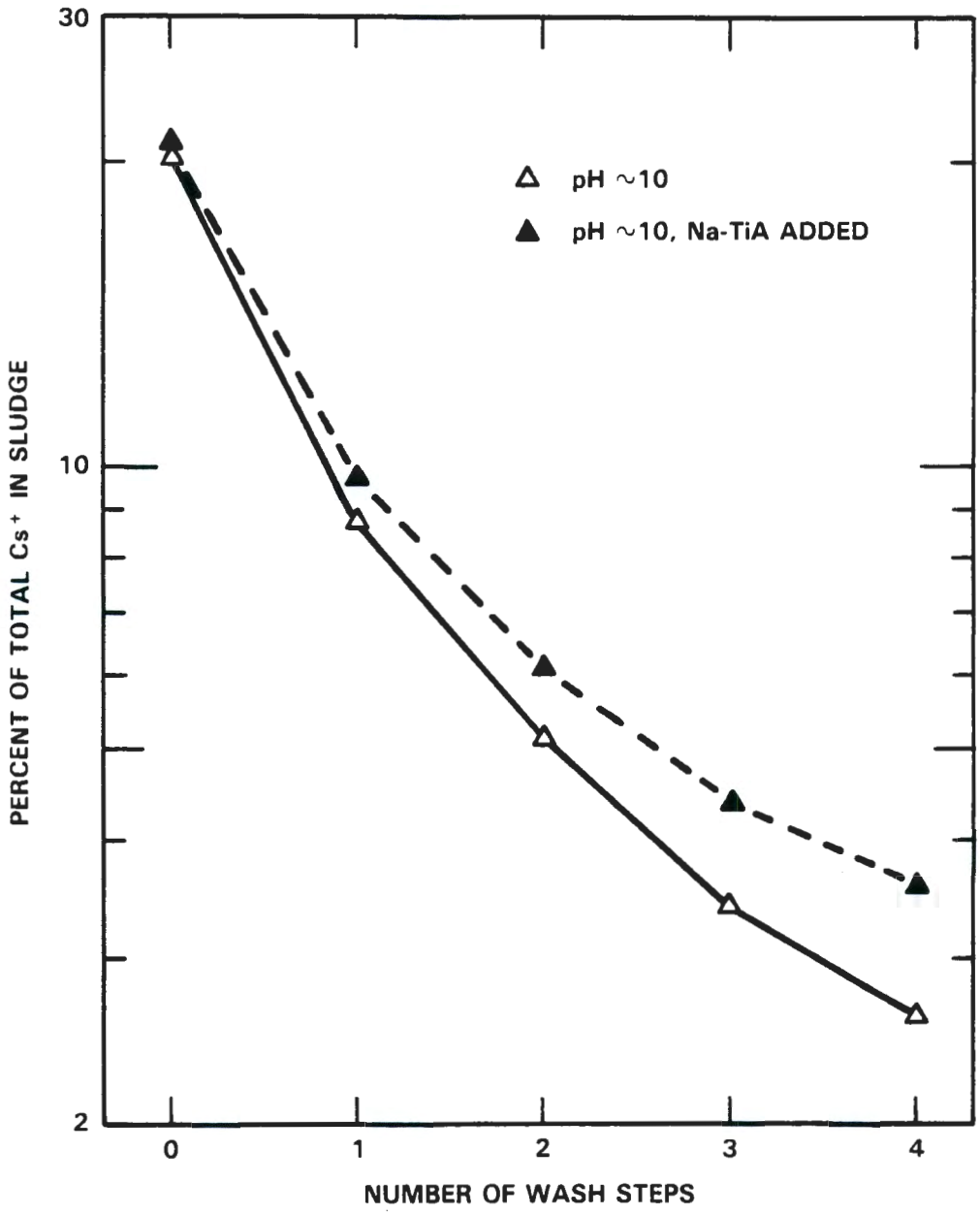


FIGURE 4. Percent of Total Cs^+ in Sludge as a Function of the Number of Wash Steps

For all species plotted, the case of pH ~10 with no Na-TiA shows the highest washing efficiency. The sulfate ion was reduced in all cases to <4% remaining in the sludge. This is equivalent to 1 wt% Na_2SO_4 in the waste glass. It is expected, however, that the sludge layer in Tank 8D2 is more

TABLE 12. Radiochemical Species Washing Data

Description	Cesium				Strontium				Plutonium			
	Volume Decanted, mL	H_2O Added, mL	pH	% in Soln.	Volume Decanted, mL	H_2O Added, mL	pH	% in Soln.	Volume Decanted, mL	H_2O Added, mL	pH	% in Soln.
Base Case (pH ~10)												
Supernatant	830	375	10.9	78.6	805	375	10.5	0.1	810	375	10.7	1.12
1st Wash	375	230	10.6	12.7	325	230	10.3	0.014	390	230	10.5	0.058
2nd Wash	230	200	10.6	3.6	245	200	10.3	0.005	235	200	10.5	0.25
3rd Wash	200	180	10.7	1.7	225	180	10.5	0.005	200	180	10.6	0.024
4th Wash	180	--	10.6	0.8	180	--	10.6	0.002	180	--	10.7	0.015
Dissolved Sludge	1000	--	--	2.8	1000	--	--	99.87	1000	--	--	98.53
pH ~10 + NaTIA												
Supernatant	850	375	11.0	78.1	830	375	10.6	0.054	840	375	11.2	0.154
1st Wash	355	230	10.9	12.2	335	230	10.5	0.006	365	230	11.0	0.048
2nd Wash	230	200	10.7	3.6	225	200	10.5	0.004	230	200	11.0	0.03
3rd Wash	200	180	10.9	1.7	200	180	10.7	0.0007	200	180	11.2	0.037
4th Wash	180	--	11.1	0.8	180	--	10.8	0.0003	180	--	11.2	0.029
Dissolved Sludge	1000	--	--	3.7	1000	--	--	99.98	1000	--	--	99.71

Description	Neptunium				Technetium				Europium				Americium			
	Volume Decanted, mL	H_2O Added, mL	pH	% in Soln.	Volume Decanted, mL	H_2O Added, mL	pH	% in Soln.	Volume Decanted, mL	H_2O Added, mL	pH	% in Soln.	Volume Decanted, mL	H_2O Added, mL	pH	% in Soln.
Base Case (pH ~10)																
Supernatant	830	375	10.4	38.8	830	375	10.6	75.3	830	375	9.9	~0.1	830	375	10.4	~0.1
1st Wash	335	230	10.0	1.0	335	230	10.4	10.6	310	230	9.9	~0.1	335	230	10.3	~0.1
2nd Wash	225	200	10.2	0.2	225	220	10.6	3.6	225	200	9.9	~0	225	200	10.4	~0
3rd Wash	200	180	10.0	0.1	200	180	10.3	1.8	200	180	9.9	~0	200	180	9.6	~0
4th Wash	180	--	10.8	--	180	--	10.4	--	180	--	10.0	~0	180	--	9.5	~0
Dissolved Sludge	1000	--	--	59.9	1000	--	--	8.6	1000	--	--	99.8	1000	--	--	99.8

TABLE 13. Percent of Total Sr and Pu in Final Washed Supernatant

Element	Percent in Final Supernatant		Na-TiA DF
	pH ~10	pH ~10 w/Na-TiA	
Strontium	0.13	0.02	6.5
Plutonium	1.5	0.29	5.1

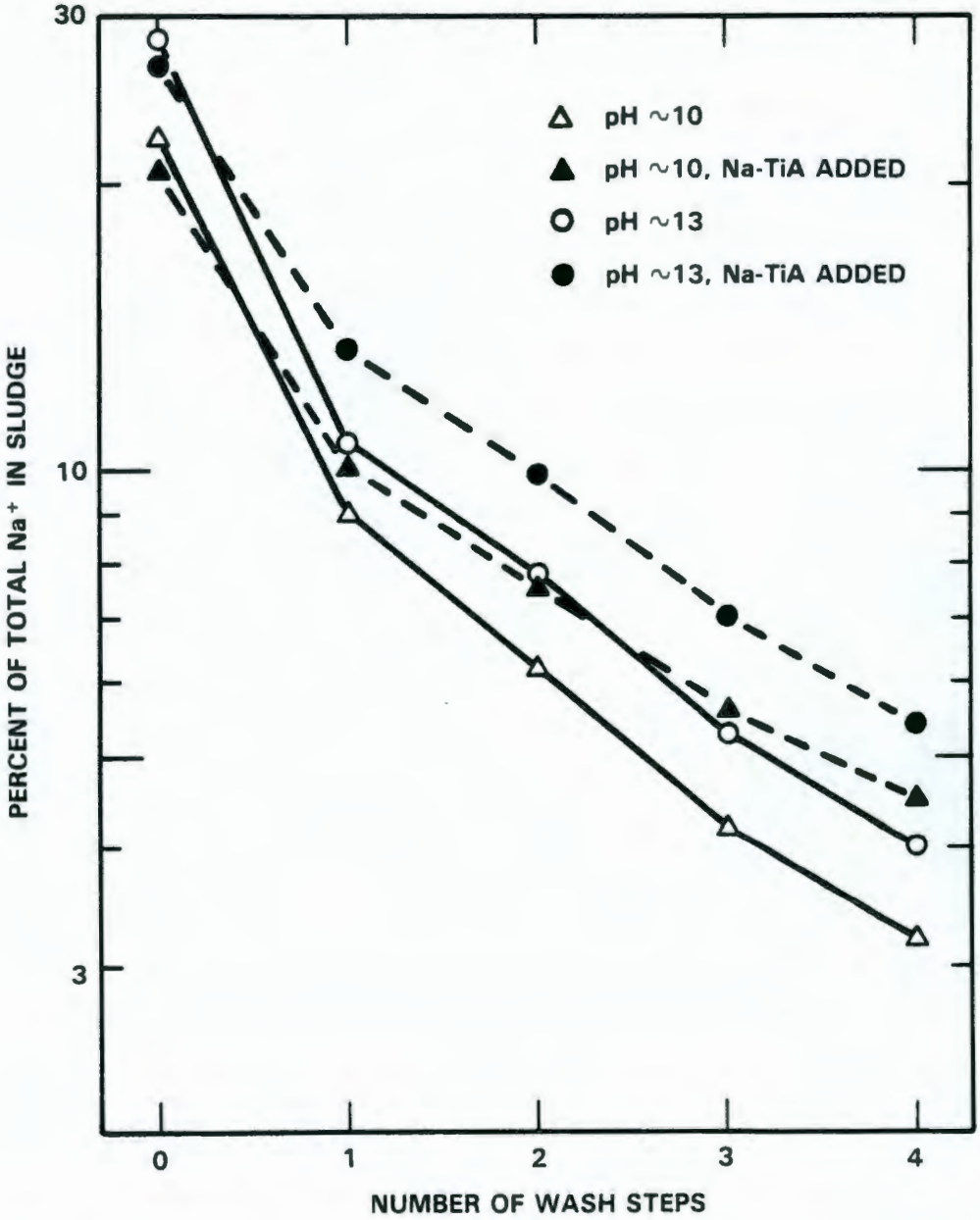


FIGURE 5. Percent of Total Na^+ in Sludge as a Function of the Number of Wash Steps

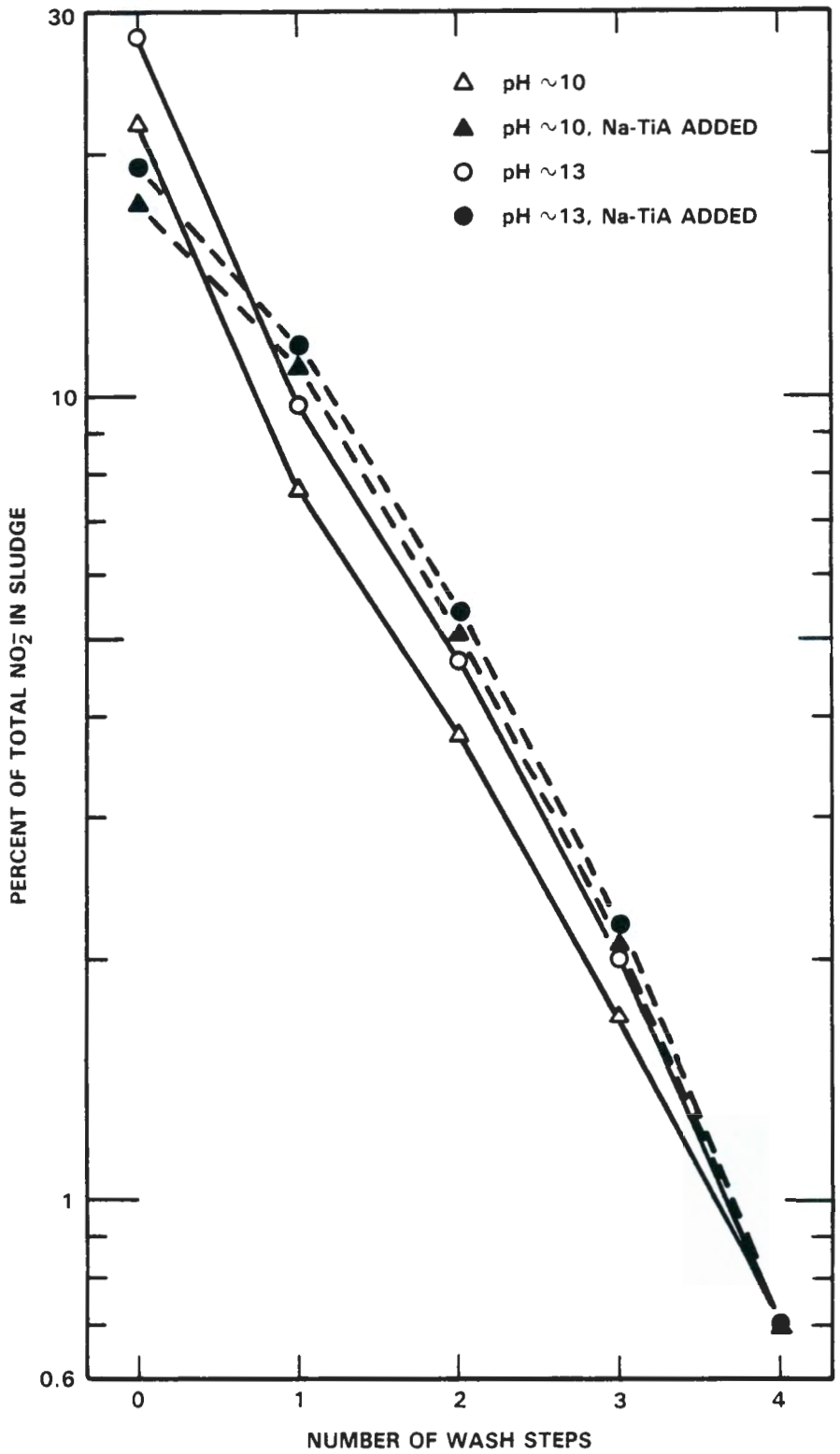


FIGURE 6. Percent of Total NO_2^- in Sludge as a Function of the Number of Wash Steps

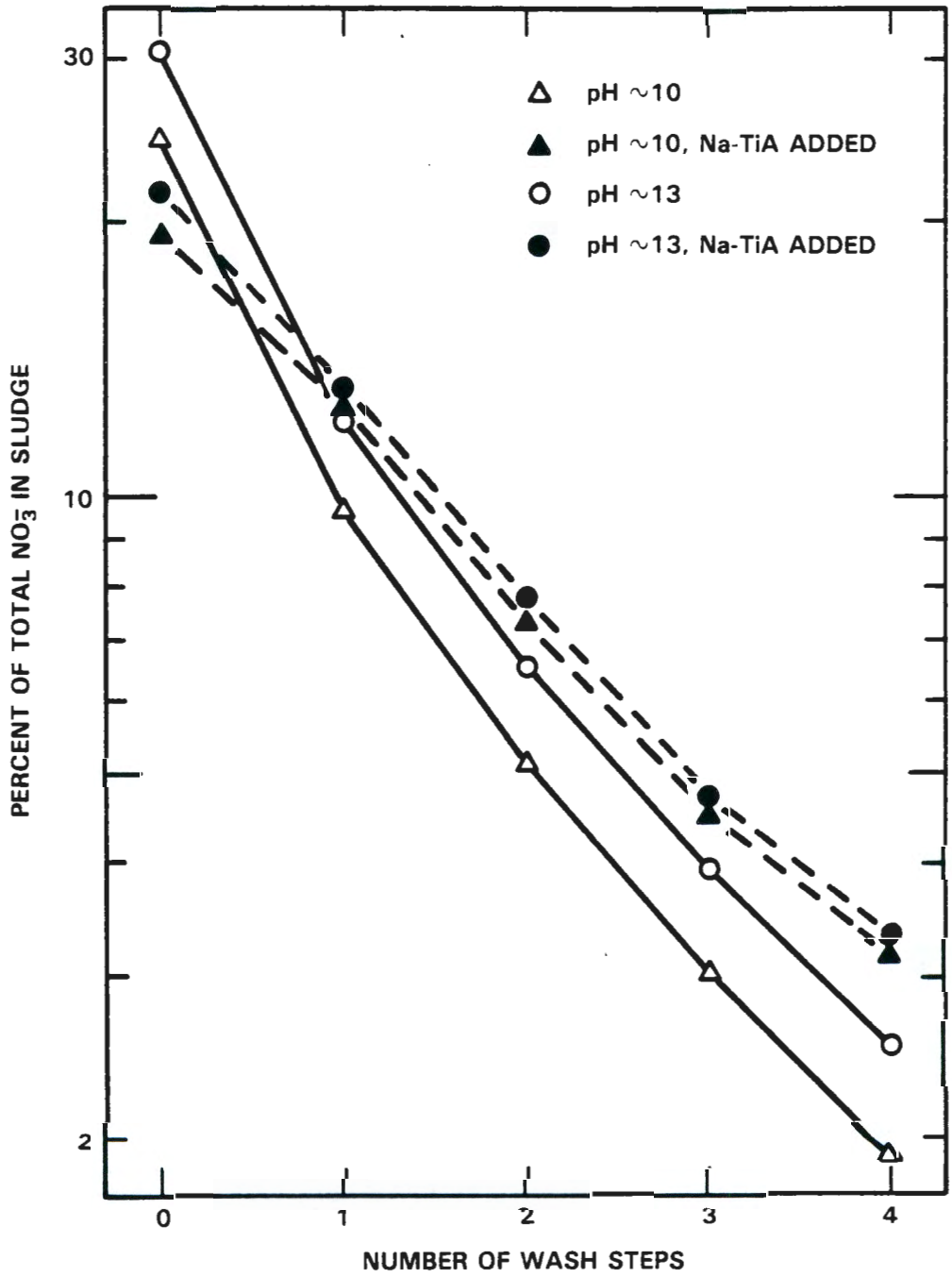


FIGURE 7. Percent of Total NO_3^- in Sludge as a Function of the Number of Wash Steps

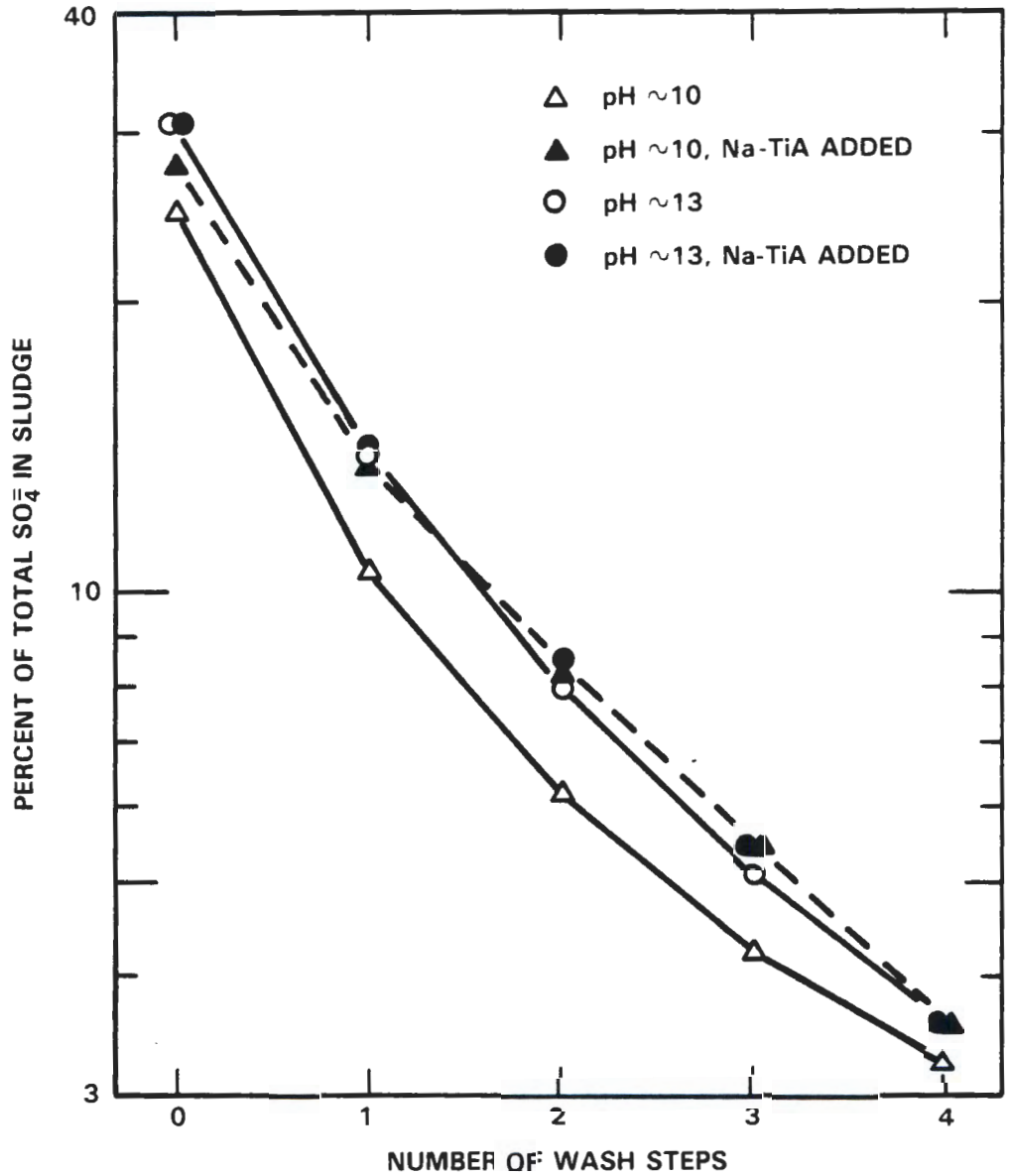


FIGURE 8. Percent of Total $SO_4^=$ in Sludge as a Function of the Number of Wash Steps

dense, and it may not be possible to achieve contacting conditions as favorable as in the laboratory.

There was no difference in the pH of the wash solutions and the supernatant.

TABLE 14. Chemical Species Washing Data, pH 10

Base Case (pH ~10)

Description	Vol Decanted, mL	H_2O Added, mL	pH	Results: % of total µg/mL																	Results: % of total mg/mL			
				Al	B	Ba	Ca	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	P	Si	Sr	Ti	Cl^-	NO_2	NO_3	SO_4
Supernatant	815	375	9.6	2.2	30.2	--	19.3	0.26	30.6	0.02	74.7	--	--	72.0	77.5	--	17.0	6.0	--	--	--	78.3	75.6	75.2
				12	3	--	5	5	2	5	2600	--	--	320	1.78 E5	--	650	4	--	2	<0.3	83	262	27.3
1st Wash	390	230	9.6	0.4	9.6	--	7.4	0.05	0.7	<0.001	10.7	--	--	14.0	13.5	--	4.4	0.6	--	--	--	14.0	14.8	14.4
				5	2	--	4	2	0.1	0.4	780	--	--	130	6.5 E4	--	350	0.8	--	0.1	<0.3	31	107	10.9
2nd Wash	225	200	9.8	0.2	1.9	--	1.2	0.02	1.3	<0.001	3.9	--	--	4.0	2.8	--	1.95	0.4	--	--	--	3.9	4.5	4.2
				3.9	0.7	--	1.1	1.1	0.3	0.8	490	0.8	--	65	2.3 E4	--	270	1	--	1	<0.3	15	57	5.5
3rd Wash	200	180	9.9	0.2	1.7	--	0.66	0.008	0.75	<0.001	2.3	--	--	3.0	2.0	--	1.45	0.4	--	--	--	2.1	2.1	1.96
				4	0.7	--	0.7	0.6	0.2	0.5	320	0.6	--	37	1.9 E4	--	225	1	--	--	<0.3	9.2	29	2.9
4th Wash	180	--	9.93	0.2	0.9	--	0.3	0.005	1.0	<0.001	1.4	--	--	1.0	1.0	--	1.16	0.7	--	--	--	1.0	1.1	0.97
				5	0.4	--	0.4	0.4	0.3	0.5	220	--	--	20	1 E4	--	200	2	--	--	<0.3	5.0	17	1.6
Dissolved Sludge	5000	--	--	96.8	55.6	100	71.1	99.7	65.7	99.98	7.0	--	100	6.9	3.2	100	74.0	92.0	100	--	--	<0.6	1.95	<3.4
				87	0.9	6.2	3	310	0.7	3700	40	--	74	5	1200	150	460	10	0.6	--	--	<0.1	1.1	<0.2
Material Balance, g				0.45	0.008	0.031	0.021	1.56	0.0054	18.5	2.84	--	0.37	0.362	187.2	0.75	3.11	0.055	0.003	--	--	86.4	282	29.6

TABLE 15. Chemical Species Washing Data, pH 10 + NaTi-A

Base Case pH 10 + NaTiA

Description	Vol Decanted, mL	H_2O Added, mL	pH	Results: % of total µg/mL																	Results: % of total mg/mL			
				Al	B	Ba	Ca	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	P	Si	Sr	Ti	Cl^-	NO_2	NO_3	SO_4
Supernatant	880	375	9.9	1.4	78.3	--	17.7	0.27	10.2	0.01	75.4	--	--	79.6	78.9	--	16.8	3.9	--	0.05	--	82.7	80.7	72.4
				13	5	--	4	5	2	2	2600	--	--	300	1.8 E5	--	560	3	--	3	<0.3	76	245	23.6
1st Wash	325	230	10.0	0.3	11.6	--	4.9	0.04	0.6	0.001	7.8	--	--	10.9	10.3	--	4.2	0.33	--	0.001	--	6.4	6.9	13.9
				8	2	--	3	2	0.3	0.7	730	--	--	120	6.3 E4	--	380	0.7	--	0.2	<0.3	16	57	12.3
2nd Wash	225	200	10.0	0.2	4.0	--	1.5	0.01	0.4	<0.001	3.4	--	--	3.9	2.5	--	2.3	0.49	--	<0.001	--	5.8	5.1	5.3
				7.4	1	--	1.3	1	0.3	0.3	460	0.9	--	63	2.2 E4	--	300	1.5	--	0.1	<0.3	20.8	60	6.8
3rd Wash	200	180	10.0	0.2	3.6	--	--	0.009	1.05	--	2.2	--	--	2.1	2.0	--	1.9	0.2	--	--	--	3.0	2.8	2.9
				8	1	--	--	0.7	0.9	--	330	--	--	38	2 E4	--	280	0.7	--	--	<0.3	12.3	38	4.2
4th Wash	180	--	10.2	0.2	2.6	--	0.63	0.006	0.6	<0.001	1.4	--	--	1.2	1.1	--	1.5	--	--	--	--	1.4	1.35	1.9
				8	0.8	--	0.7	0.5	0.6	0.4	230	--	--	2.4	1.2 E4	--	250	--	--	--	<0.3	6.3	20	3.0
Dissolved Sludge	5000	--	--	97.7	--	100	75.3	99.7	87.1	100	9.9	--	100	8.4	4.5	100	73.3	95.1	100	99.95	--	<0.6	3.2	<1.5
				160	--	7	3	320	3	3600	60	--	73	6	1800	150	430	13	0.5	1100	--	<0.1	1.7	<0.2
Material Balance, g				0.819	0.006	0.035	0.02	1.61	0.017	18.0	3.04	--	0.365	0.359	199.4	0.75	2.94	0.069	0.003	5.5	--	80.9	267	28.7

TABLE 16. Chemical Species Washing Data, pH 13

Base Case pH ~13

Description	Vol Decanted, mL	H_2O Added, mL	pH	Results: % of total / µg/mL																		Results: % of total / mg/mL			
				Al	B	Be	Ca	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	P	Si	Sr	Ti	Cl^-	NO_2	NO_3	SO_4
Supernatant	760	575	12.4	1.6	81.6	--	8.7	0.7	29.0	0.008	68.6	--	--	69.5	71.8	--	60.3	39.3	--	21.8	--	72.1	69.5	69.4
				13	350	--	4	14	2	2	2600	--	--	420	1.9 E5	--	1900	370	--	1.5	<0.3	81	258	24.5
1st Wash	345	250	12.5	0.2	2.3	--	5.1	0.2	0.9	0.001	13.4	--	--	18.4	17.5	--	22.3	14.9	--	0.85	--	18.2	18.4	16.6
				3	170	--	4	6	0.1	0.3	870	--	--	190	7.9 E4	--	1200	240	--	0.1	<0.3	35	117	10.0
2nd Wash	225	200	12.2	0.07	6.2	--	0.65	0.05	1.7	0.002	4.2	1.0	--	4.8	3.0	--	6.3	6.9	--	0.86	--	5.0	5.6	6.1
				1.9	90	--	1	3.5	0.4	1.4	540	0.9	--	100	2.7 E4	--	670	220	--	0.2	<0.3	19	70	7.3
3rd Wash	200	180	12.4	0.06	3.4	--	--	0.025	0.8	<0.001	2.6	0.6	--	2.6	2.4	--	3.1	5.6	--	--	--	2.7	2.6	2.8
				2	55	--	--	2	0.2	0.4	380	0.6	--	60	2.4 E4	--	370	200	--	--	<0.3	11.5	37	3.7
4th Wash	180	--	12.2	0.03	1.9	--	--	0.01	1.0	<0.001	1.6	--	--	1.4	1.3	--	1.8	5.3	--	--	--	1.4	1.4	1.5
				1	35	--	--	1	0.3	0.6	260	--	--	35	1.5 E4	--	240	210	--	--	<0.3	6.6	22	2.2
Dissolved Sludge	5000	--	--	98.0	4.6	100	85.6	99.1	66.7	99.99	9.5	98.4	100	3.3	4.0	100	6.3	28.0	100	76.5	--	<0.6	2.5	<3.7
				120	3	5	6	320	0.7	3800	55	4	75	3	1600	150	30	40	0.6	0.8	--	<0.1	1.4	<0.2
Material Balance, g				0.61	0.33	0.025	0.035	1.62	0.005	19.0	2.88	0.02	0.375	0.46	201	0.75	2.40	0.72	0.003	0.005	--	85.4	282	26.9

TABLE 17. Chemical Species Washing Data, pH 13 + Na-TiA

Base Case pH ~13 + NaTiA

Description	Vol Decanted, mL	H_2O Added, mL	pH	Results: % of total / µg/mL																		Results: % of total / mg/mL			
				Al	B	Be	Ca	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	P	Si	Sr	Ti	Cl^-	NO_2	NO_3	SO_4
Supernatant	825	575	13.1	5.3	68.5	--	15.6	9.6	7.5	0.009	71.2	--	--	71.4	73.5	--	47.3	1.2	--	0.01	--	81.8	78.6	69.5
				57	115	--	4	180	2	2	2500	--	--	380	1.8 E5	--	1700	20	--	1	<0.3	76	245	23.6
1st Wash	370	250	13.0	2.3	14.2	--	7.0	2.0	0.5	0.002	9.6	--	--	15.2	13.2	--	21.2	0.3	--	0.002	--	7.6	8.2	16.3
				55	53	--	4	84	0.3	1	750	--	--	180	7.2 E4	--	1700	11	--	0.3	<0.3	16	57	12.3
2nd Wash	255	200	12.6	1.2	5.4	--	1.1	0.8	0.3	<0.001	4.4	0.8	--	5.4	3.4	--	7.9	0.2	--	<0.001	--	6.2	5.5	5.7
				45	32	--	1	50	0.3	0.5	540	0.7	--	100	2.9 E4	--	1000	10	--	0.2	<0.3	20.6	60	6.8
3rd Wash	200	180	12.6	1.0	2.9	--	2.8	0.4	0.5	0.001	2.8	--	--	3.0	2.9	--	4.2	0.2	--	--	--	3.2	3.0	3.0
				44	20	--	3	33	0.6	1	400	--	--	65	2.9 E4	--	630	11	--	--	<0.3	12.3	38	4.2
4th Wash	180	--	12.5	0.8	1.8	--	2.6	0.2	--	<0.001	1.7	--	--	1.6	1.6	--	2.5	0.1	--	--	--	1.5	1.4	1.9
				39	14	--	3	20	--	0.9	270	--	--	40	1.8 E4	--	420	10	--	--	<0.3	6.3	20	3.0
Dissolved Sludge	5000	--	--	89.5	7.2	100	70.9	87.0	91.1	99.99	10.4	99.2	100	3.4	5.4	100	16.8	98.0	100	99.98	--	<0.6	3.3	<3.6
				160	2	6	3	270	4	3700	60	4	75	3	2200	150	100	270	0.6	1200	--	<0.1	1.7	<0.2
Material Balance, g				0.89	0.14	0.03	0.022	1.55	0.022	18.5	2.90	0.02	0.375	0.44	202	0.75	2.97	1.38	0.003	6.0	--	77.6	257	28.0

Radiochemical Species

The Cs and Tc in the alkaline waste behaved much like Na. Plutonium and Sr behave as expected in the alkaline waste; however, when Na-TiA was added to the sludge/supernatant mixture, it failed to achieve the DFs possible when it is added to the supernatant only. We believe that the Na-TiA removes the Sr and Pu from the supernatant, but that the supernatant then reequilibrates with the Sr- and Pu-laden sludge phase, putting more Sr and Pu back into the supernatant. It is not feasible, then, to add Na-TiA directly to Tank 8D2. If Na-TiA is used, it should be added only to the washed supernatant solution. Greater than 98% of the Sr, Pu, Eu, and Am remain with the sludge after four washes. The distribution of Np is split between the supernatant (~40%) and the washed sludge (~60%).

PRECIPITATION AND SORPTION PROCESSES

The objective of the following section was to provide data using synthetic alkaline supernatant to support the precipitation process. A simplified schematic for this approach is shown in Figure 9. The precipitation process which uses Na-TPB [$Na(C_6H_5)_4B$] to selectively precipitate Cs^+, K^+ and Rb^+, and Na-TiA ($Na_2Ti_3O_7$) to adsorb Sr^{2+} and Pu from the alkaline supernatant was developed at Savannah River Laboratory by Lee and Kilpatrick (1982) as an alternative to ion exchange. The attractive features of the process include its ability to provide high DFs for Cs (~10^4) and Sr (~200) from alkaline supernatant in a single batch contact. The process has been demonstrated in a full-scale test at SRP in 1983.

Laboratory-scale experiments were conducted to study the performance of the Na-TPB precipitation process for recovery of Cs, and the Na-TiA precipitation process for recovery of Sr and Pu from simulated West Valley alkaline supernatant. The effects of the following process variables were examined: temperature (25 and 50°C), pH (10.4 and 13.7), contact time (1 to 14 days), and quantity of precipitant chemical added. The experimental procedure is given in Appendix C.

The Na-TiA process showed enhanced recovery of Sr and Pu at a pH of 13.7 compared to 10.4, and a temperature of 50°C compared to 25°C. Recovery of Sr

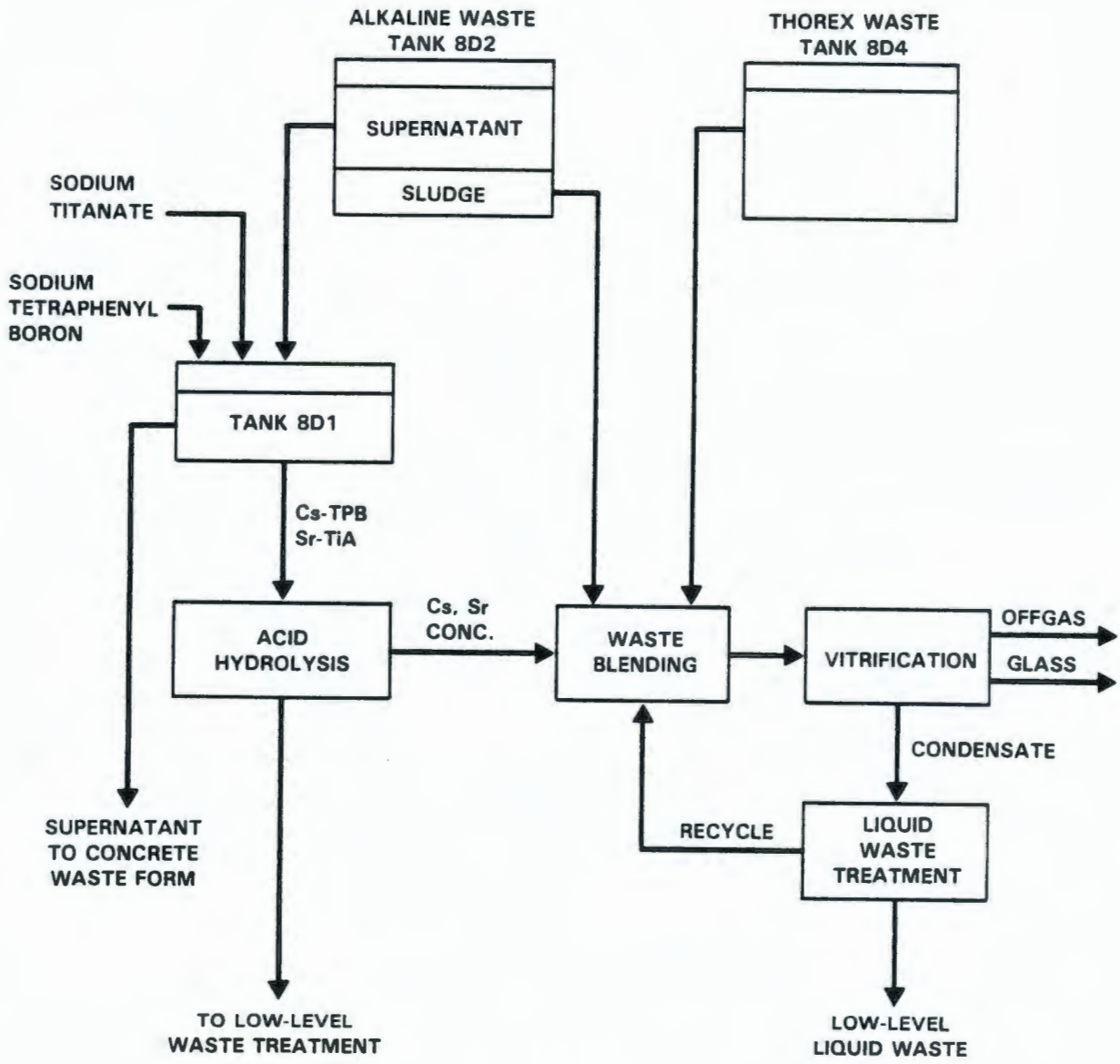


FIGURE 9. Precipitation Process

was independent of Sr concentration, indicating that Sr concentration is not a controlling factor. The Na-TiA precipitation process reached equilibrium with respect to recovery of Sr and Pu within 2 days. The performance of the Na-TiA recovery process improved with increasing concentrations of Na-TiA; however, the relative decontamination performance of the Na-TiA process decreased with increasing additions of Na-TiA. The Na-TiA recovery process is not selective for Sr or Pu.

Cesium Precipitation Using Na-TPB

The following test parameters were examined for the Cs precipitation process:

- mole ratio Na-TPB/Cs+K+Rb (0.007 to 2.3)
- pH (~10 and ~13)
- contact time (1 to 14 days)
- temperature (25 and 50°C)
- Na concentration in the alkaline supernatant (3 to 6M).

The experimental results for recovery of Cs from the alkaline supernatant using Na-TPB are summarized in Tables 18 and 19 and are shown graphically in Figures 10 and 11.

TABLE 18. Precipitation of Cesium Using Na-TPB[a]

Na-TPB/Cs+K+Rb, Mole Ratio	Fraction Cesium in Solution, C/Co		Final Na^+ Concentration, M	
	pH 12.8	pH 10.0	pH 12.8	pH 10.0
7.0 E-3	9.9 E-1	9.6 E-1	6.8	6.6
1.4 E-2	9.1 E-1	9.1 E-1	6.8	6.6
2.1 E-2	8.9 E-1	8.7 E-1	6.8	6.6
7.0 E-2	5.6 E-1	4.7 E-1	5.7	5.4
1.1 E-1	4.8 E-1	3.2 E-1	5.7	5.4
1.4 E-1	3.0 E-1	3.1 E-1	5.7	5.4
1.7 E-1	2.8 E-1	2.8 E-1	5.7	5.4
4.6 E-1	3.0 E-1	2.6 E-1	5.8	5.6
6.8 E-1	1.3 E-1	1.1 E-1	5.8	5.6
9.1 E-1	8.7 E-2	5.4 E-2	5.8	5.6
1.1 E+0	2.8 E-2	1.3 E-2	5.8	5.6
1.7 E+0	8.5 E-5	9.0 E-5	5.0	4.8
2.3 E+0	6.8 E-5	1.0 E-4	5.0	4.8

(a) Feed: ~7M Na^+; 1.1 x 10^{-3}M Cs^+; 0.069M K^+; 1 x 10^{-4}M Rb^+.
Contact Time: 16 to 24 hours.
Temperature: ~25°C.

TABLE 19. Removal of Cesium from Alkaline Supernatant Using Na-TPB at Different Temperatures and Sodium Concentrations[a]

Na-TPB/ Cs+K+Rb, Mole Ratio	Final Na^+ Conc., M	Temp., °C	Fraction Cesium in Solution, C/Co			
			1 Day	3 Days	7 Days	14 Days
7.0 E-1	4	25	9.3 E-2	8.8 E-2	8.7 E-2	8.4 E-2
7.0 E-1	4	50	1.1 E-1	1.1 E-1	1.1 E-1	1.1 E-2
1.0 E+0	4	25	2.4 E-3	2.3 E-2	2.0 E-2	2.0 E-2
1.0 E+0	4	50	1.4 E-2	2.5 E-2	2.3 E-2	2.3 E-2
1.1 E+0	4	25	4.0 E-3	8.0 E-3	6.0 E-3	5.0 E-3
1.1 E+0	4	50	2.0 E-3	7.0 E-3	5.0 E-3	4.0 E-3
1.4 E+0	4	25	2.0 E-3	7.0 E-6	2.0 E-5	3.0 E-4
1.4 E+0	4	50	2.0 E-5	4.0 E-5	2.0 E-5	2.0 E-4
1.8 E+0	4	25	6.0 E-5	~0	~0	3.0 E-4
1.8 E+0	4	50	3.0 E-5	4.0 E-5	~0	2.0 E-4
1.1 E+0	6	25	2.3 E-1	1.9 E-1	1.5 E-1	1.3 E-1
1.1 E+0	6	50	1.8 E-1	1.6 E-1	1.4 E-1	1.3 E-1
1.1 E+0	5	25	5.2 E-2	3.3 E-2	2.4 E-2	2.0 E-2
1.1 E+0	5	50	4.9 E-2	2.9 E-2	2.3 E-2	2.0 E-2
1.1 E+0	4	25	1.0 E-2	6.0 E-3	6.0 E-3	3.0 E-3
1.1 E+0	4	50	8.0 E-3	2.0 E-4	7.0 E-5	7.0 E-4
1.1 E+0	3	25	~0	2.0 E-4	~0	7.0 E-4
1.1 E+0	3	50	1.5 E-2	4.0 E-3	8.0 E-5	5.0 E-4

(a) Feed: 7M Na^+; 0.001M Cs^+; 0.16M K^+; 1 x 10^{-4}M Rb^+; pH 10.4.

Cs recovery using Na-TPB is dramatically improved when the mole ratio Na-TPB to Cs+K+Rb is >1. This indicates strong competition between the cations (Cs, K, and Rb) in the precipitation reaction. Once the cation concentration is equivalent to the Na-TPB concentration, the recovery of Cs by Na-TPB is very efficient. To achieve a Cs DF of $>10^4$, this ratio must be at least 1.4 (Na-TPB required was estimated to be 2 x 10^5 kg for Tank 8D2). However, at mole ratios >1, the soluble Na-TPB concentration increases in the supernatant. This situation may pose difficulties in supernatant disposal because soluble Na-TPB could complex radionuclides, making them more leachable from the LLW form. Also, the

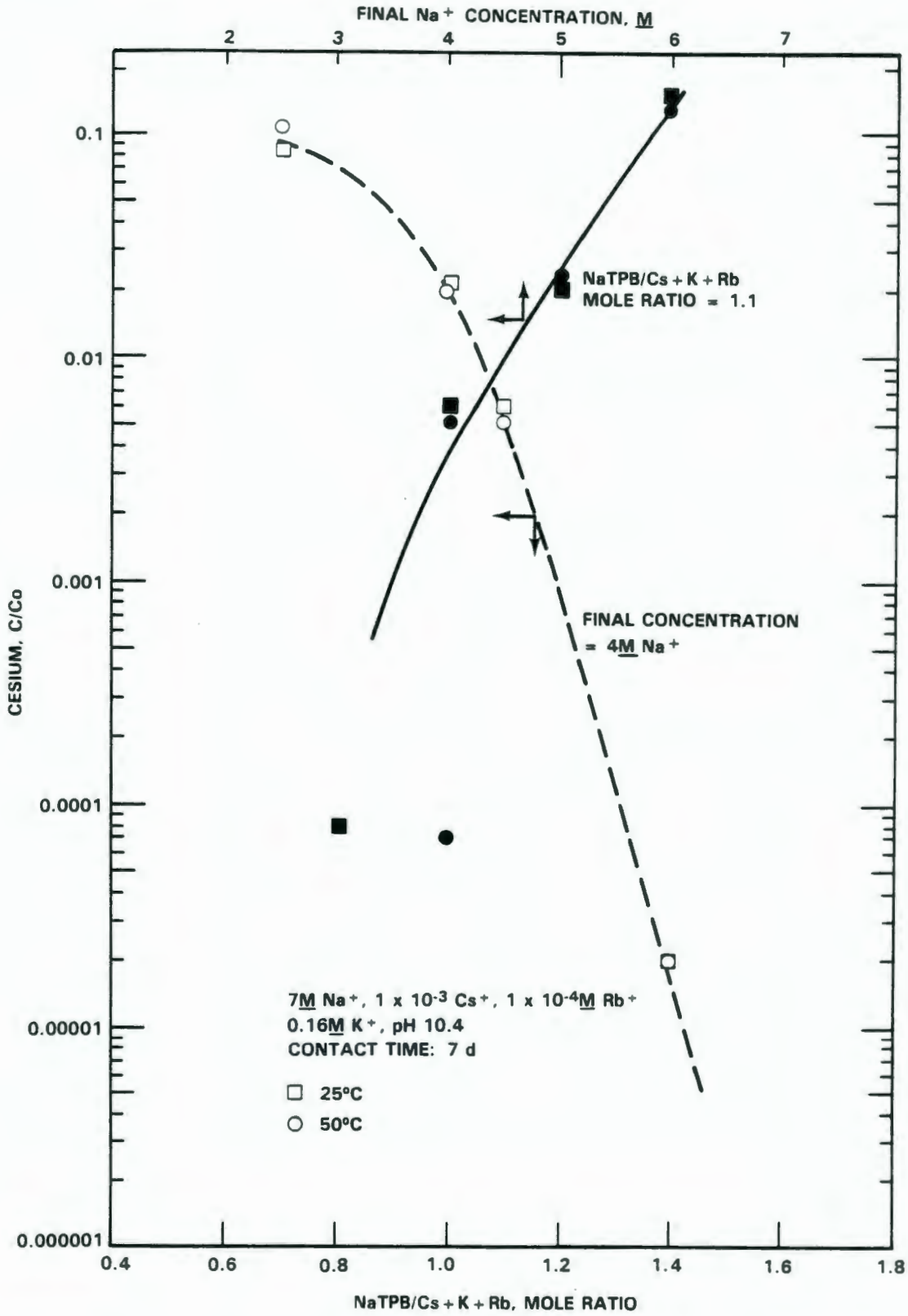


FIGURE 10. Cesium Precipitation from Simulated West Valley Alkaline Supernatant as a Function of Na-TPB/Cs+K+Rb Mole Ratio, 4M Na^+

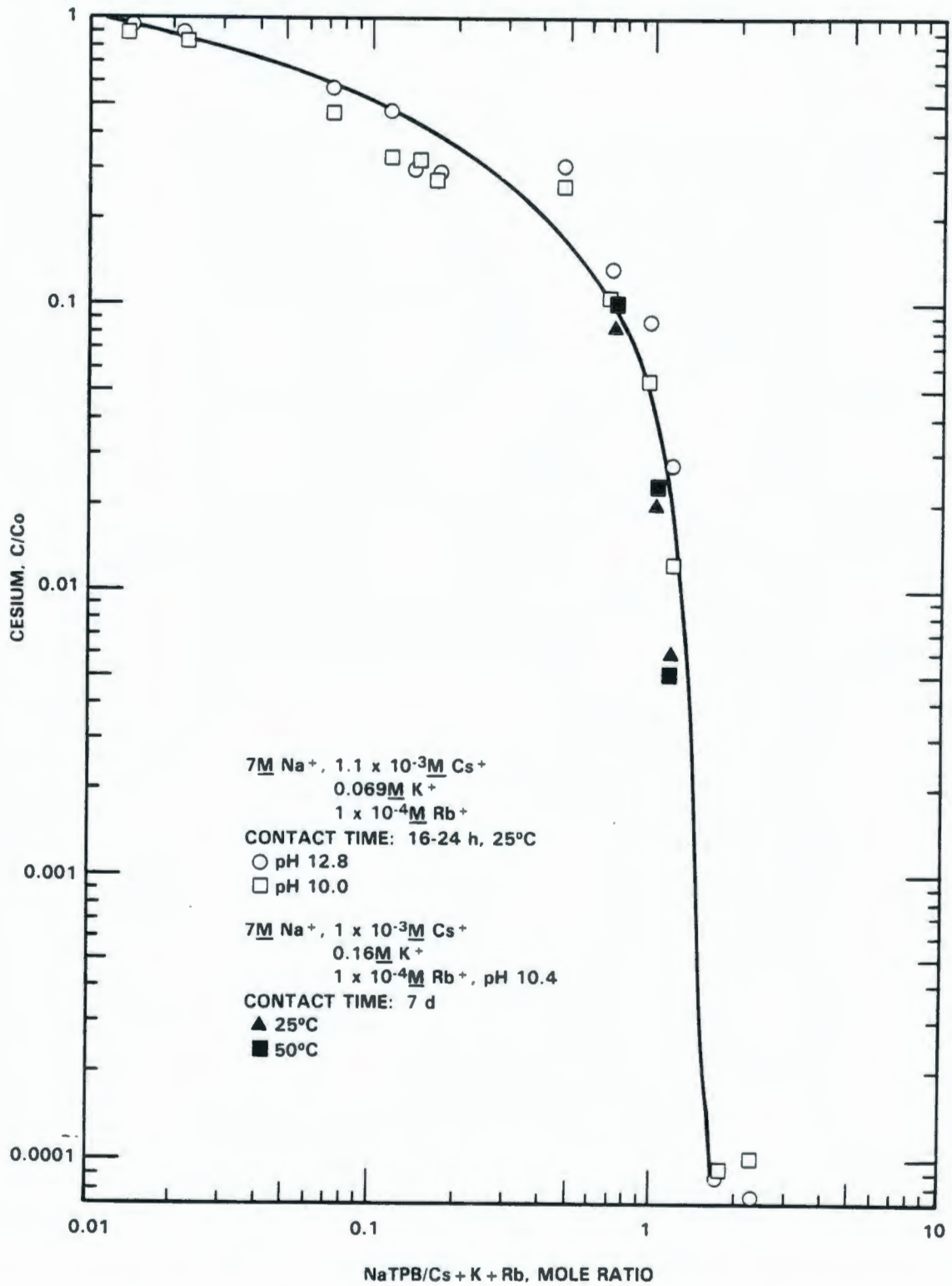


FIGURE 11. Cesium Precipitation from Simulated West Valley Alkaline Supernatant as a Function of Na-TPB/Cs+K+Rb Mole Ratio, 7M Na^+

soluble Na-TPB may interfere with Tc recovery by organic anion exchange because the TPB anion will use up resin capacity.

The recovery of Cs from the alkaline supernatant is independent of solution pH in the range of 10.4 to 12.8, as shown in Figure 10 and Table 18.

Recovery of Cs from alkaline supernatant with Na-TPB is dependent on contact time at times <7 days as shown in Table 19. The recovery fractions were erratic with <7 days of contact time. After 7 days, the system became stable with a consistent recovery fraction for Cs.

The recovery of Cs from the alkaline waste supernatant using Na-TPB is essentially temperature independent in the range 25 to 50°C as shown in Table 19 and Figures 10 and 11.

Both the Na-TPB and the Na-TiA should be added to the supernatant after it has been separated from the sludge. The Na-TPB precipitate has a gelatinous consistency and floats on the top of the supernatant when sludge is present. Adding the Na-TPB to the supernatant/sludge mixture will complicate the sludge washing operation and treatment of the organic precipitate prior to vitrification of the waste. Adding the Na-TPB mixture to a separate supernatant phase simplifies processing operations.

Strontium and Plutonium Adsorption Using Na-TiA

The following test parameters were examined for the Sr/Pu recovery process:

- mole ratio Na-TiA/Sr (740 to 6100)
- pH (~10 and ~13)
- contact time (1 to 14 days)
- temperature (25 and 50°C).

Initial experiments involved recovery of Sr and Pu with Na-TiA in which the stock supernatants were prepared by neutralization of simulated acidic PUREX waste. The experimental results are summarized in Table 20 and Figure 12.

TABLE 20. Removal of Strontium from Alkaline Supernatant Using Na-TiA Slurry

Na-TiA, M[a]	Na-TiA to Sr Mole Ratio	Fraction Sr in Solution, C/Co
	2.74×10^{-8} M Sr^{2+}; pH 12.8	
1.5 E-2	5.5 E+5	1.1 E-2
2.3 E-2	7.9 E+5	6.6 E-3
4.3 E-2	1.6 E+6	2.2 E-3
6.2 E-2	2.3 E+6	9.0 E-4
	2.16×10^{-8} M Sr^{2+}; pH 10.0	
1.6 E-2	7.6 E+5	4.1 E-2
2.2 E-2	1.0 E+6	3.3 E-2
3.6 E-2	1.7 E+6	1.5 E-2
6.7 E-2	3.1 E+6	6.5 E-3

(a) Feed: ~7M Na^+; 16 hour contact.
(b) Assuming 1.5 E-3 moles/g of centrifuged Na-TiA.

Additional experiments were then completed to determine the removal of Pu and Sr from alkaline supernatant as a function of pH, temperature, and contact time. These results are shown in Figures 12 and 13 and Table 21.

The recoveries of Sr and Pu from the supernatant were dependent on solution pH in the range 10 to 14. Both the Sr and Pu systems showed greater recovery with the use of Na-TiA at higher pH levels; Sr recovery improved by a factor of 10 as the pH is raised from 10.4 to 13.7, and Pu recovery improved by a factor up to 3 (Figure 13) when the pH is increased from 10.4 to 13.7. This improvement in recovery for Sr and Pu with increasing pH is not understood. Figure 12 shows that for two concentrations of Sr in the alkaline waste (1.3×10^{-5} M and 2.7×10^{-8} M), there was no increase in Sr recovery at a given pH level. This suggests that Na-TiA is not specific for Sr. Other ions in solution that may be controlling have not been identified.

Strontium recovery using Na-TiA is independent of temperature (Table 21 and Figure 12), but the recovery of Pu by Na-TiA is sensitive to temperature

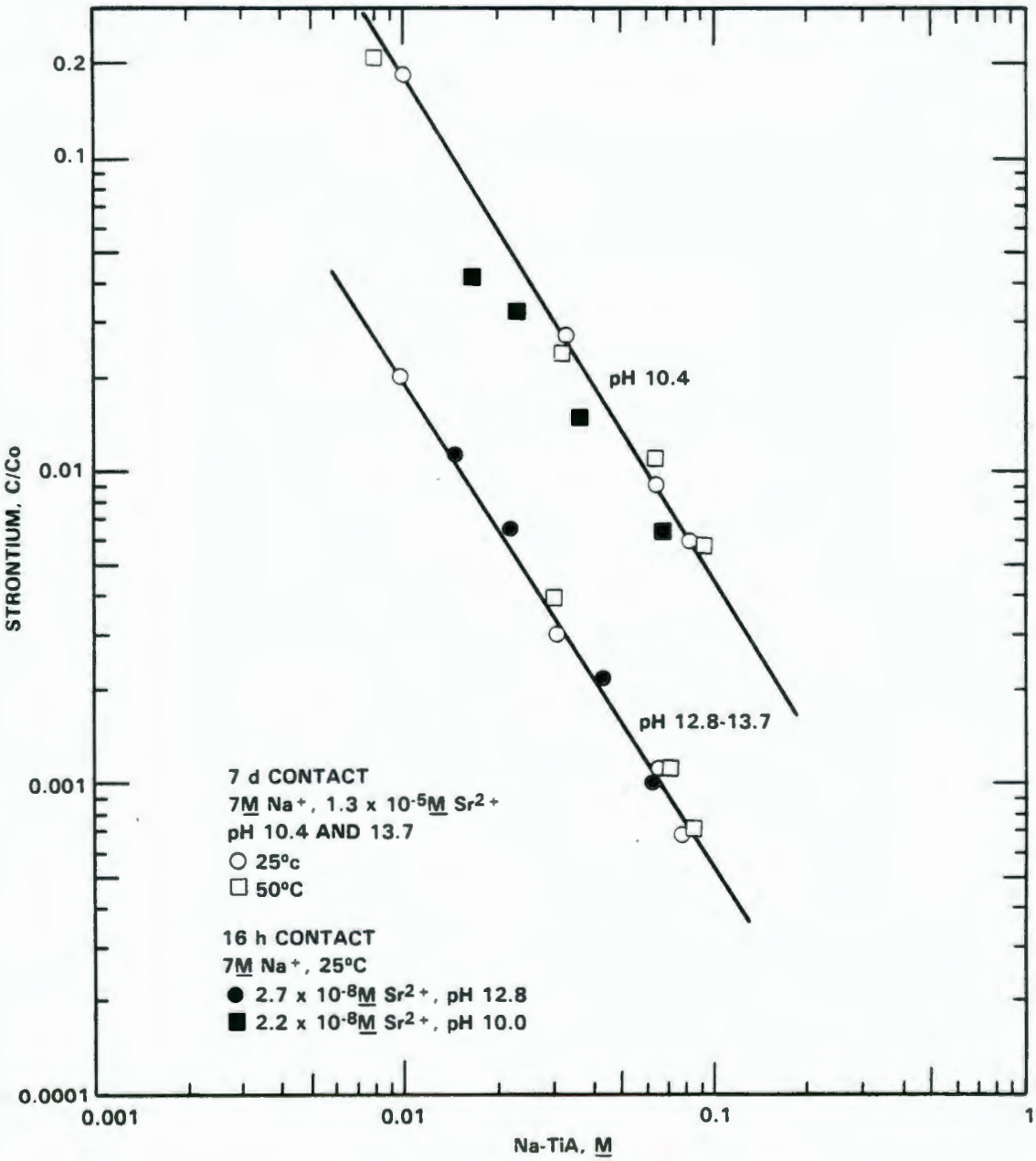


FIGURE 12. Adsorption of Strontium from Simulated West Valley Alkaline Supernatant Using Na-TiA

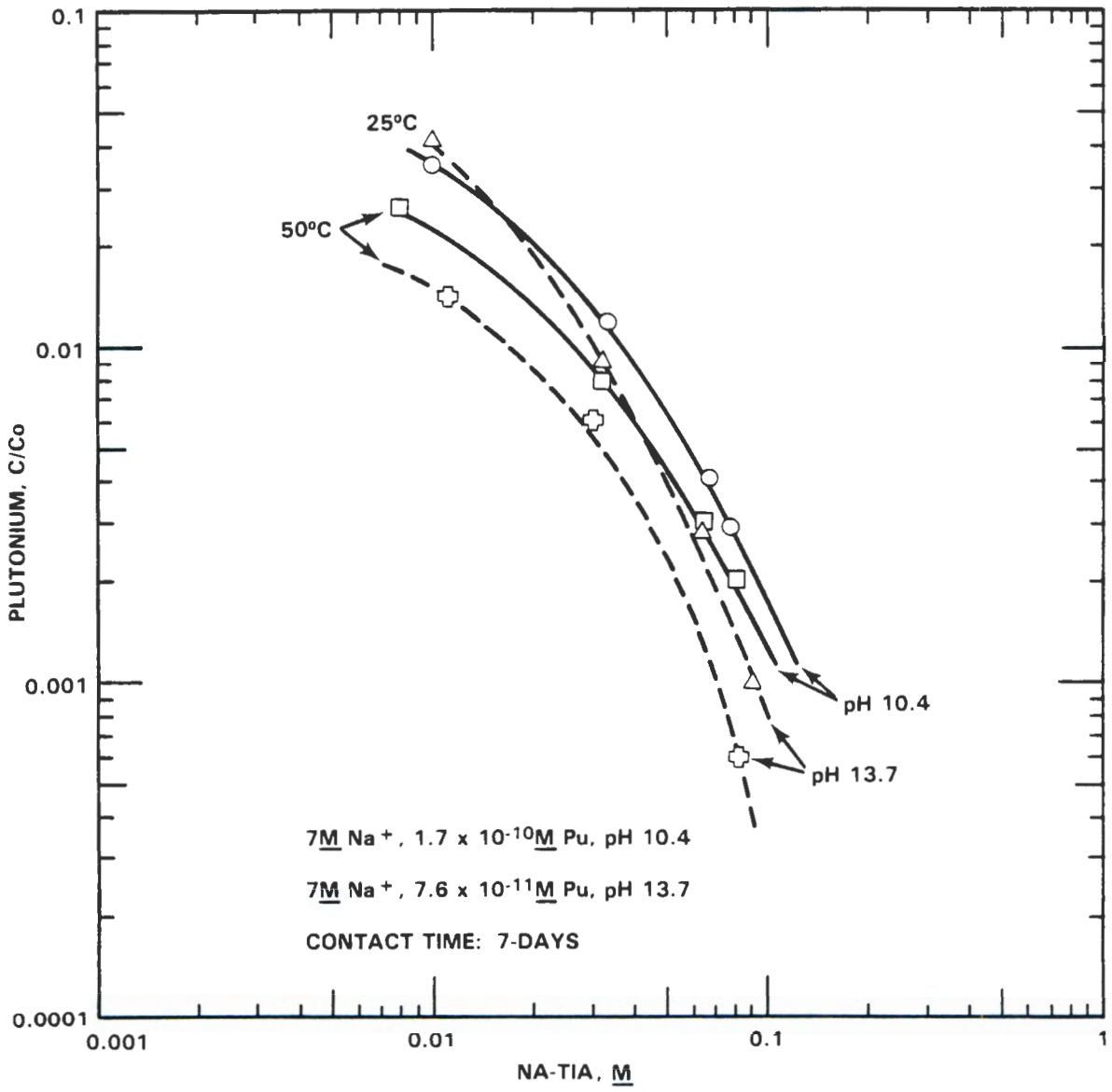


FIGURE 13. Adsorption of Plutonium from Simulated West Valley Alkaline Supernatant Using Na-TiA

(Table 21, Figure 13). At concentrations between 1 x 10^{-2}M and 8 x 10^{-2}M of Na-TiA, 1.5 to 3 times more Pu is removed at a temperature of 50°C compared to 25°C.

Strontium and Pu recovery is dependent upon contact time. As shown in Table 21, the recovery of Sr and Pu improved with contact times up to 2 days. At this time the system had stabilized at equilibrium. In general, Sr recovery

TABLE 21. Removal of Plutonium and Strontium from Alkaline Supernatant Using Na-TiA as a Function of pH and Temperature

Feed: ~7M Na^+; 1.3×10^{-5}M Sr^{2+}; pH 10.4; 1.7×10^{-10}M Pu; supernatant prepared by chemical mixing approach.

	Na-TiA, M	Na-TiA/Sr Mole Ratio	Fraction Sr in Solution, C/Co				Fraction Pu in Solution, C/Co			
			1 Day	2 Days	7 Days	14 Days	1 Day	2 Days	7 Days	14 Days
25°C	1.0 E-2	7.7 E+2	3.5 E-1	1.9 E-1	1.9 E-1	8.1 E-2	1.7 E-1	5.5 E-2	3.5 E-2	4.0 E-2
	3.3 E-2	2.6 E+3	6.4 E-2	2.7 E-2	2.7 E-2	2.6 E-2	3.5 E-2	2.0 E-2	1.2 E-2	1.9 E-2
	6.5 E-2	5.0 E+3	2.0 E-2	9.0 E-3	9.0 E-3	8.0 E-3	6.0 E-3	9.0 E-3	4.0 E-3	2.0 E-3
	7.7 E-2	6.0 E+3	1.8 E-2	6.0 E-3	5.0 E-3	5.0 E-3	1.3 E-2	7.0 E-3	3.0 E-3	2.0 E-3
50°C	8.0 E-3	6.2 E+2	3.1 E-1	2.0 E-1	2.2 E-1	2.2 E-1	6.8 E-2	3.7 E-2	2.6 E-2	--
	3.2 E-2	2.5 E+3	5.3 E-2	3.1 E-2	3.4 E-2	3.6 E-2	1.9 E-2	1.6 E-2	8.0 E-3	8.0 E-3
	6.4 E-2	5.0 E+3	4.7 E-2	1.0 E-2	1.1 E-2	1.1 E-2	1.8 E-2	7.0 E-3	3.0 E-3	2.0 E-3
	7.9 E-2	6.1 E+3	9.0 E-3	6.0 E-3	6.0 E-3	7.0 E-3	7.0 E-3	1.0 E-3	2.0 E-3	1.4 E-3
	Feed: ~7M Na^+; 1.2×10^{-5}M Sr^{2+}; pH 13.7; 7.6×10^{-11}M Pu									
25°C	9.6 E-3	7.4 E+2	6.2 E-2	2.1 E-2	2.0 E-2	1.7 E-2	--	--	4.1 E-2	2.4 E-2
	3.1 E-2	2.4 E+3	1.1 E-2	3.0 E-3	3.0 E-3	3.0 E-3	--	--	9.0 E-3	7.0 E-3
	6.5 E-2	5.0 E+3	3.0 E-3	1.3 E-3	1.2 E-3	1.0 E-1	--	--	3.0 E-3	5.0 E-4
	7.8 E-2	6.0 E+3	2.0 E-3	9.0 E-4	7.0 E-4	7.0 E-4	--	--	<1.0 E-3	1.4 E-3
50°C	1.1 E-2	8.1 E+2	5.2 E-2	2.0 E-2	2.7 E-2	2.9 E-2	--	--	1.4 E-2	1.1 E-2
	3.0 E-2	2.3 E+3	7.0 E-3	3.0 E-3	4.0 E-3	4.6 E-3	--	--	6.0 E-3	4.4 E-3
	6.6 E-2	5.1 E+3	2.0 E-3	1.0 E-3	1.0 E-3	1.2 E-3	--	--	<1.0 E-4	1.6 E-3
	7.9 E-2	6.1 E+3	1.0 E-3	6.0 E-4	7.0 E-4	1.2 E-3	--	--	<6.0 E-4	<5.0 E-4

improved by a factor of 1.3 to 2 after 2 days of contact; the Pu recovery improved by a factor of ~2 after 2 days of contact.

Strontium recovery improved with increased additions of Na-TiA. However, the relative rate of recovery decreased. For example, at a pH = 10.4, 0.01M Na-TiA removed 82% of Sr in solution. Doubling the Na-TiA concentration increased the decontamination performance only by an additional 12%. Absolute and relative rates of recovery for Pu also showed the same behavior, indicating that Na-TiA is not specific for Sr or Pu, and that competing ions (possibly Cr, Fe, or Ni) have a strong influence in the system.

To achieve DFs of 225 for Sr and >6 for Pu, the mole ratio of Na-TiA to Sr must be 10,000 or greater at a pH of 10.4 and a temperature of 25°C. The mass of Na-TiA required for this DF was estimated to be 1.2×10^5 kg for West Valley Tank 8D2. No adverse effects were noted when combining Na-TPB and Na-TiA in the experimental studies. However, as mentioned previously, the precipitant chemicals should be added to supernatant separated from the sludge.

Based on the above laboratory data and minimum process requirements, conditions that should assure optimum performance for a precipitation system are shown in Table 22.

ION-EXCHANGE PROCESS

Laboratory-scale experiments were conducted to study the performance of organic and inorganic ion exchangers for the decontamination of West Valley alkaline supernatant from Sr, Cs, and Pu; and the recovery of Tc by the use of an organic anion exchange resin. Simulated supernatant prepared by direct chemical mixing (see Appendix A), was used for these experiments. Batch distribution ratios (R_d) were measured to determine the ability of a select group of organic and inorganic exchangers to remove the radionuclides of interest from solution. The results for the batch sorption tests showed that the organic ion-exchange process (with Duolite CS-100 and Amberlite IRC-718) was viable for ion-exchange column testing, and that a zeolite inorganic exchanger should also be investigated.

TABLE 22. Optimum Conditions for a Precipitation System

Process Parameters	Precipitation	
	Optimum Conditions	Comments
Temperature	25 to 50°C	Higher temperatures enhance Pu recovery by Na-TiA.
pH	10.4 to 13	Increased pH enhances Sr/Pu recovery at a constant Na-TiA concentration.
Contact time	7 days minimum	Equilibrium is readily achieved in well-mixed laboratory-scale system. Engineering-scale system has not been evaluated.
Mass of Na-TPB required for Tank 8D2	Coverage: 1.4 moles Na-TPB/mole Cs+K+Rb	About 2×10^5 kg Na-TPB are required for Cs DF of 10^4, ~1.6×10^5 kg Na-TPB for Cs DF of 130, and <0.5×10^5 kg Na-TPB for Cs DF of 1.3.
Mass of Na-TiA required for Tank 8D2	Coverage: 10,000 moles Na-TiA/mole Sr	About 1.5×10^5 kg of Na-TiA are required based on 0.1M Na-TiA at pH = 10.4. This mass of Na-TiA will increase glass mass by a factor of up to 7.
Precipitant chemical addition	Na-TPB and Na-TiA addition to supernatant separated from sludge	Na-TPB interferes with sludge washing. A large mass of Na-TiA will be required to achieve equilibrium with total Sr in tank if sludge is present.
		Precipitation will not remove Tc from solution.

An experimental ion-exchange system consisting of a 1.8-cm-dia ID glass ion-exchange column containing 100 mL^3 of exchanger was used to provide reproducible tests. Experiments were completed to examine the effects of temperature, pH, flow rate, and Na/Cs mole ratio in the feed.

Batch Sorption

To select ion-exchange materials for the recovery of Cs, Sr, and Pu from alkaline supernatant, a batch sorption screening test was completed. The laboratory test, described in Appendix D, provides a rapid and cost-effective method for comparing the selectivity of a wide variety of materials for specific radionuclides. When this work was initiated (October 1982), the need for radionuclide decontamination had not been completely assessed because the actual composition of the West Valley alkaline supernatant had not been determined. Therefore, a wide variety of candidate radionuclides were included in this initial study.

Batch ion-exchange experiments involved contacting a sample of supernatant containing the radionuclide under investigation with a small weighed sample of ion-exchange material. Contact was maintained 7 days at room temperature. The alkaline supernatant was adjusted to pH 10 or 13. Because only one contact time was tested, radionuclides that slowly equilibrate with the exchange material were not identified. Additional tests as a function of time and temperature would be required to identify kinetic and equilibrium problems. The batch test was used to rank the candidate exchangers, but did not eliminate the need to conduct flow-through ion-exchange column testing on selected exchangers.

The R_d values for the radionuclides are shown in Table 23 for each exchanger type. A general description of each exchanger is given in the Experimental section of this report.

A comparison of R_d values for Cs at pH 10 shows that IE-95 and AW-500 rank above CS-100. At a pH of 13, IE-95, AW-500, and CS-100 are equal. Strontium results show that the organic exchanger IRC-718 ranks above IE-95 and AW-500 at pH 10, but that AW-500 has a higher R_d value at pH 13. Plutonium results at pH 10 show that IRC-718 and ARC-359 are superior to IE-95 or AW-500. Technetium is removed only by charcoal and a group of organic anion exchange resins. Neptunium, Eu, and Am show some exchange using AW-500, IE-95, CS-100, and ARC-718 at pH 10. Iodine is removed by the organic resins at both pH 10 and 13. Ruthenium is removed only by charcoal.

TABLE 23. Batch R_d Values for Radionuclides for Different Exchanger Types

Element	pH	AW-500 & IE-95 (Average)	CS-100	ARC-359	IRC-718	A-51	IRC-84 & IRC-50S (Average)	Charcoal	Dowex-1,X8 IRA-401 IRA-402 (Average)	IRA-458
Cs	10	39	14	12	2	<1	<1	<1	--	--
	13	34	34	24	1.7	<1	<1	<1	--	--
Sr	10	386	82	11	1517	30	--[a]	14	--	--
	13	1408	<1	<1	177	21	--	<1	--	--
Pu	10	19	284	108	<1	<1	--	<1	--	--
Tc	10	<1	<1	<1	<1	<1	--	67	223	138
	13	<1	<1	<1	<1	<1	--	37	212	134
Np	10	2	32	12	<1	<1	--	<1	--	--
	13	28	<1	19	<1	<1	--	<1	--	--
I	10	1	56	17	36	1.5	--	4	--	--
	13	~2	34	11	22	<1	--	3	--	--
Eu	10	790	683	101	100	1.2	--	3	--	--
	13	9300	2760	132	<1	892	--	71	--	--
Ru	10	<1	8	5	10	<1	<1	386	--	--
	13	1	6	2	<1	<1	<1	16	--	--
Am	10	24	11	7	46	11	<1	2	--	--
	13	--	--	--	--	--	--	--	--	--

(a) Not determined.

The overall results for the batch sorption tests show that the organic ion-exchange resins CS-100 and IRC-718 and the IE-95 inorganic exchanger are viable candidates for the removal of Cs, Sr, and Pu from alkaline supernatant. Removal of Tc using any of the quaternary ammonium polystyrene anion resins such as Dowex-1,X8 appears feasible.

Organic Ion Exchange

The objective of the following section is to provide data to support the organic resin ion exchange process using synthetic alkaline supernatant. A simplified schematic for this approach is shown in Figure 14. In the alkaline supernatant from Tank 8D2, Cs is removed using a granular Duolite CS-100 organic ion exchanger, followed by an organic macroporous cation exchanger (Amberlite IRC-718) to remove Sr.

Duolite CS-100 performance for Cs was found to be dependent upon the resin particle size, temperature, and feed pH. Higher Cs loadings were achieved at smaller resin size classifications. Cesium loadings improved by a factor of 1.3 as the feed temperature was lowered from 50 to 6°C. When the alkaline supernatant feed pH was increased from 10.4 to 13.6, the loading capacity increased by a factor of 3.3 at a Cs breakthrough of 0.5 C/Co. At a feed pH of 13.8, the maximum Cs decontamination performance for CS-100 ion exchanger was determined to be ~1560. No Pu decontamination was found. Elution was achieved by passing 10 cv of 0.1M formic acid (HCOOH) upflow through the resin bed. The eluate consists of Cs and Na formate.

Amberlite IRC-718 performance for Sr was dependent upon feed pH. Strontium DFs of 100 and 1000 were achieved after 10 cv of feed were loaded downflow (0.6 cv/h) at alkaline supernatant pH values of 10.8 and 13.3, respectively. After loading, the column was rinsed with water and eluted upflow with 5 cv of 2M HCOOH.

CS-100 Loading and Elution

Experience with CS-100 has been limited to laboratory-scale loading and elution testing at SRP. Further experimentation with this resin was necessary to provide more complete characterization as it applied to the West Valley alkaline supernatant. These results are shown below.

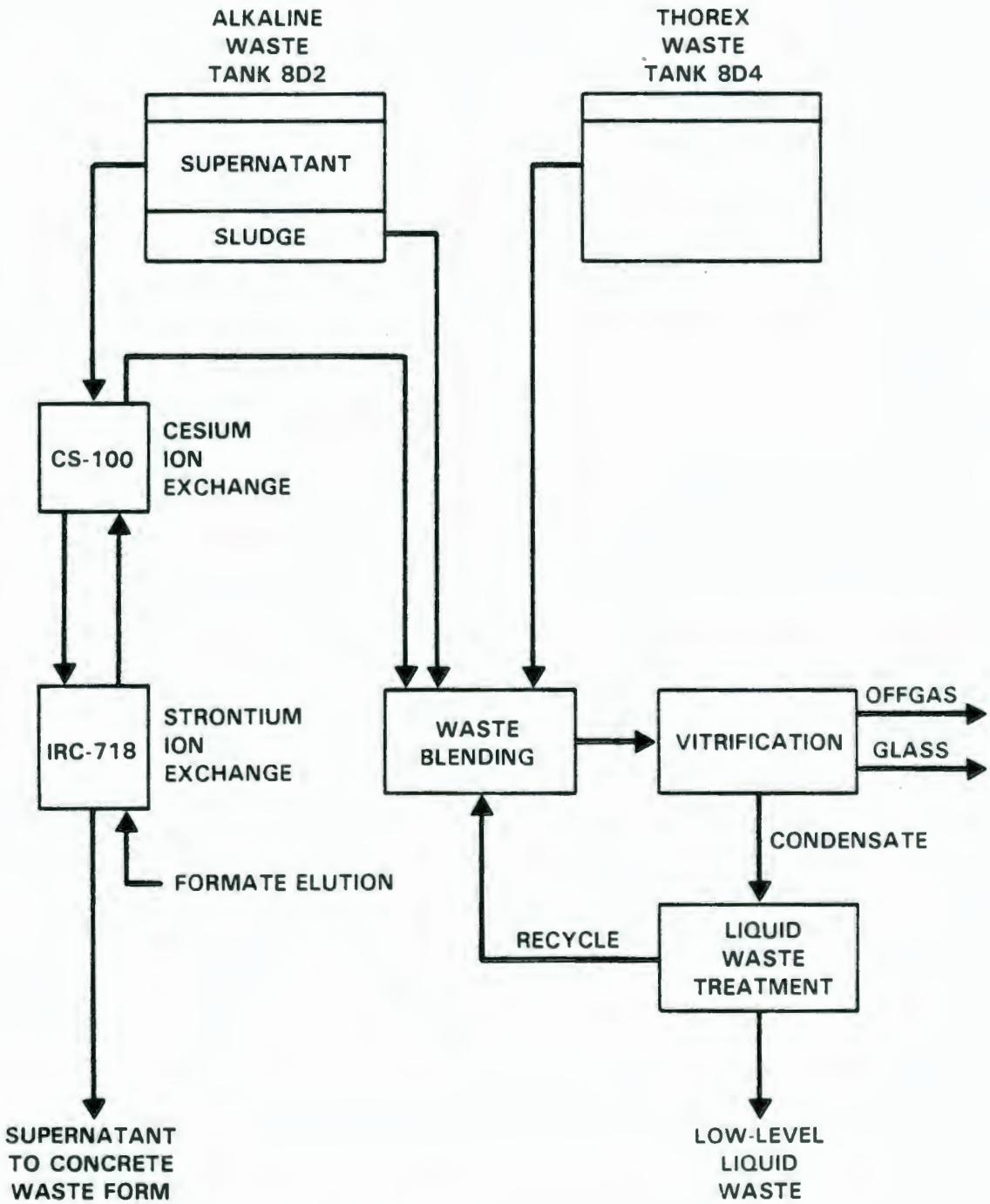


FIGURE 14. Organic Ion-Exchange Process

The CS-100 was found to be very particle-size dependent. The "as-received" resin was sieved to determine its size (Table 2). Approximately 22 wt% was retained on 20-mesh (0.85 mm) screen, and 75 wt% on 40-mesh (0.425 mm) screen. Figure 15 shows Cs breakthrough curves for pH 13.6 alkaline supernatant for 3 mesh sizes: as received, 60-mesh, and 80-mesh, with a 0.01 C/Co Cs breakthrough occurring at 2, 4.7, and 6.4 cv, respectively. The fine mesh resin was prepared by grinding the resin under water and sizing.

The CS-100 resin was very temperature dependent as shown in Figure 16. Using 60-mesh resin, pH 13.6 feed at 0.6 cv/h, the 0.01 C/Co breakthrough for Cs at 50, 25, and 6°C was 2.1, 5, and 7.3 cv, respectively. The Cs^+ loading at 0.01 C/Co increased by a factor of 3.5 as the temperature decreased from 50 to 6°C. Although the feed remained physically stable at 6°C, application may be difficult in a large-scale plant.

The capacity of CS-100 to retain Cs^+ from pH 13.6 alkaline supernatant (8.2M Na^+) decreased with an increasing Na/Cs mole ratio as shown in Figure 17 and Table 24. As the Na/Cs mole ratio was increased by a factor of 100, the number of cv's of feed loaded increased by a factor of 2.3 at 0.01 C/Co, and the mass of Cs loaded decreased by a factor of 43.

The Cs loading of CS-100 increased with increasing pH since the phenolic resins are more selective (Cs versus Na) with increasing pH. The West Valley waste would therefore require a pH adjustment from pH 10 to 13.8 to take advantage of the increased capacity. When feed was prepared at pH 10.4 rather than pH 13.6, and Cs breakthrough values obtained (Figures 16 and 18) for 60-mesh CS-100, a 0.01 C/Co breakthrough occurred at 0.5 and 4.7 cv, respectively.

Batch R_d measurements for Sr and Pu (Table 23) using CS-100 gave values of 82 and 284, indicating that they should be retained on ion-exchange columns at alkaline supernatant pH values of 10.4. However, a CS-100 column test (Figure 18) shows no retention, with a 0.5 C/Co breakthrough at 2 cv for both Sr and Pu.

Detailed elution and Na scrubbing studies were completed by Grant (1983) and Wallace and Ferguson (1980) using formic acid. Therefore, we completed

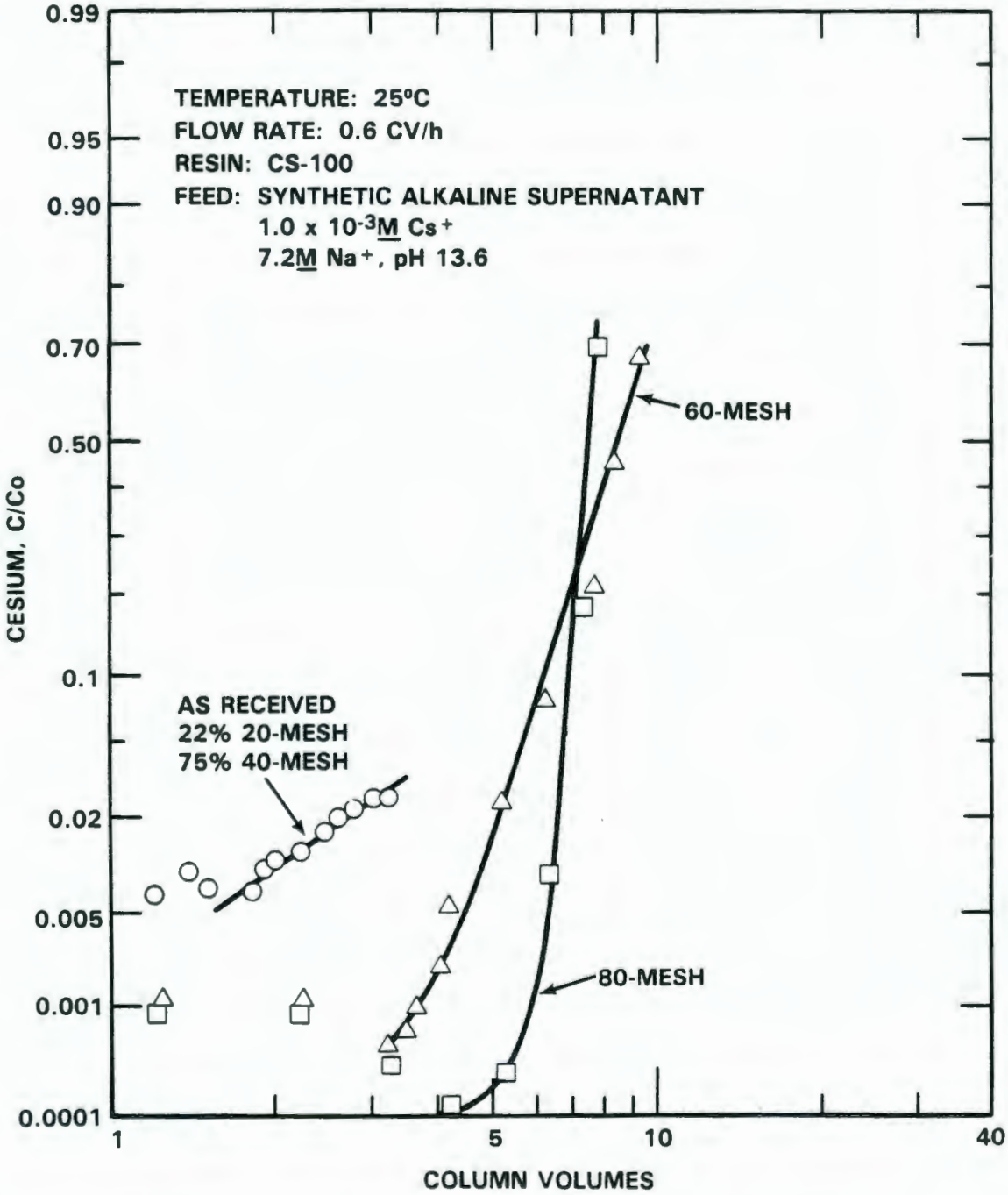


FIGURE 15. Cesium Breakthrough as a Function of Mesh Size for Organic Exchanger CS-100

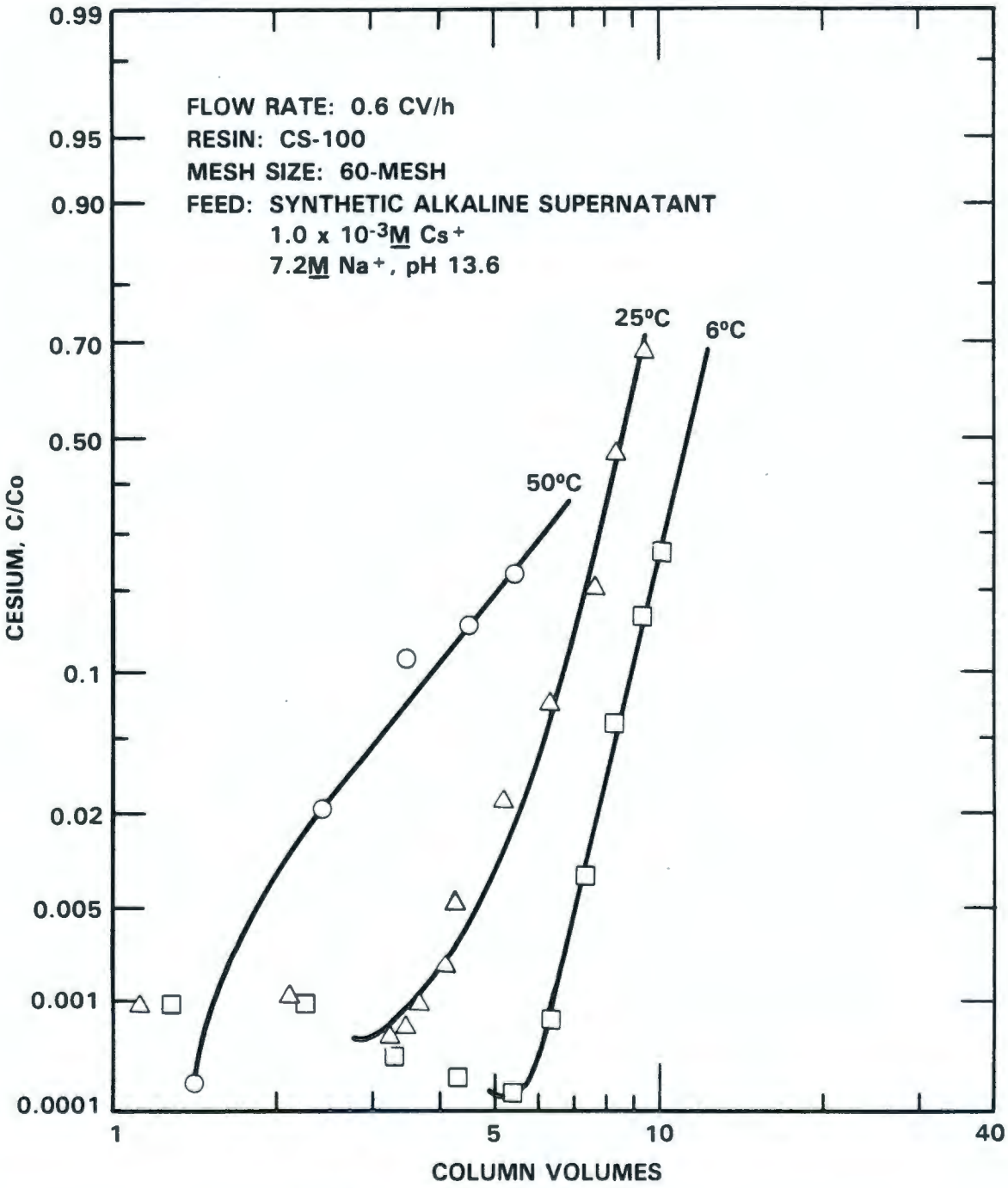


FIGURE 16. Cesium Breakthrough as a Function of Temperature for Organic Exchanger CS-100

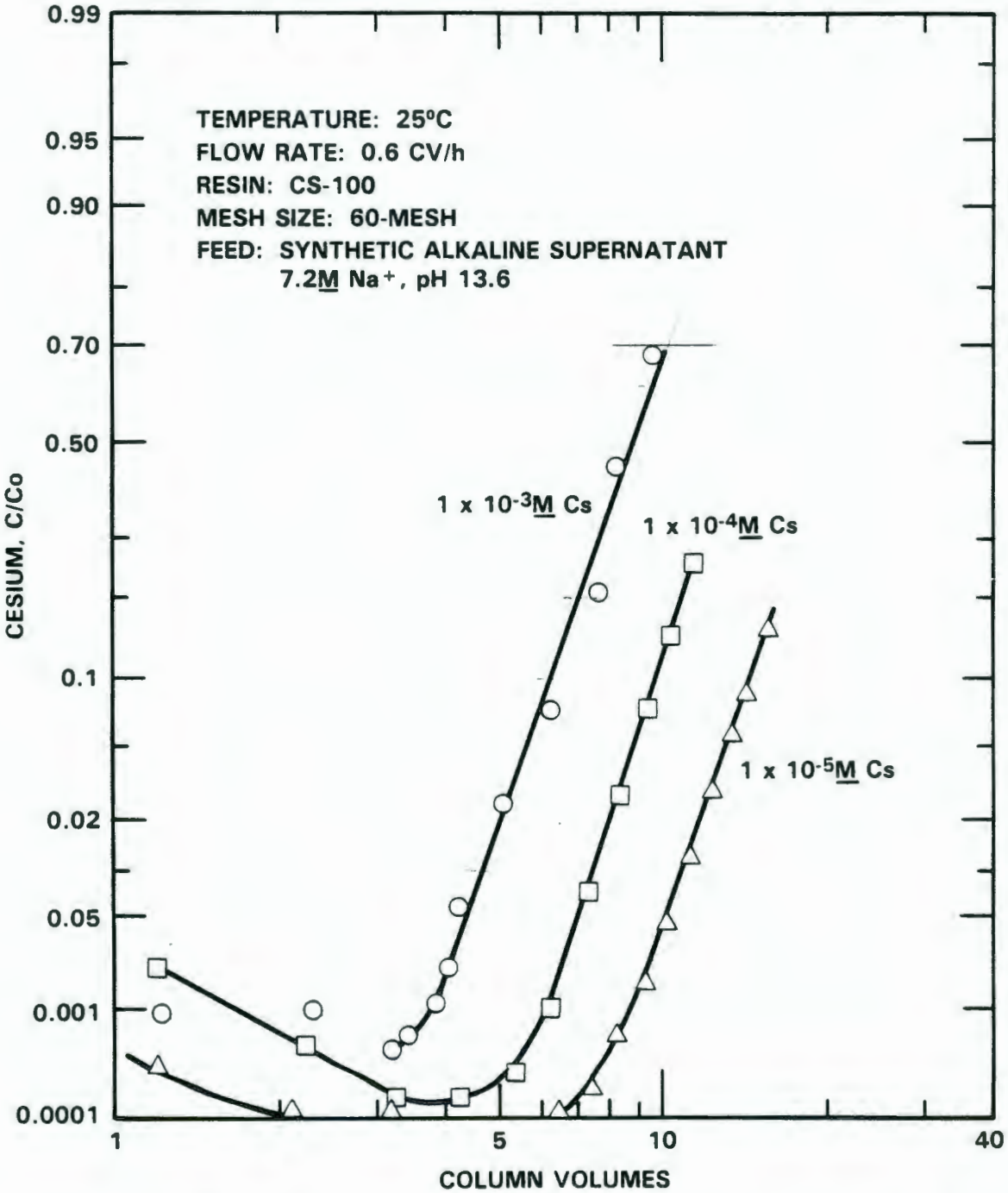


FIGURE 17. Cesium Breakthrough as a Function of the Influent Cesium Feed Concentration for Organic Exchanger CS-100

TABLE 24. Cesium Loaded on CS-100 as a Function of Na/Cs Mole Ratio

Na/Cs Mole Ratio	Column Volumes at 0.01 C/Co	Moles Cs Loaded/L of CS-100
7.2 E+3	4.7	4.7 E-3
7.2 E+4	6.5	6.4 E-4
7.2 E+5	11	1.1 E-5

only one loading, washing, and elution test. The alkaline supernatant containing ^{137}Cs and ^{22}Na tracers was adjusted to pH 13.8 (Na/Cs mole ratio = 6550), and 10 cv of feed was loaded downflow at 0.6 cv/h. A 0.01 C/Co breakthrough was observed at 3.5 cv (Figure 19). Approximately 18% Cs and 94% Na were found in the feed effluent. After washing the column downflow to displace the remaining feed, a 0.1M HCOOH scrub solution (intended to preferentially remove Na^+) was started upflow. After 7 cv, 0.6% Na^+ and 3% Cs^+ of the initial feed was eluted. Unexpectedly, the next two column volumes of 0.1M HCOOH removed 79% Cs^+ and 2% Na^+ (equivalent to 95% Cs and 77% Na initially loaded). The peak concentration of both the Na^+ and Cs^+ ions occurred simultaneously, indicating that the 0.1M HCOOH does not selectively remove Na^+ in preference to Cs^+. The intended elution cycle solution, 2M HCOOH, was then introduced into the column, but was not required since the 0.1M HCOOH had already efficiently removed the Na-Cs product.

IRC-718 Loading and Elution

Amberlite IRC-718 is a chelating, macroreticular polystyrene divinylbenzene resin. It is highly selective for Sr and other polyvalent cations in highly alkaline systems such as Savannah River supernatant. Further experimentation with this resin was necessary to provide more complete characterization as it applied to the West Valley alkaline supernatant. These results are given below.

The macroreticular cation exchange resin, IRC-718, provided a Sr DF of ~100 and ~1000 after 10 cv of feed were loaded downflow (0.6 cv/h) at alkaline supernatant pH values of 10.8 and 13.3, respectively (Figures 20 and 21). No significant Pu decontamination was observed.

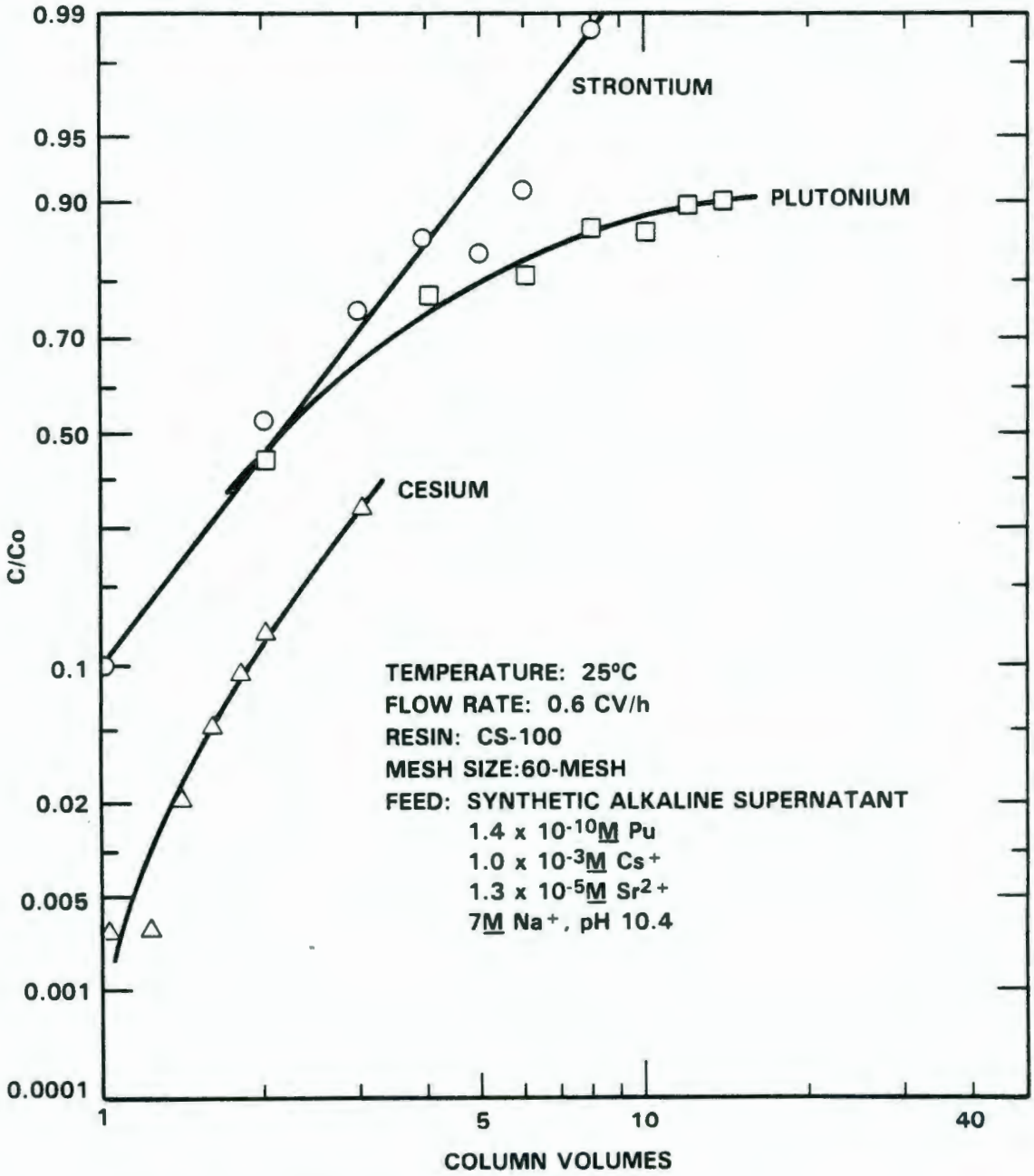
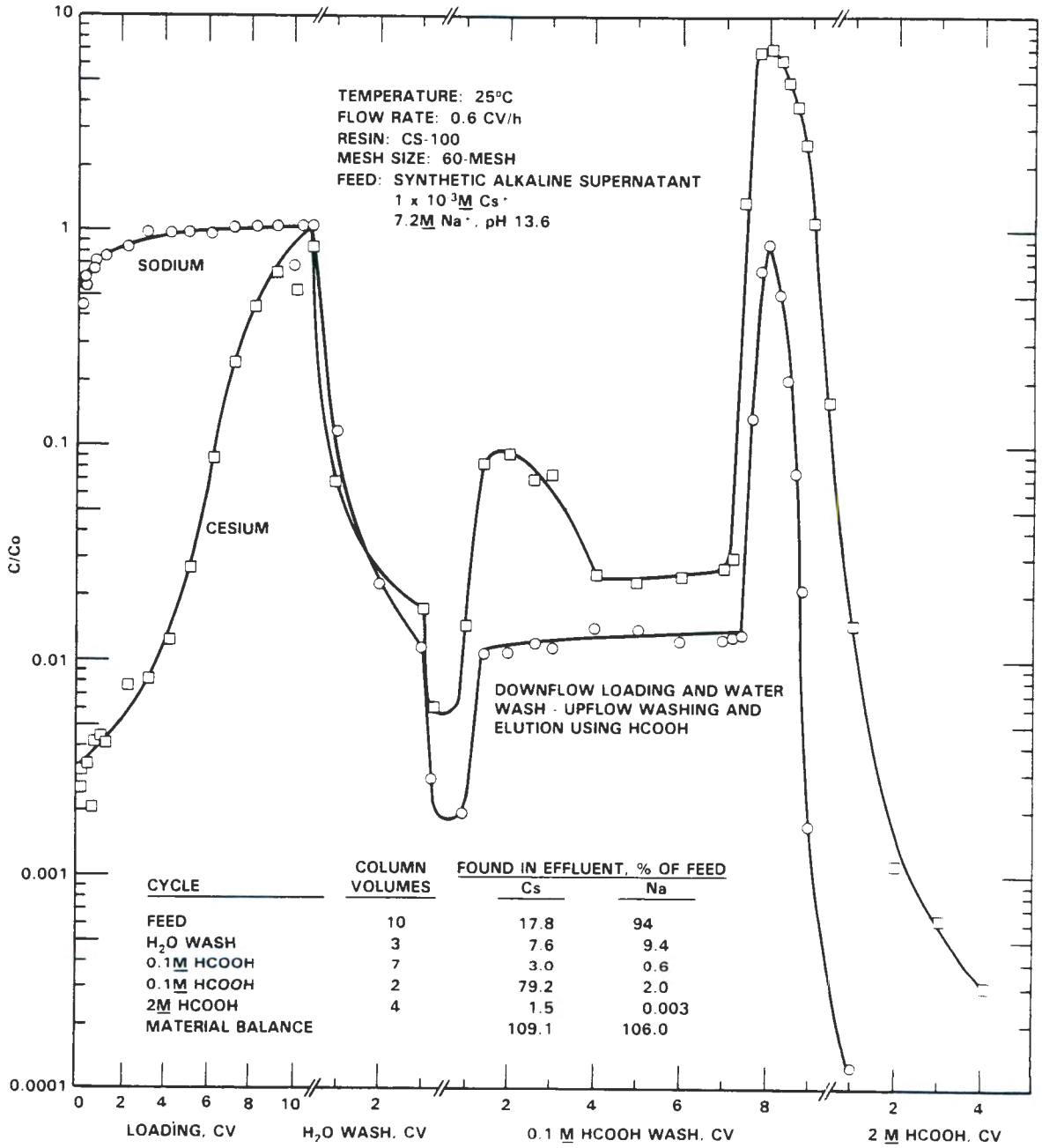


FIGURE 18. Cesium, Plutonium and Strontium Breakthrough for Organic Exchanger CS-100 at pH 10.4



CYCLE	COLUMN VOLUMES	FOUND IN EFFLUENT, % OF FEED Cs	Na
FEED	10	17.8	94
H_2O WASH	3	7.6	9.4
0.1M HCOOH	7	3.0	0.6
0.1M HCOOH	2	79.2	2.0
2M HCOOH	4	1.5	0.003
MATERIAL BALANCE		109.1	106.0

FIGURE 19. Cesium Breakthrough for Loading and Elution Cycle of Organic Exchanger CS-100

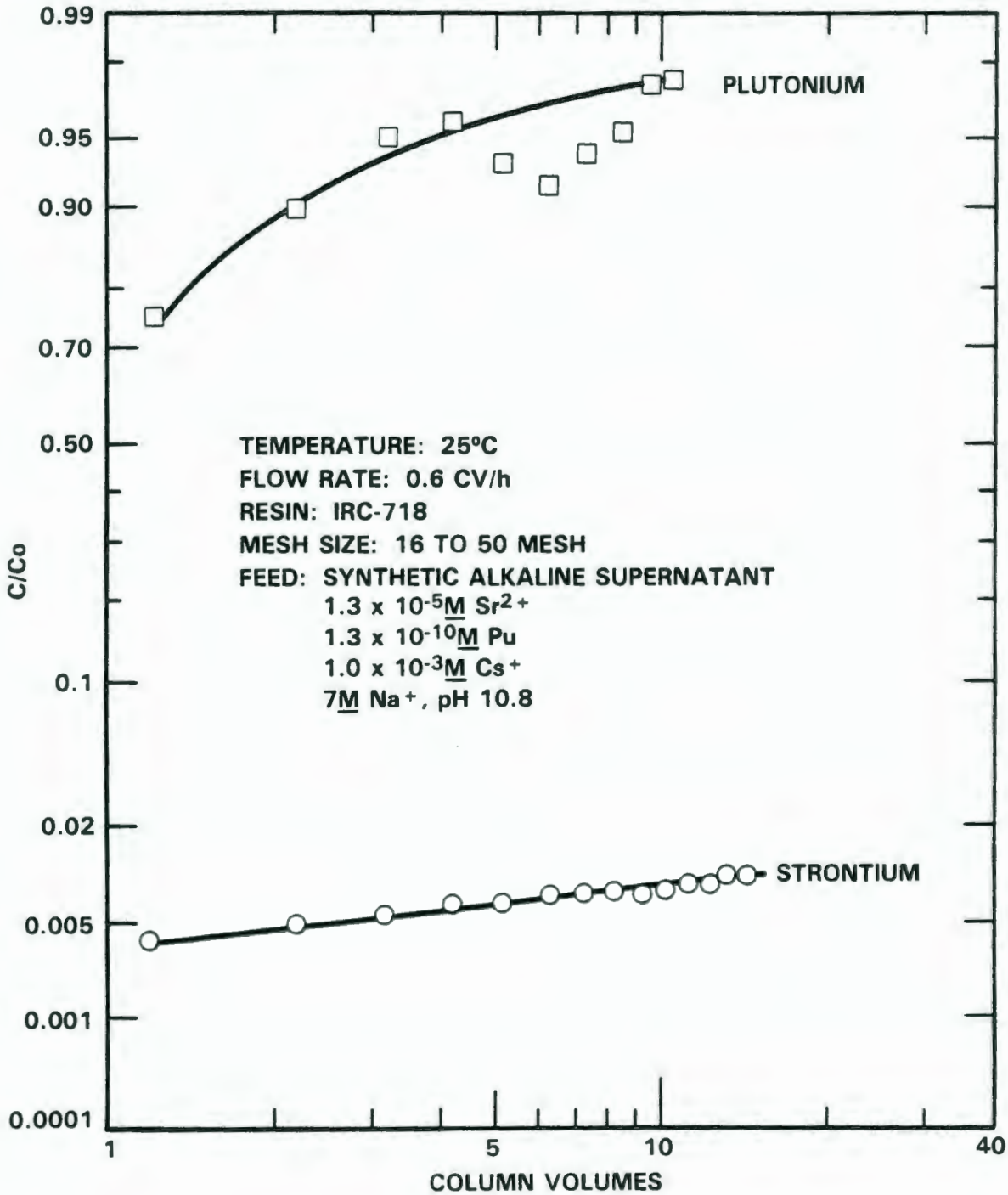


FIGURE 20. Strontium and Plutonium Breakthrough as a Function of Column Volumes Loaded for Organic Exchanger IRC-718 at pH 10.8

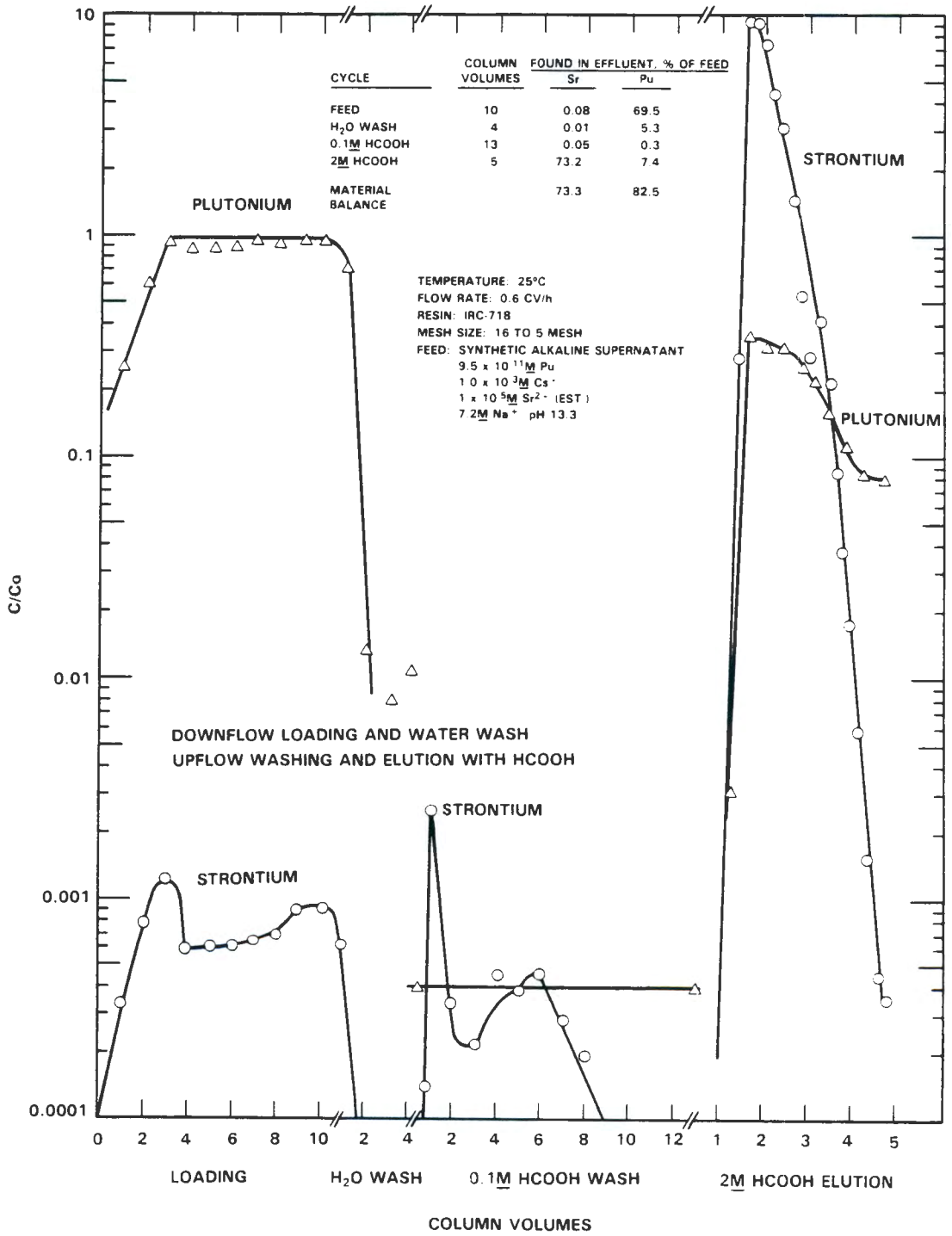


FIGURE 21. Strontium and Plutonium Breakthrough for Loading and Elution Cycle of Organic Exchanger IRC-718 at pH 13.3

An upflow elution test (Figure 21) showed that 0.1M formic acid will not elute Sr^{2+} or Pu (Na^+ data were not obtained), and that 5 cv of 2M HCOOH will be required to elute the Sr and Pu from the column.

Based on the above laboratory data and minimum process requirements, conditions that should achieve optimum performance for an organic ion exchange process are shown in Table 25.

Inorganic Ion Exchange

A simplified schematic for the inorganic ion-exchange approach at West Valley is shown in Figure 22. Alkaline supernatant (2×10^6 L) is separated from Tank 8D2 and processed through inorganic ion exchange to remove Cs, Sr, and Pu. The loaded and washed exchanger is fed to the vitrification process

TABLE 25. Optimum Conditions for an Organic Ion-Exchange System

Process Parameters	Organic Ion Exchange	
	Optimum Conditions	Comments
Temperature	25°C	Lower temperatures (6°C) will enhance Cs capacity on CS-100 by a factor of 1.3, but may be impractical to achieve.
pH	13.8	CS-100 will achieve a Cs DF of ~1600 at 13.8. IRC-718 requires a pH of 13.8 to decrease Pu and Sr solubility and to achieve a Sr DF of 225.
Flow rate	<0.6 cv/h	Cs, Sr, and Pu loadings are enhanced by lower flow rates.
Na to Cs mole ratio in feed	<7000	Cs loading on CS-100 is enhanced by lower Na/Cs mole ratios.
Elution	Formic acid	0.1 to 2 M.
Anion resin		Technetium recovery on an anion exchange resin will exceed a DF of 100. Loadings to 90 cv, followed by a H_2O wash and elution using 8 cv of 8M HNO_3, will allow recycling of the resin during processing of the supernatant.

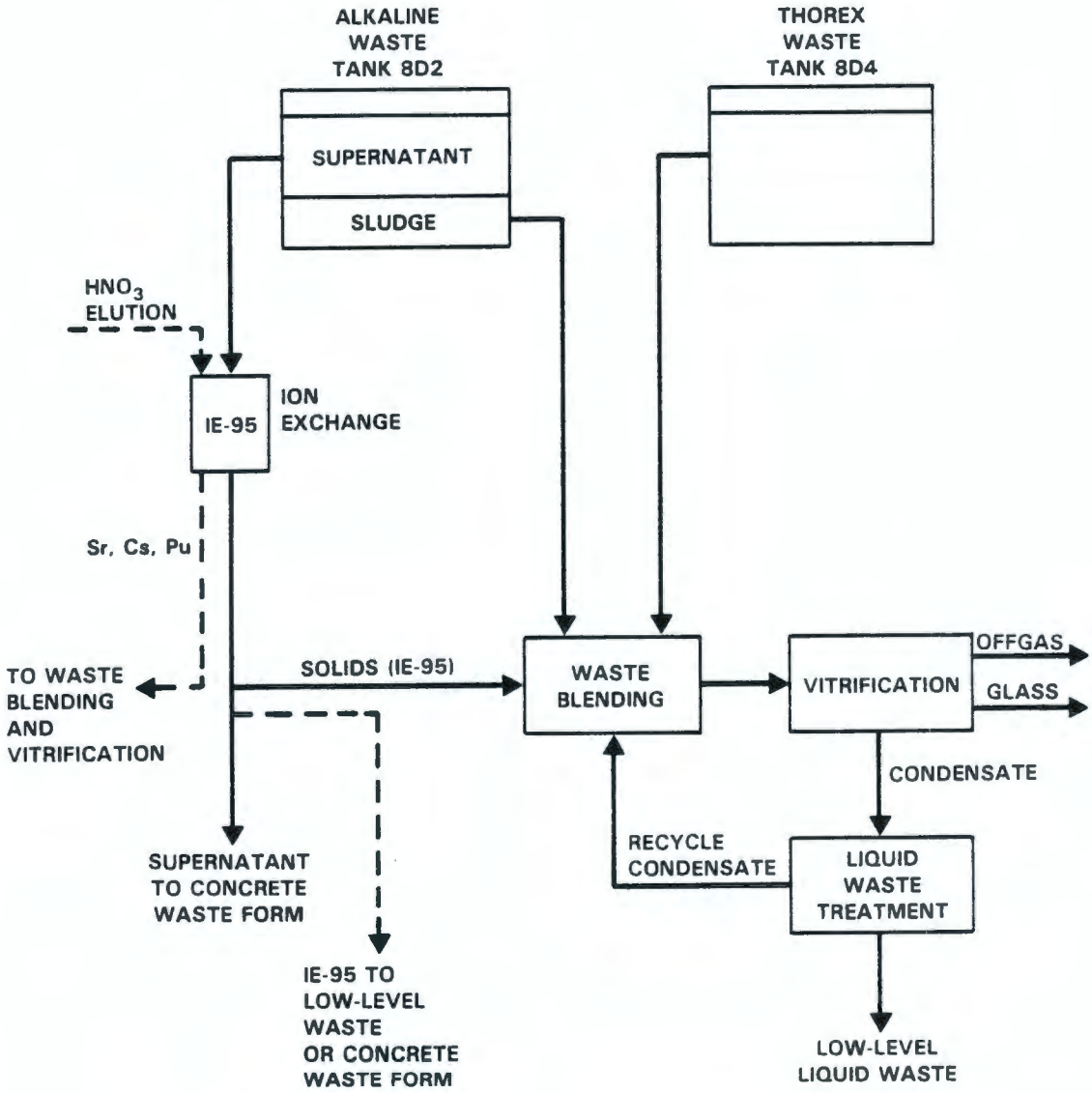


FIGURE 22. Inorganic Ion-Exchange Process

and will replace ~32% of the glass former chemicals. An alternative method is to elute the inorganic exchanger with acid and process the IE-95 as low-level waste, or to add it to the concrete waste form. The acidic eluate waste containing Cs, Sr, and Pu is blended and processed through vitrification. Both pH 10 and 13 alkaline supernatants were used in the study for comparison with the organic ion-exchange option.

The performance of inorganic zeolite ion exchanger Linde IE-95 was found to be dependent on temperature, flow rate, Na/Cs feed ratio, and pH. Loadings

for Cs improved by a factor of 1.5 as the temperature was lowered from 50 to 6°C at 0.01 C/Co. Cesium loadings decreased by a factor of 1.4 as the feed pH increased from 10.4 to 13.8. At 8 cv of feed loaded, Cs loading breakthrough fractions (C/Co) decreased by a factor of 50 as the flow rate varied from 1.75 to 0.6 cv/h. Decontamination factors for Cs ($>10^4$), Sr ($\sim 10^3$), and Pu (~ 10) were achieved at the following ion-exchange column conditions: 0.6 cv/h, pH 10.4, 8 cv, and 25°C. The basis for this summary is shown below.

IE-95 Batch Loading

Powdered IE-95 (>80 mesh) was added to alkaline supernatant and stirred for 8 days. The test was designed to determine the value of adding zeolite directly to Tank 8D2 to remove Cs (Figure 23). The batch sorption ratios (R_d) were 20 and 42 for pH 13.6 and 10.4 alkaline supernatant, respectively. At an IE-95 concentration of 0.1 g/mL of alkaline supernatant, the C/Co Cs values for pH 13.6 and 10.4 alkaline waste were 0.32 and 0.19, respectively. The results show that a very large mass (4.3×10^5 kg) of powdered IE-95 would be required to provide a DF of 10 for Cs in Tank 8D2.

IE-95 Loading

Breakthrough studies were completed using IE-95 in ion-exchange columns to determine Cs loading as a function of temperature and feed pH. The results show that Cs loading on IE-95 is increased by lower temperatures and lower feed pH values (Figures 24, 25 and Table 26). At a Cs breakthrough of 0.01 C/Co, the volumes of feed (at pH 10.4) loaded varied from 17 (at 6°C) to 11 (at 50°C). At a feed pH of 13.6, the volumes of feed loaded decreased to 13.5 (at 6°C) and 9.6 (at 50°C).

Cesium loading on IE-95 was enhanced by lower alkaline supernatant flow rates (see Figure 26). At feed flow rates (cv/h) of 0.6, 1.0 and 1.8, the Cs breakthrough fraction (C/Co) was determined to be 4.0 E-5, 2.0 E-4 and 2.0 E-3, respectively, after eight column volumes of feed had passed through the column.

A series of experiments was completed using alkaline supernatant at pH 10.4 containing 6×10^{-5} M Cs^+, 4.5×10^{-4} M Cs^+, or 1×10^{-3} M Cs^+ at 7 M Na^+ (see Figure 27). The cesium feed concentration was adjusted by using the effluent from one run as the feed for the next. A similar series was completed

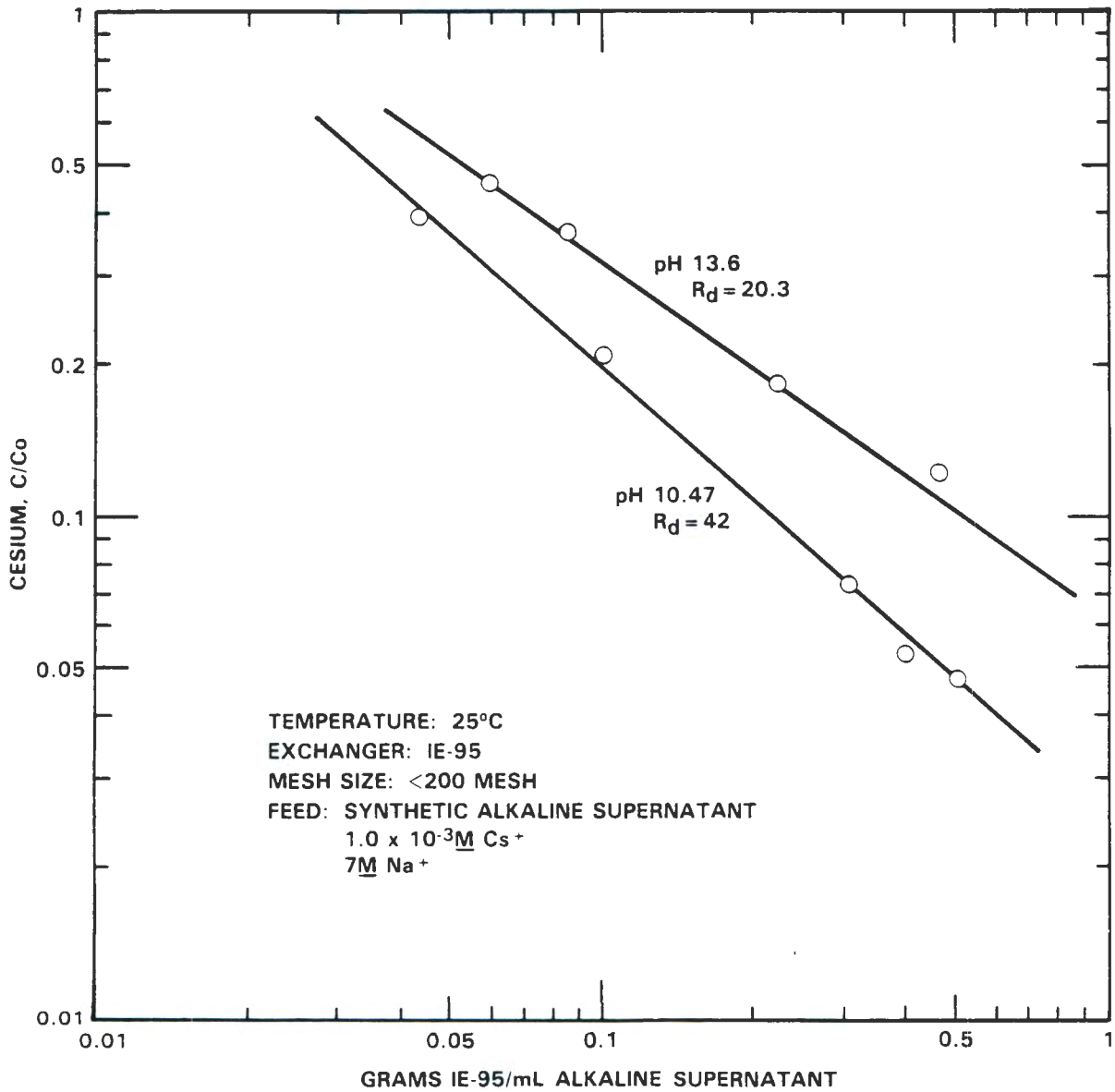


FIGURE 23. Cesium in Solution as a Function of Added Powdered Zeolite Exchanger IE-95

in which the Cs was varied in the initial feed. The breakthrough results for the two methods of feed preparation were similar, indicating that K^+ and Rb^+ ions do not interfere with the IE-95 Cs-loading capacity. The Cs capacity of IE-95 decreased with increasing Na/Cs mole ratio in the alkaline supernatant as shown in Table 27.

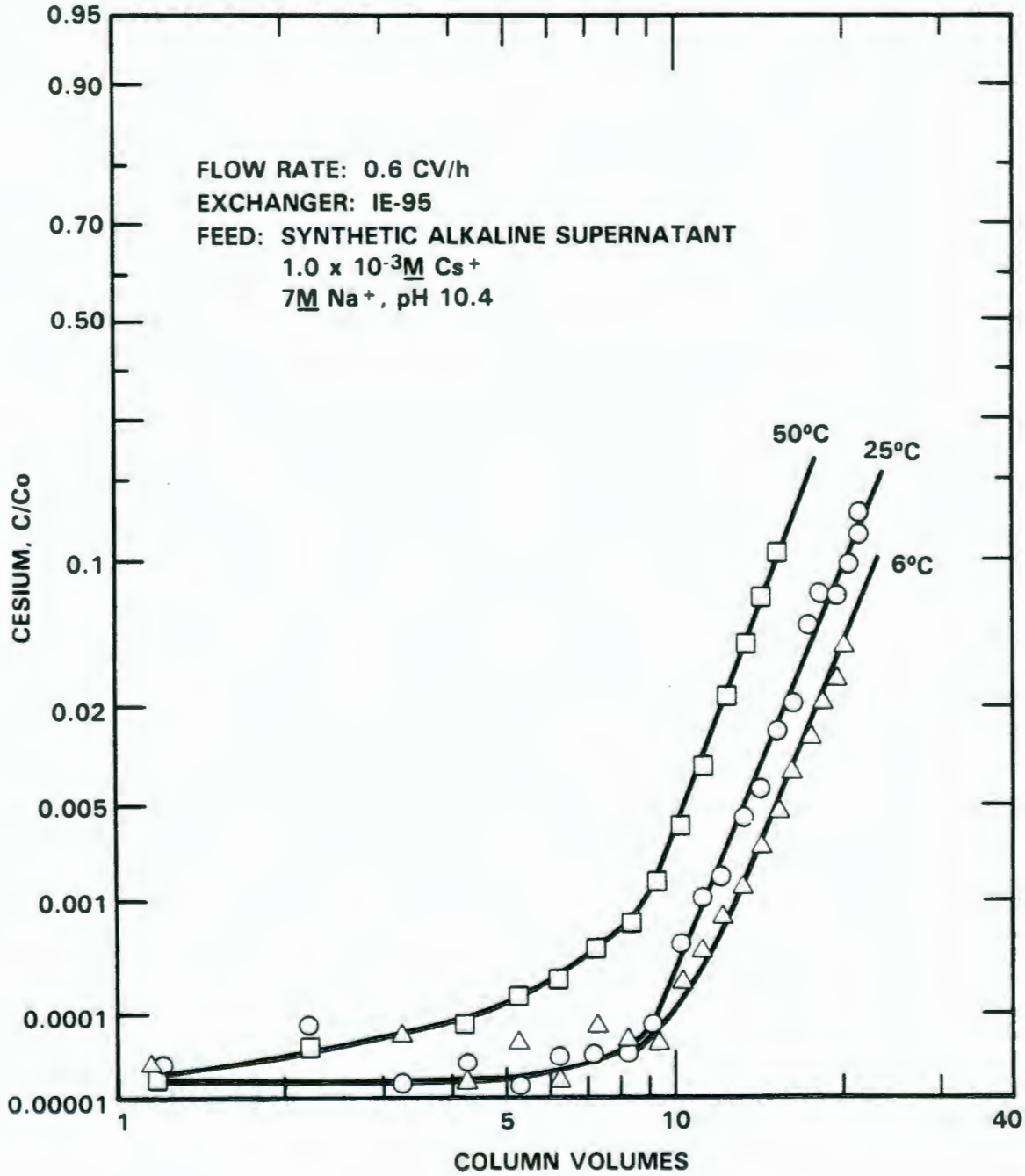


FIGURE 24. Cesium Breakthrough as a Function of Temperature for the Zeolite Exchanger IE-95 at pH 10.4

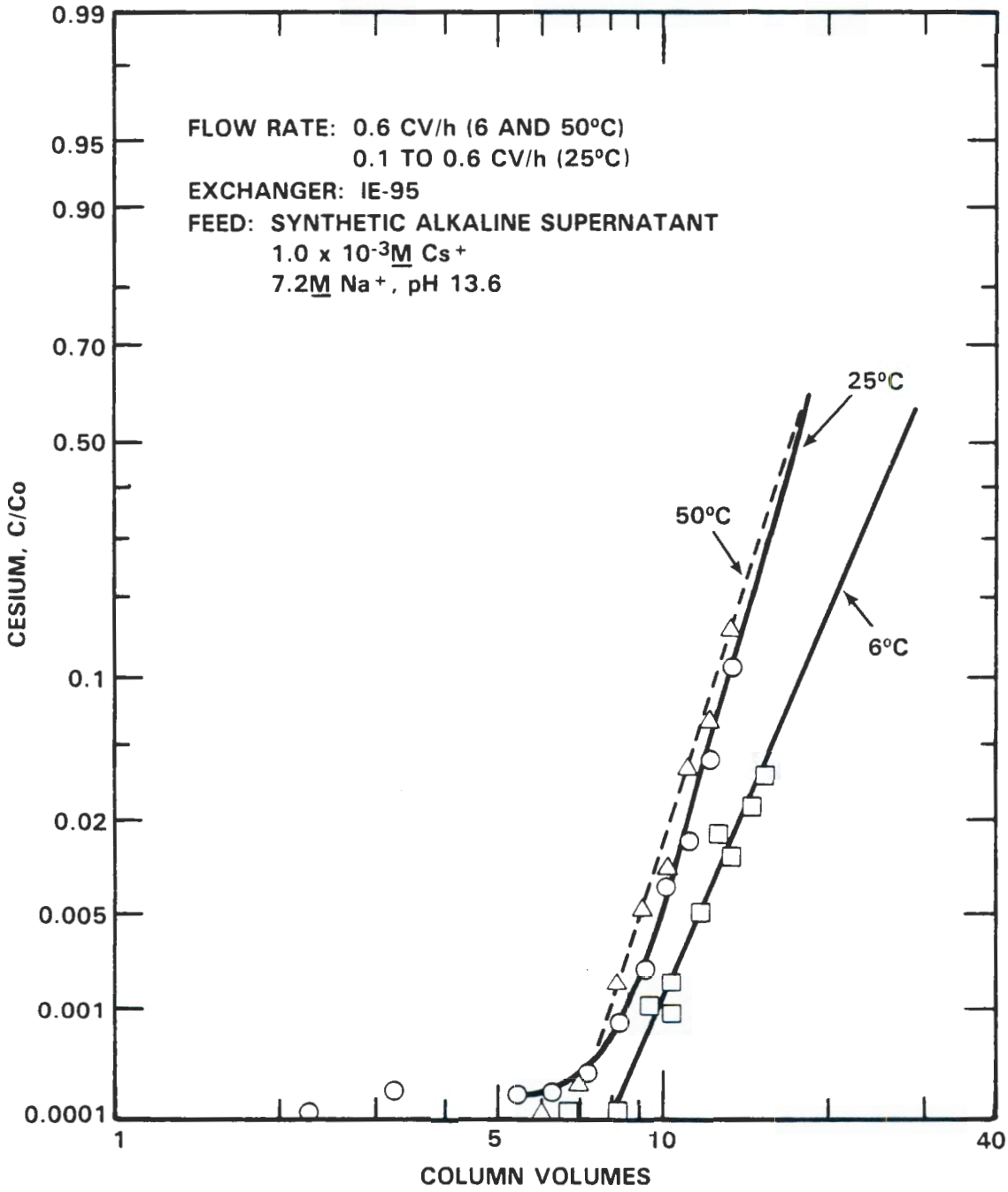


FIGURE 25. Cesium Breakthrough as a Function of Temperature for the Zeolite Exchanger IE-95 at pH 13.6

TABLE 26. Volumes of Feed Loaded as a Function of Temperature and pH

Alkaline Supernatant, pH	Column Volumes at 0.01 C/Co		
	6°C	25°C	50°C
10.4	17	14.5	11
13.6	13.5	10.4	9.6

Cesium, Pu, and Sr IE-95 inorganic ion-exchange results are shown in Figures 24, 28, and 29 as a function of throughput temperatures for different, using pH 10.4 alkaline supernatant. The results at 25°C show that the instantaneous Cs, Sr, and Pu DFs of 10^4, 224, and 6 are not exceeded until more than 9, 12, and 8 cv of feed are passed through the column, respectively. Loading of Cs, Sr, and Pu is temperature dependent. However, the Pu and Sr curves show kinetic and equilibrium problems not identified in the batch equilibrium studies. At 8 cv, the C/Co values shown in Table 28 were obtained.

IE-95 Elution

Cesium, Sr, and Pu are effectively eluted from IE-95 using 4M HNO_3. However, in an ion-exchange column, gas due to the presence of carbonate ion will tend to disrupt the flow of the eluate. Batch may be more viable than column elution.

Cesium can be removed from zeolites by cations that are similar in size and charge to Cs (K^+, Rb^+, and NH_4^+). At Hanford (Buckingham 1967), sodium is selectively scrubbed from AW-500 with 0.2M $(NH_4)_2CO_3$ - 0.1M NH_4OH, and then the Cs^+ is eluted at 55°C with 4 to 8M NH_4^+ with about 75% of the NH_4^+ added as $(NH_4)_2CO_3$, and 25% added as NH_4OH.

Acid elution of IE-95 was considered as an option to direct waste blending (Figure 22). Initial batch contacts of Cs-loaded IE-95 (Table 29) show that Cs can be stripped. Cesium R_d values of 3 and 0.1 were obtained using 0.5 and 2M HNO_3, respectively. Formic acid was not efficient in the removal of Cs from IE-95.

Based on the Cs batch contacts, IE-95 column tests were completed by loading 20 cv of pH 10.4 alkaline supernatant; washing the column with water; and eluting the Sr, Cs, and Pu using 1M HNO_3 (Figure 30) or 4M HNO_3

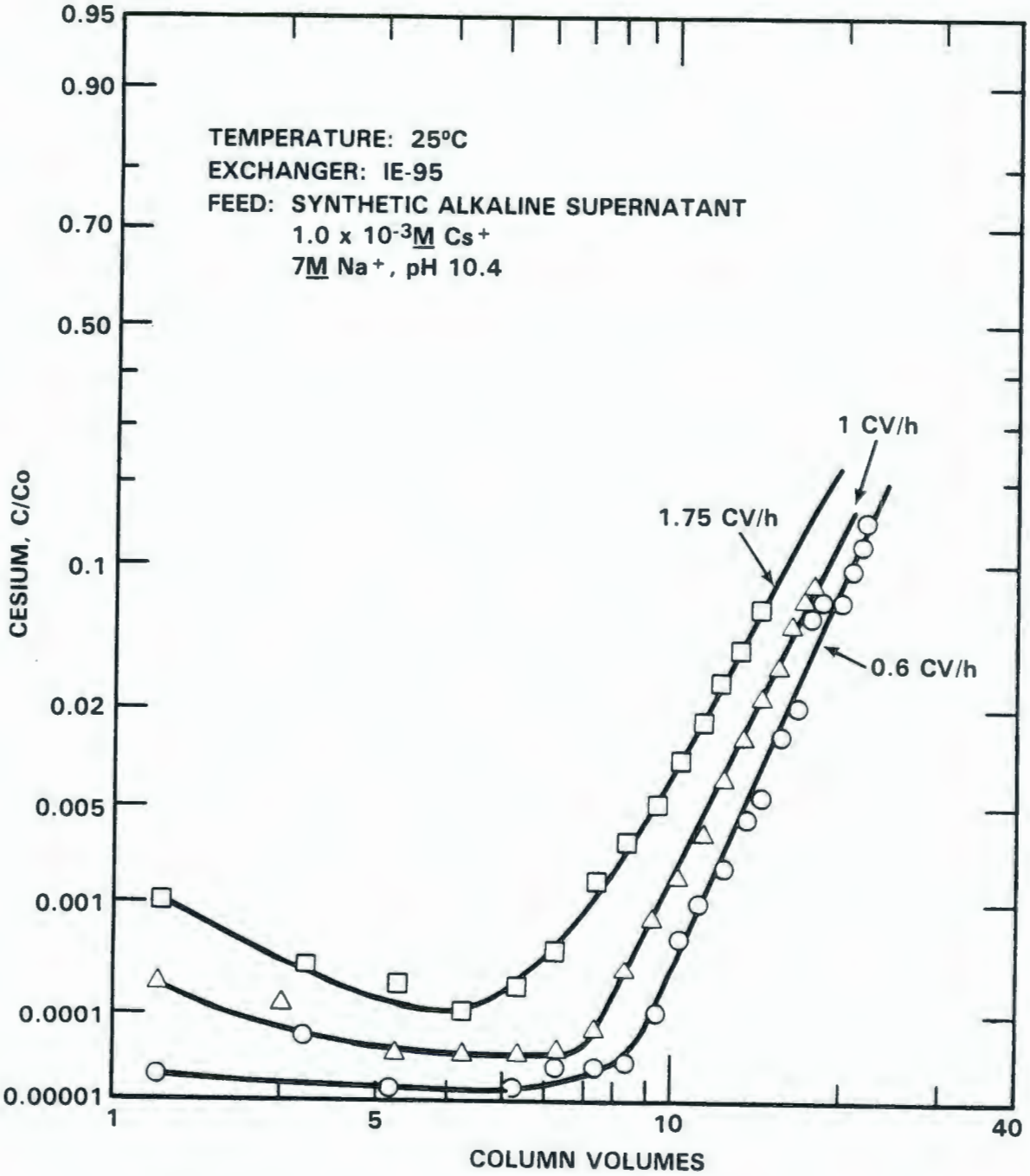


FIGURE 26. Cesium Breakthrough as a Function of Flow Rate for Zeolite Exchanger IE-95 at pH 10.4

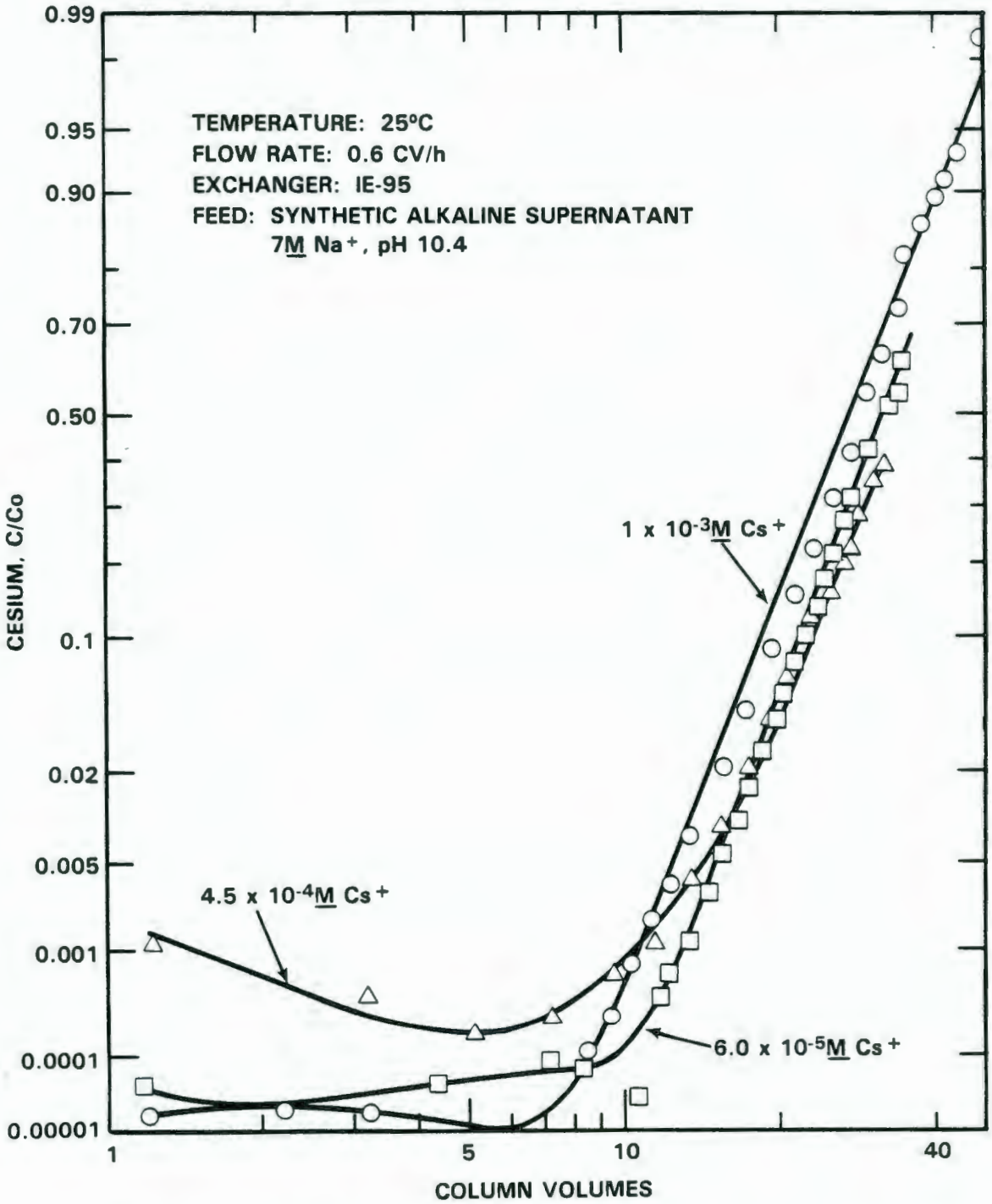


FIGURE 27. Cesium Breakthrough as a Function of the Influent Cesium Concentration for the Zeolite Exchanger IE-95

TABLE 27. Cesium Loaded on IE-95 as a Function of Na/Cs Mole Ratio

Na/Cs Mole Ratio	Column Volumes at 0.01 C/Co	Moles Cs Loaded/L of IE-95
7.0 E+3	13	1.3 E-2
1.56 E+4	16	7.1 E-3
1.17 E+5	16	9.6 E-4

(Figure 31). To obtain a C/Co value of 0.01, 21 and 6.5 cv of 1 and 4M HNO_3 were required, respectively. The zeolite bed was disrupted during acid elution due to the formation of CO_2 gas in both tests, which may account for the unusual elution profiles. However, the Sr may be associated with the calcium carbonate, which dissolves readily in HNO_3. The resulting eluted exchangers were sized to determine physical destruction due to the NHO_3 eluated. No major size reduction was noted. Reuse of the exchanger has not been tested, but nearly total loss in cesium loading is expected.

Based on the above laboratory data and minimum process requirements, conditions that should achieve optimum performance for an inorganic ion-exchange system are shown in Table 30.

Technetium Organic Anion Exchange

Recovery of Tc from alkaline supernatant has been studied at Hanford (Buckingham 1967). Roberts, Smith, and Wheelwright (1963) recovered more than 1 kg of Tc from the PUREX alkaline supernatant as part of an early fission product utilization study, and a flowsheet was developed (Beard 1964). Technetium is found in the West Valley waste supernatant as a soluble pertechnetate anion, TcO_4^-. Initial reports on the radiochemical composition of Tank 3D2 predicted that the Tc would be found as $Ba(TcO_4)_2$ in the sludge phase. More recent studies show that 92 kg (1600 Ci) of Tc (90%) will be found in the supernatant phase.

Technetium R_d values (Table 23) show that the quaternary ammonium polystyrene, strong-base anion exchange resins will recover (Tc R_d = 223) the TcO_4^- anion from synthetic West Valley supernatant of pH 10.4. The results for a single ion exchange column loading and elution test using Dowex-1,X8 resin are summarized below.

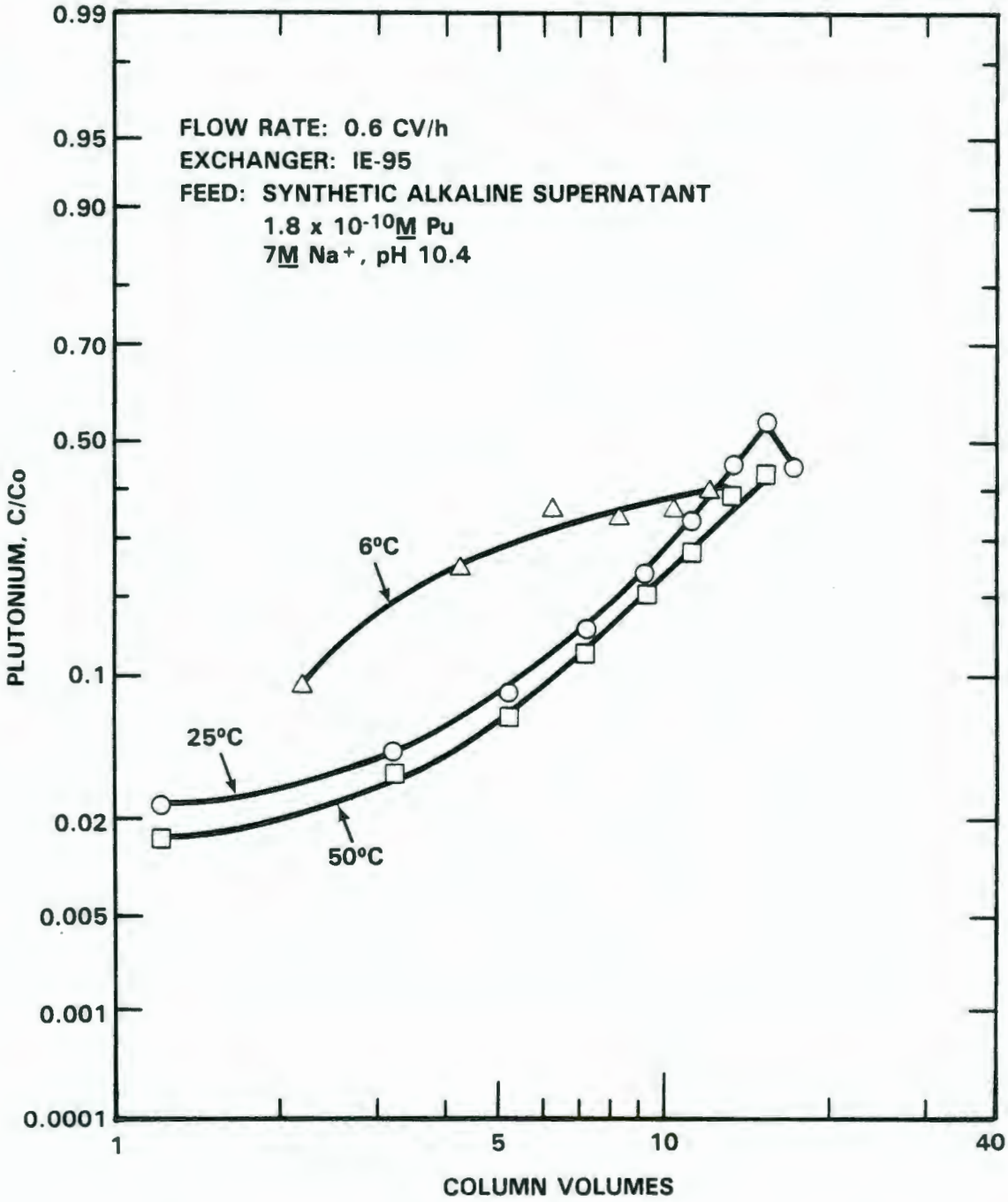


FIGURE 28. Plutonium Breakthrough as a Function of Temperature for Zeolite Exchanger IE-95

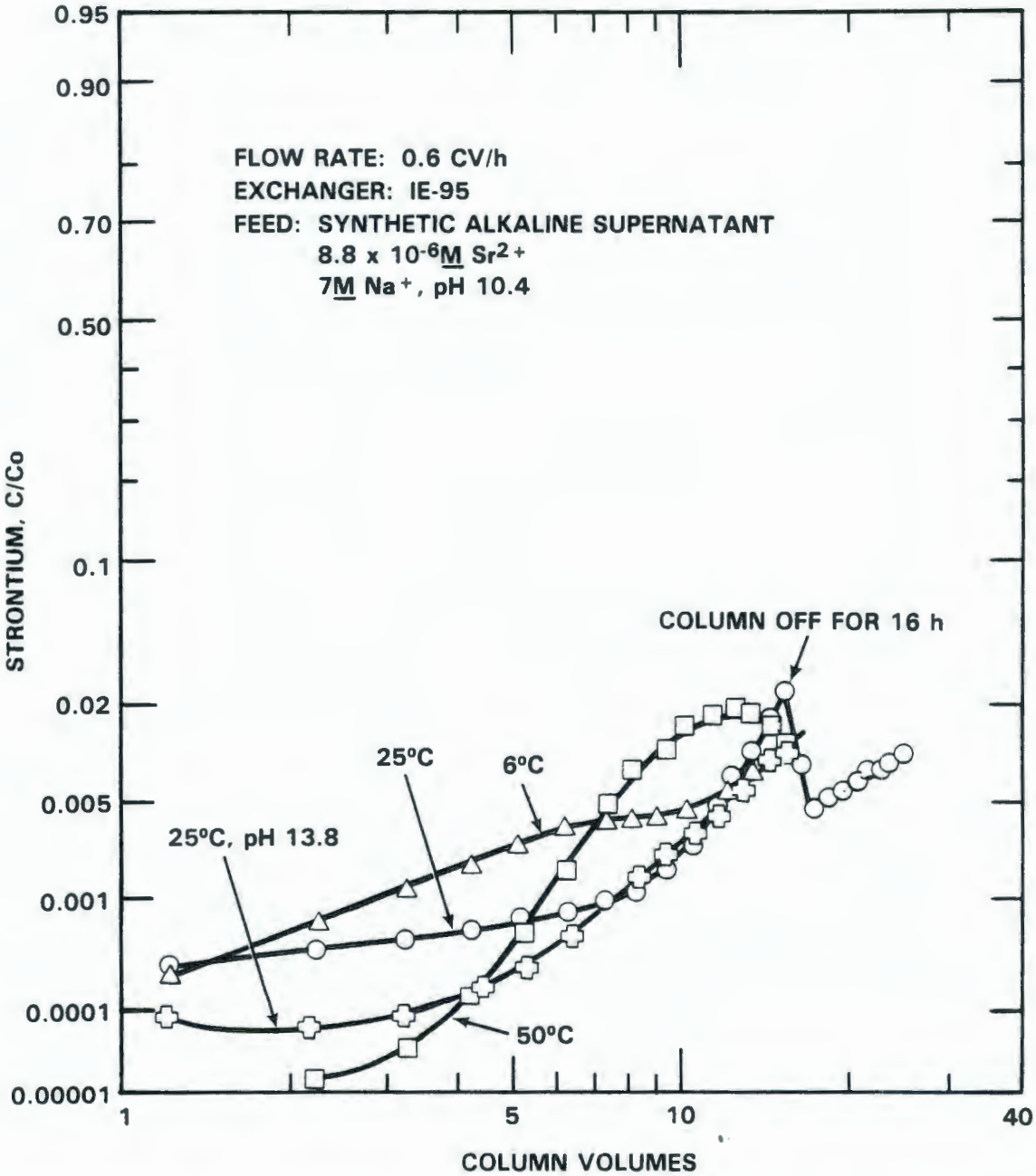


FIGURE 29. Strontium Breakthrough as a Function of Temperature for Zeolite Exchanger IE-95

TABLE 28. Breakthrough Values for IE-95 as a Function of Temperature

Element	Breakthrough Fraction, C/Co 6°C	25°C	50°C
Cs	4.0 E-5	5.0 E-5	6.5 E-4
Sr	4.0 E-3	1.0 E-3	7.0 E-3
Pu	3.5 E-1	1.9 E-1	1.5 E-1

TABLE 29. Batch Elution of IE-95 Using Nitric and Formic Acid[a]

Acid	Loading, Cs R_d	% of Initial Cs That Loaded	Stripping, Cs R_d	% of Initial Cs That Stripped
0.5M HNO_3	3.3 E+1	23.8	3.1 E+0	23.2
2M HNO_3	3.4 E+1	24.0	0.1 E-1	24.5
0.1M HCOOH	3.4 E+1	23.8	1.3 E+4	0.2
2M HCOOH	3.4 E+1	24.0	4.7 E+2	4.5

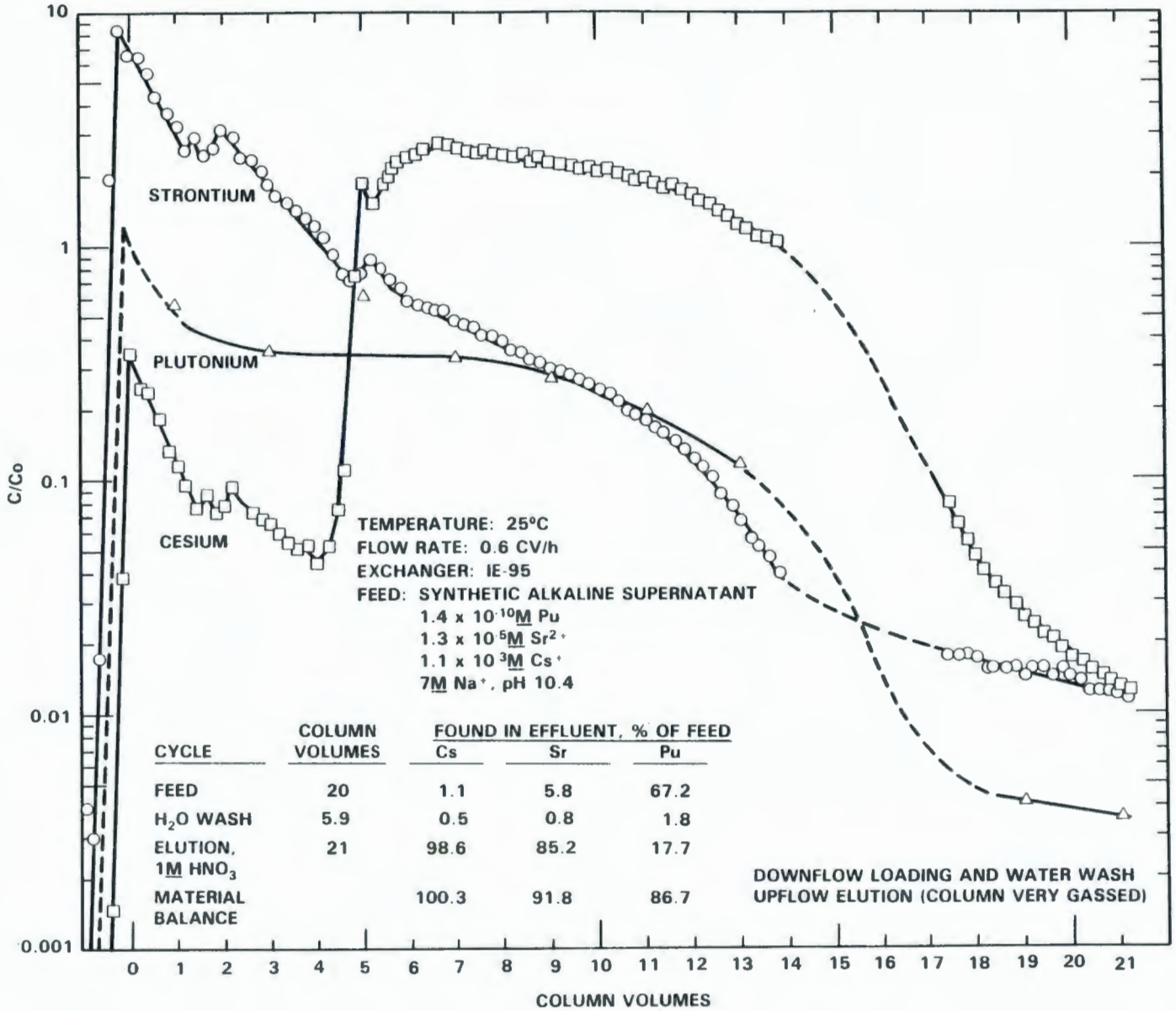
(a) Conditions: Batch contact 0.1 g of IE-95 with 10 mL of West Valley synthetic waste, pH 10.8, 1.1 x 10^{-3}M Cs^+, for 24 hours. Determine R_d value for loading. Wash exchanger with two 10-mL contacts of H_2O. Contact exchanger with formic or nitric acid for 24 hours.

Dowex-1,X8 Loading and Elution

Synthetic alkaline supernatant (pH 10.4) was adjusted to a Tc content of 0.044 g/L. The feed was passed through a 100 mL ion-exchange column containing Dowex-1,X8 resin in the nitrate form at 0.6 cv/h (Figure 32). A 0.01, 0.1, and 0.5 C/Co Tc breakthrough occurred at 84, 91, and 100 cv, respectively. After washing the column of resin with H_2O, the TcO_4^- was eluted with 9 cv of 8M HNO_3, with an average concentration of ~0.5 g Tc/L (Figure 33). The maximum eluate concentration was 30 times the feed concentration, or 1.3 g Tc/L. A DF of ~100 was achieved after 90 cv of feed were loaded. Greater than 99% of the Tc was recovered from the Dowex-1,X8 resin with 9 cv of 8M HNO_3.

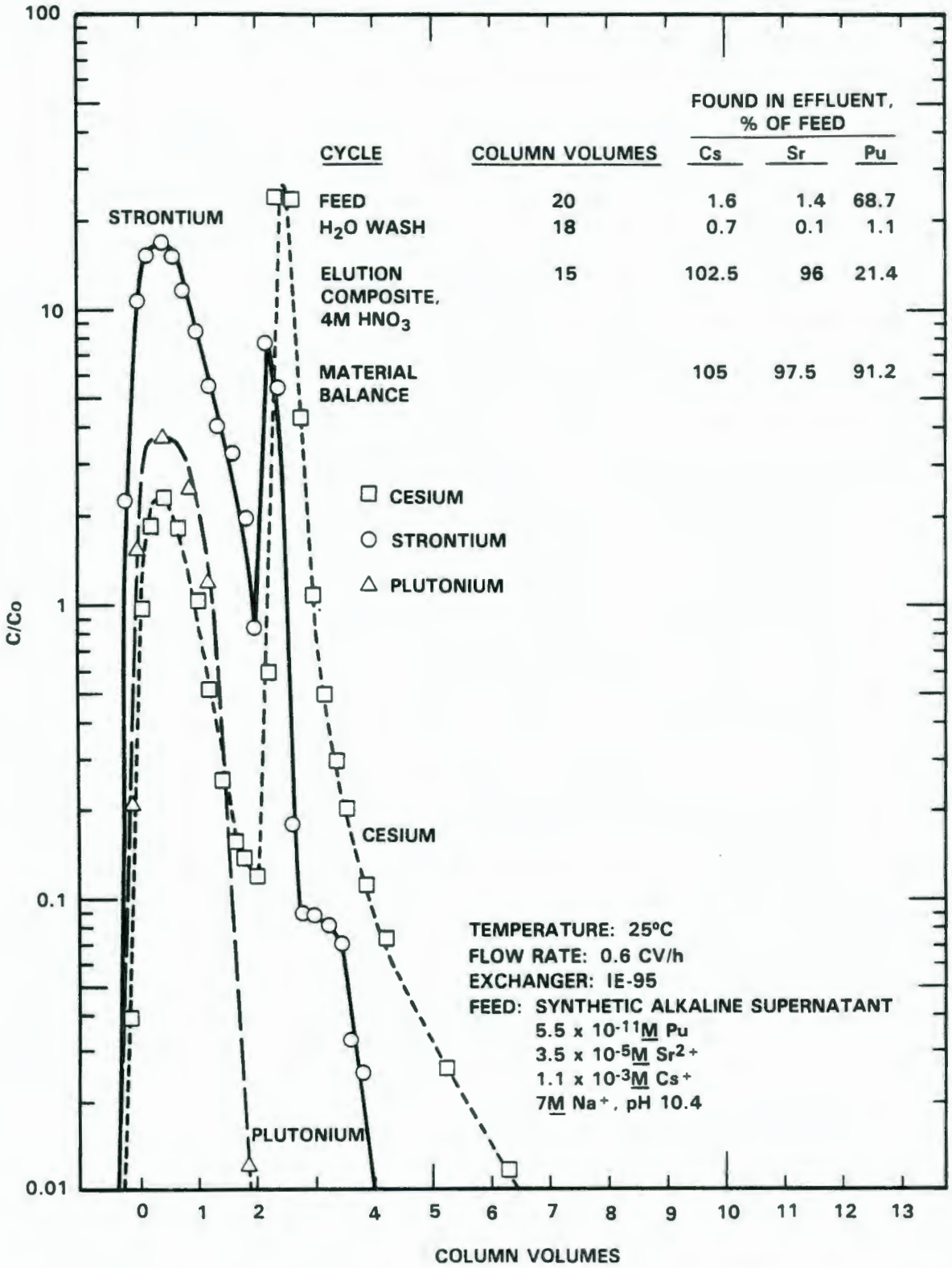
ASSESSMENT OF ION-EXCHANGE CANDIDATES FOR CESIUM RECOVERY

Organic ion-exchange resin CS-100 and inorganic exchanger IE-95 were selected for ion-exchange column testing based on an initial batch screening



CYCLE	COLUMN VOLUMES	FOUND IN EFFLUENT, % OF FEED Cs	Sr	Pu
FEED	20	1.1	5.8	67.2
H_2O WASH	5.9	0.5	0.8	1.8
ELUTION, 1M HNO_3	21	98.6	85.2	17.7
MATERIAL BALANCE		100.3	91.8	86.7

FIGURE 30. Elution of the Zeolite Exchanger IE-95 Using 1M HNO_3



CYCLE	COLUMN VOLUMES	FOUND IN EFFLUENT, % OF FEED Cs	Sr	Pu
FEED	20	1.6	1.4	68.7
H_2O WASH	18	0.7	0.1	1.1
ELUTION COMPOSITE, 4M HNO_3	15	102.5	96	21.4
MATERIAL BALANCE		105	97.5	91.2

FIGURE 31. Elution of the Zeolite Exchanger IE-95 Using 4M HNO_3

TABLE 30. Optimum Conditions for an Inorganic Ion-Exchange System

Process Parameters	Inorganic Ion Exchange	
	Optimum Conditions	Comments
Temperature	25°C	Lower temperatures (6°C) will enhance Cs capacity on both CS-100 and IE-95 by a factor of 1.2. Higher temperatures may enhance Pu and Sr recovery on IE-95. However, higher temperatures provide adverse Cs loadings.
pH	10.4	IE-95 will provide a Cs DF of 10^4, a Sr DF of 225 and a Pu DF of 6.
Flow rate	0.6 cv/h	Cs, Sr, and Pu loadings are enhanced by lower flow rates.
Na to Cs mole ratio in feed	<7000	Cs loading on IE-95 is enhanced by lower Na/Cs mole ratios.
Mass of IE-95 required for Tank 8D2	1×10^5 kg	Process will use three or more ion-exchange beds in series, front bed loaded to capacity (~20 cv) to optimize the process. Zeolite does not impact the glass mass (Al_2O_3 in glass ~6 wt%).
Elution (optional)	HNO_3	Zeolite loading/elution cycling is impractical due to exchanger breakup. Eluted zeolite can be packaged and disposed of as LLW or added to the concrete. Eluate (nitric acid) may require acid destruction. Batch elution may be viable. Column elution may not be viable due to gas formation during elution.

process. They were tested in a 100-mL ion-exchange column with synthetic West Valley alkaline supernatant to examine key process variables such as pH, temperature, and loading capacity. A comparative evaluation of the ion-exchange candidates is discussed below.

pH

The West Valley Tank 8D2 contains 2.1×10^6 L of alkaline supernatant at a pH of ~10. The exchangers were tested to determine the effect of pH. The capacity for Cs as a function of pH showed that IE-95 inorganic exchanger provided more Cs capacity at either pH 10 or 13, as compared to CS-100 (see

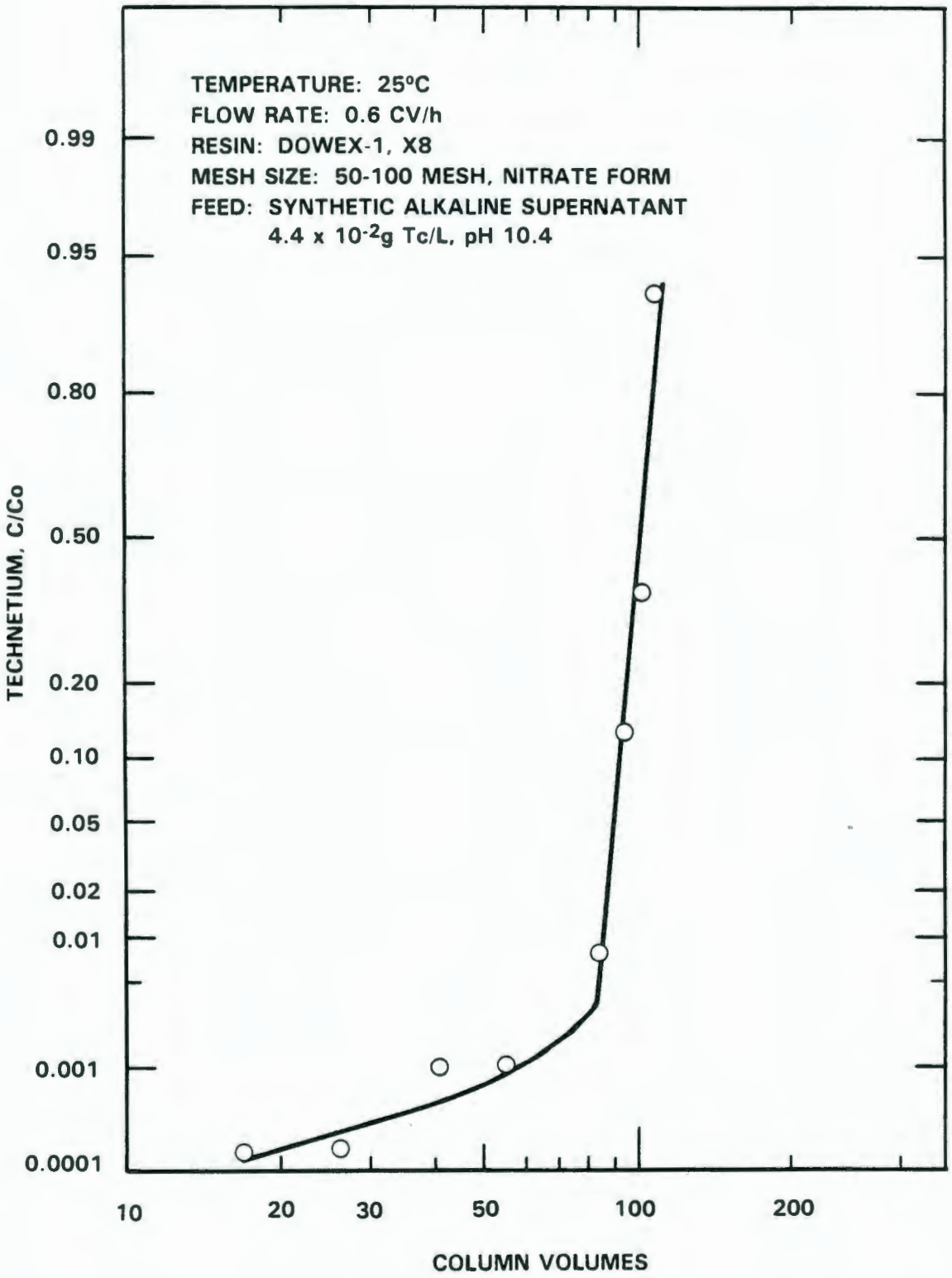


FIGURE 32. Technetium Breakthrough for Organic Anion Resin Dowex-1,X8

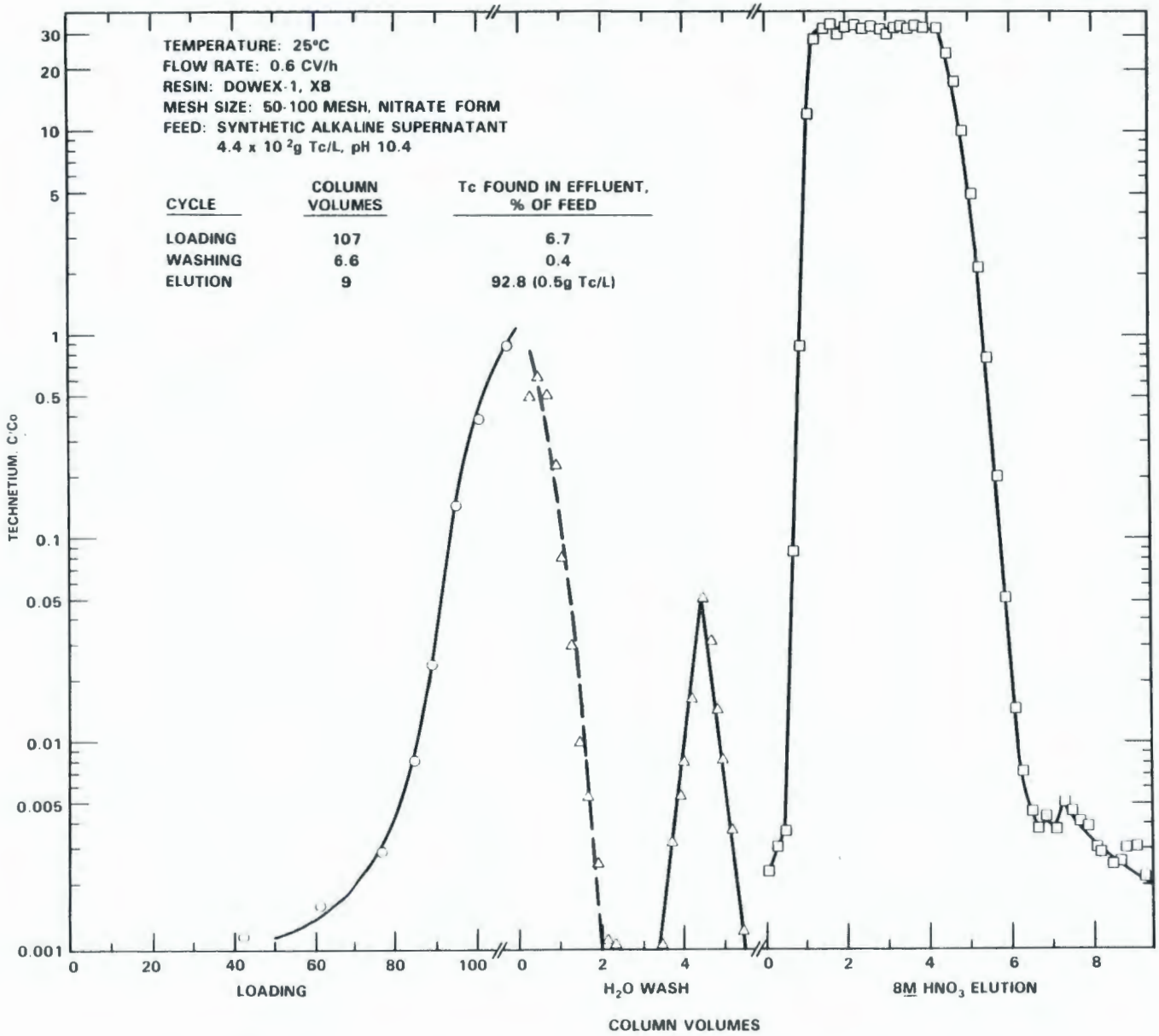


FIGURE 33. Technetium Breakthrough for Loading and Elution Cycles of Organic Anion Resin Dowex-1,X8

Figure 34 and Table 31). The Cs capacity expressed in cv of feed loaded at 0.5 C/Co breakthrough increased from 2.6 to 8.5 cv for CS-100, while the capacity on IE-95 decreased from 31 to 19 cv, as the feed pH varied from 10.4 to 13.6. The ratio of IE-95 capacity for Cs to CS-100 capacity was 12 at pH 10.4, and 2.2 at pH 13.6.

Temperature

Increased temperature had an adverse effect on Cs^+ loading for both IE-95 (Figure 16) and CS-100 (Figure 24). This effect was caused by partial dehydration of the Na^+ ion at elevated temperatures, which increased its ability to compete with the unhydrated Cs^+ ion. The Cs^+ capacity of IE-95 is higher than CS-100 at 0.5 C/Co by a factor of ~3, as the temperature is varied from 6 to 50°C (see Figure 35 and Table 32).

Cesium Loading Capacity

The Cs loading capacity for both IE-95 (Figure 27) and CS-100 (Figure 17) at 0.5 C/Co is dependent on the Na/Cs mole ratio of the alkaline supernatant feed. The loading results are compared in Table 33 and Figure 36. Assuming that loading is independent of pH, Cs loads onto IE-95 by a factor of >2 more than onto CS-100 for the same Na/Cs mole ratio. The Na to Cs mole ratio for the West Valley alkaline supernatant was assumed to be ~7000 for this study, and the Cs-loading capacity on IE-95 (pH 10.4) was greater by a factor of 3.6 than on CS-100 (pH 13.6).

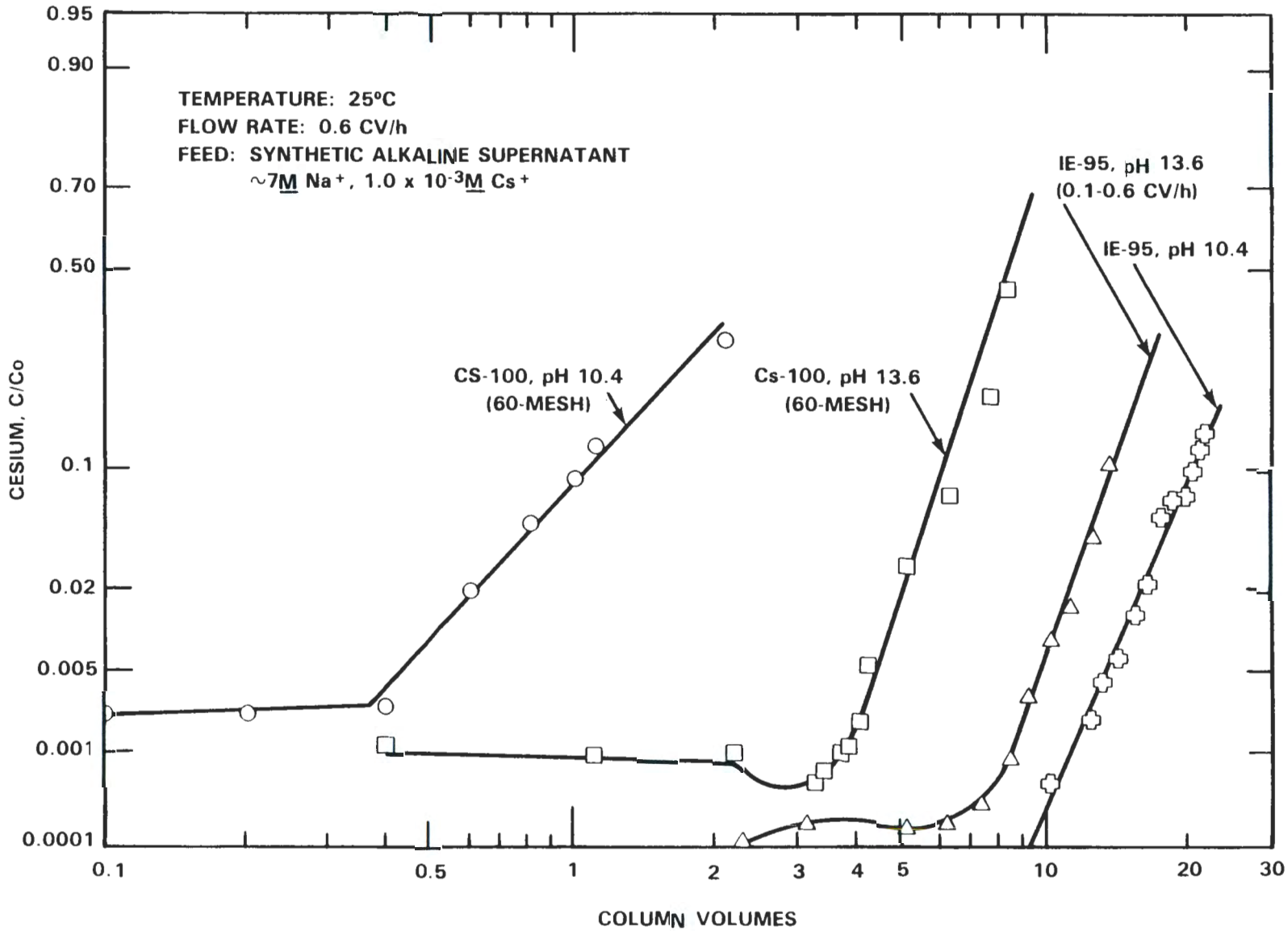


FIGURE 34. Cesium Breakthrough as a Function of Exchanger and Feed pH

TABLE 31. Cesium Loading Capacity on IE-95 and CS-100 as a Function of pH for the West Valley Synthetic Alkaline Supernatant[a]

	Alkaline Supernatant pH 10.4	Alkaline Supernatant pH 13.6	pH 10.4/pH 13.6 Cs Capacity Ratio
CS-100			
Column volumes	2.6 E+0	8.5 E+0	
Moles Cs loaded per L of CS-100	2.6 E-3	8.5 E-3	3.0 E-1
IE-95			
Column volumes	3.1 E+1	1.9 E+1	
Moles Cs loaded per L of IE-95	3.1 E-2	1.9 E-2	1.6 E+0
IE-95/CS-100 Cs capacity ratio	1.2 E+1	2.2 E+0	

(a) Conditions: ~7M Na^+, 1 x 10^{-3}M Cs^+, 25°C.
Breakthrough: C/Co = 0.5.

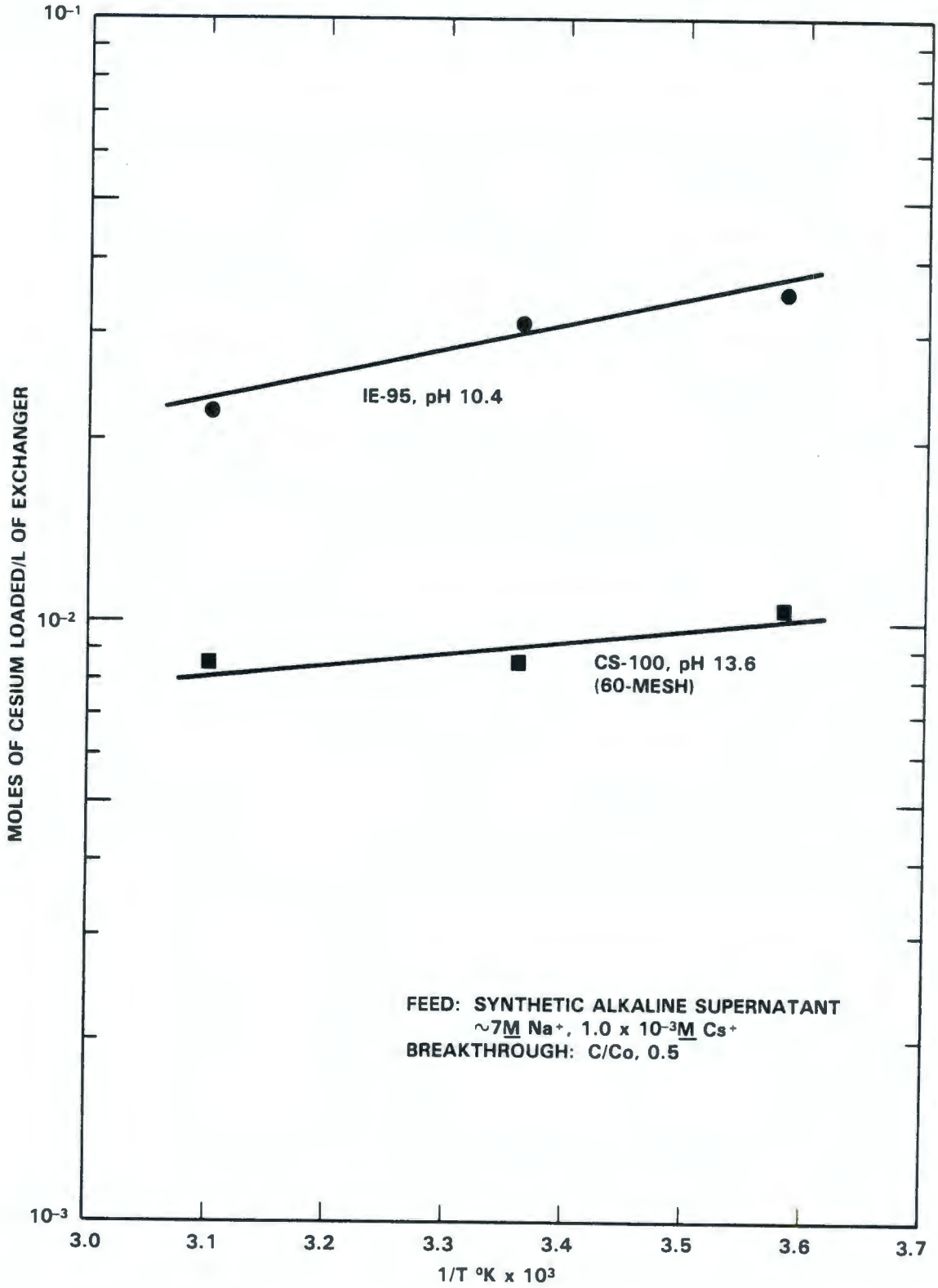


FIGURE 35. Cesium Loading Capacity as a Function of Temperature

TABLE 32. Cesium Loading Capacity on IE-95 and CS-100 as a Function of Temperature for the West Valley Alkaline Supernatant[a]

	Temperature		
	50°C	25°C	6°C
CS-100 (pH 13.6)			
Column volumes	8.5 E+0	8.5 E+0	1.1 E+1
Moles Cs loaded per L of CS-100	8.5 E-3	8.5 E-3	1.1 E-2
IE-95 (pH 10.4)			
Column volume	2.2 E+1	3.1 E+1	3.5 E+1
Moles Cs loaded per L of IE-95	2.2 E-2	3.1 E-2	3.5 E-2
1/T°K	3.10 E-3	3.36 E-3	3.58 E-3
IE-95/CS-100 Cs capacity ratio	2.6 E+0	3.6 E+0	3.2 E+0

(a) Conditions: 7M Na^+, 1×10^{-3}M Cs^+.
Breakthrough: C/Co = 0.5.

TABLE 33. Cesium Loading Capacity on IE-95 and CS-100 as a Function of the Na/Cs Mole Ratio for the West Valley Alkaline Supernatant

	Na/Cs Mole Ratio	Column Volumes at 0.5 C/Co	Moles Cs Loaded/ L of Exchanger
IE-95 (pH 10.4)	7.0 E+3	27.2	2.7 E-2
	1.6 E+4	31.5	1.4 E-2
	1.2 E+5	34	2.0 E-3
CS-100 (pH 13.6)	7.2 E+3	8.7	8.7 E-3
	7.2 E+4	13.2	1.3 E-3
	7.2 E+5	20.3	2.0 E-4

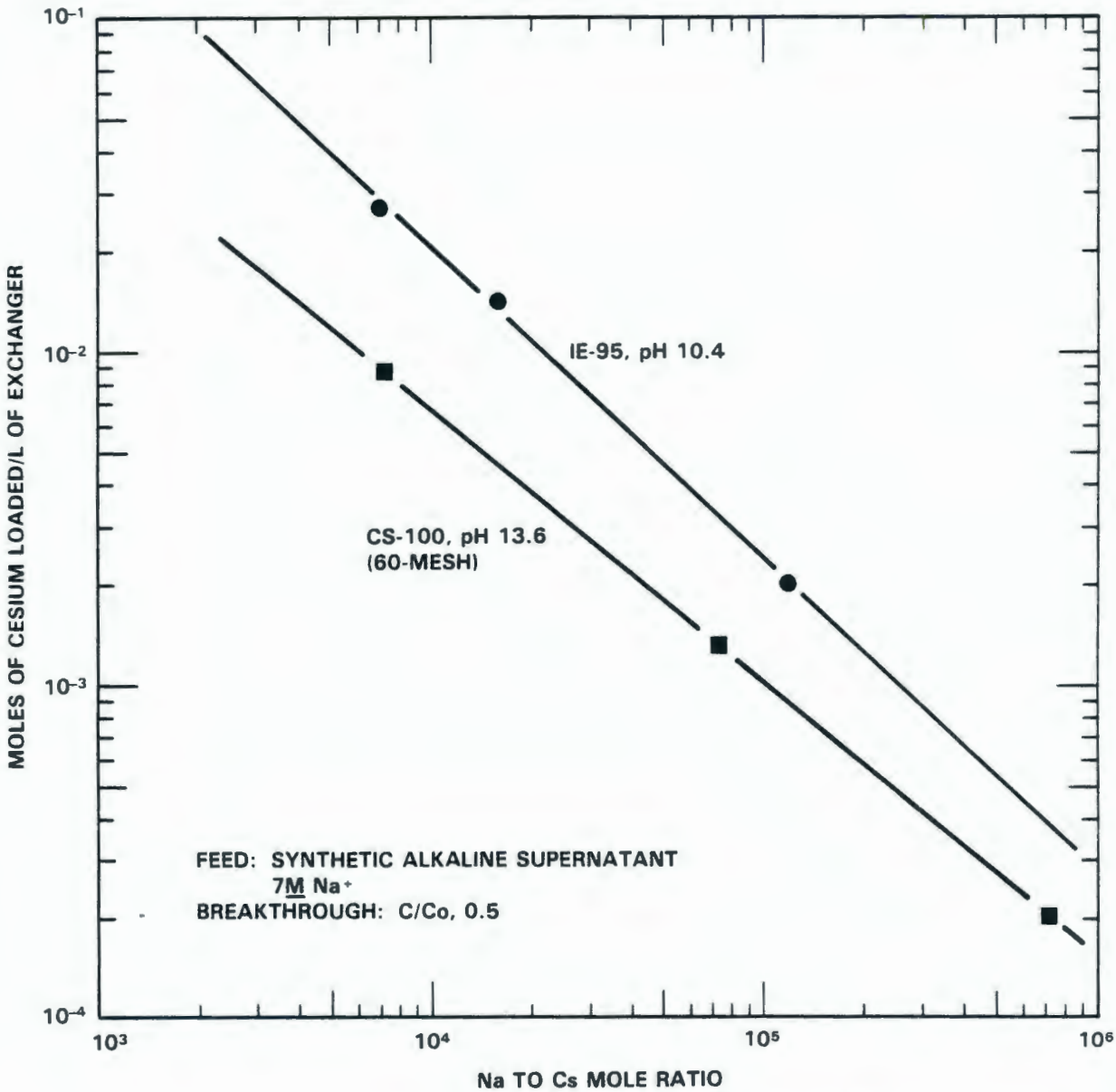


FIGURE 36. Cesium Loading Capacity as a Function of Na/Cs Mole Ratio

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APPENDIX A

PREPARATION OF WEST VALLEY SIMULATED ALKALINE WASTE

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PREPARATION OF WEST VALLEY SIMULATED ALKALINE WASTE

Two approaches have been used to prepare the simulated West Valley alkaline waste. In earlier studies, the simulated wastes were prepared by neutralization of acidic PUREX wastes, resulting in formation of a sludge phase and a supernatant phase. Based upon this initial work, it was recommended that the precipitant chemicals be added to a separated supernatant phase only. Experimental work was then continued using an alkaline supernatant starting feed prepared by mixing the appropriate chemicals. Both experimental approaches are summarized below.

PRECIPITATION APPROACH TO SUPERNATANT PREPARATION

The procedure involves preparation of simulated acidic PUREX wastes with the addition of either ^{137}Cs, ^{85}Sr, ^{237}Np, ^{241}Am, ^{99}Tc, ^{154}Eu, or ^{238}Pu. The acidic waste is neutralized and the pH adjusted to 10 or 12.8 with excess sodium hydroxide (NaOH). The solution is then thermally digested for 24 hours. Upon neutralization, a solid phase forms and settles to the bottom of the test beaker. The supernatant is clarified by centrifugation, and the amount of Cs, Sr, Np, Am, Tc, Eu, or Pu remaining in solution is then determined by beta or gamma analysis. The sludge and supernatant contain the following:

Component	Concentration, M	Component	Concentration, M
Na	~7 E+0	Al	1.5 E-2
K	1.6 E-1	Zr	3.4 E-4
Rb	1.1 E-4	Sm	4.4 E-3
Cs	1.1 E-3	NO_3	4.4 E+0
Sr	2.7 E-5	NO_2	1.8 E+0
Ba	3.0 E-4	OH (Free)	0-2.5 E-1
Mn	1.3 E-2	SO_4	3.2 E-1
Mo	6.0 E-3	PO_4	1.0 E-1
Fe	3.3 E-1	Cl	4.3 E-3

Component	Concentration, M	Component	Concentration, M
Cr	2.9 E-2	CO_3	3.9 E-1
Ni	1.3 E-2	F	2.7 E-2

One-liter batches of spiked alkaline waste are prepared by the following procedure.

600 mL of Stock A, a solution containing mostly metal nitrates and $NaNO_3$, is spiked with the radionuclide of interest. To this spiked solution, 17.8 mL of concentrated H_2SO_4 and 6.8 mL of concentrated H_3PO_4 are added. The pH of the solution is then adjusted by addition of either 100 mL of Stock B, an NaOH solution (for pH ~10 waste), or 126 mL of Stock B (for pH ~13 waste). Finally, 352 mL of Stock C, containing $NaNO_2$ and Na_2CO_3, is added to the simulated waste and the mixture digested at 90 to 95°C for 24 hours, and then cooled.

COMPOSITION OF STOCK SOLUTIONS

Stock solutions A, B, and C were composed of the components listed below with their concentrations in moles.

Stock Solution A

Component	Concentration, M
NaCl	7.2 E-3
$NaNO_3$	5.4 E+0
$Al(NO_3)_3 \cdot 9H_2O$	2.4 E-2
$Ni(NO_3)_2 \cdot 6H_2O$	2.2 E-2
$Cr(NO_3)_3 \cdot 9H_2O$	4.8 E-2
KNO_3	2.1 E-1
$Fe(NO_3)_3 \cdot 9H_2O$	5.5 E-1
$CsNO_3$	1.8 E-3
$Sr(NO_3)_2$	4.6 E-5
$RbNO_3$	1.8 E-4
$Ba(NO_3)_2$	5.0 E-4

Stock Solution B

Component	Concentration, M
NaOH	1.9 E+1
MoO_3	9.8 E-2

Stock Solution C

$NaNO_2$	5.0 E+0
Na_2CO_3	1.1 E+0

Stock Solution A

Component	Concentration, M
$Zr(NO_3)_4 \cdot 5H_2O$	5.7 E-4
$Sm(NO_3)_3$	7.3 E-3
$Mn(NO_3)_2$	2.2 E-2
HF	4.5 E-2
specific gravity, g/mL	1.4 E+0

CHEMICAL MIXING APPROACH TO SUPERNATANT PREPARATION

This procedure for preparation of alkaline supernatant containing ^{238}Pu, ^{85}Sr, or ^{137}Cs involves direct mixing of the appropriate chemicals. The following table summarizes the chemicals used to prepare the simulated supernatant and the element concentrations as determined by chemical makeup.

West Valley Synthetic Supernatant Prepared by Chemical Mixing

Chemical Makeup[a]

Component	Concentration, g/L	Element	Concentration, M
$NaNO_3$	2.9 E+2	Na	~7.0 E+0
Na_2SO_4	3.6 E+1	K	1.6 E-1
KNO_3	1.6 E+1	Cs	1.0 E-3
$Cr(NO_3)_3 \cdot 9H_2O$	2.6 E-2	Rb	1.0 E-4
$Fe(NO_3)_3 \cdot 9H_2O$	1.2 E-2	Cr	2.0 E-3
NaCl	2.3 E+0	Fe	3.0 E-5
$RbNO_3$	5.9 E-2	NO_3	3.4 E+0
$CsNO_3$	1.8 E-1	NO_2	2.2 E+0
Na_2CO_3	4.1 E+1	SO_4	2.5 E-1
$NaNO_2$	1.5 E+2	Cl	4.0 E-2
H_3PO_4, mL	6.7	P	1.0 E-2
NaOH	0 (pH 10.4)	CO_3	3.9 E-1
	1.9 E+1 (pH 13.7)	OH	0 to 2.2 E-1
		pH	10.4 to 13.7

(a) After dissolution, the liter of solution is adjusted to weigh 1340 g, and is filtered through prepleated, medium porosity filter paper to remove any foreign material.

Strontium-85 and ^{238}Pu are added to the supernatant solutions together. Five milliliters of Sr stock solution (0.19M $Sr[NO_3]_2$ stock solution spiked with ^{85}Sr) is added to 1 L of simulated supernatant. Plutonium-238 is also added ($\sim 10^{-9}$ M) to the supernatant solution in a similar manner. The concentration of Sr and Pu in the stock solutions added to the supernatant is greater than the quantity of each isotope which is soluble in the supernatant. Consequently, the majority of Sr and Pu was precipitated over a 48-hour digestion period. The resulting alkaline supernatant is filtered through 0.2 μm filter paper prior to use in the experiments. Cesium-137 is added to samples of alkaline supernatant without additional filtering. Technetium-99 is added to obtain a concentration of 0.044 g/L in the supernatant.

Concentrations of ^{85}Sr, ^{137}Cs, and ^{238}Pu are determined by counting the stock solution. The solubility of the Sr in this feed is $\sim 10^{-5}$M. The ^{85}Sr count rate in the prepared supernatant is lower than acceptable for use in the experiment. Therefore, additional ^{85}Sr is added to the supernatant to achieve acceptable counting statistics. The mass quanitity of ^{85}Sr added in this manner does not significantly increase the total concentration of Sr in the simulated supernatant. The concentration of ^{238}Pu is $\sim 10^{-11}$ M in the supernatant; however, the Pu valence has not been determined.

RADIOTRACER ANALYSIS

Gamma counting is used for radiotracers of ^{137}Cs, ^{22}Na, $^{152-154}Eu$, and ^{85}Sr. These tracers do not significantly increase the total concentration of the specific ion in the simulated supernatant but are used to follow the ions pathway. A 4 mL sample of the initial "spiked" feed is used as the standard. During the test program, 4 mL samples of waste effluent or eluate are compared with the standard. Gamma counting is performed by the use of a multichannel analyzer and a NaI well detector.

Samples containing alpha or beta emitters such as I, Np, Am, and Tc are counted using a Tri-Carb 300-C scintillation counter after mixing 1 mL of standard or sample with 15 mL of xylene-surfactant-based scintillation cocktail such as PCS.

To analyze for Pu, samples containing ^{238}Pu or mixtures of ^{238}Pu-^{137}Cs or ^{238}Pu-^{85}Sr require a Pu extraction prior to scintillation counting. Samples (1 mL) are mixed with 1 mL of 10M HNO_3 and heated to destroy nitrates. The sample is then mixed with 10 mL of 2M HNO_3 containing 0.1 mL of 200 g/L urea. The resulting aqueous solution is contacted with 10 mL of Pu extractant/scintillation cocktail. This organic mixture is prepared by mixing 0.0225M p-terphenyl, 0.22M HDEHP[a], and 0.0014M POPOP[b] in toluene. The organic and aqueous phases are allowed to separate after stirring for 15 minutes. Five mL of the organic phase containing the Pu is transferred into a second vial containing 10 mL of new 2M HNO_3. The sample is again stirred for 15 minutes to scrub traces of the aqueous phase ^{137}Cs or ^{85}Sr from the organic phase. The organic phase on top of the aqueous phase is then counted by liquid scintillation without further separation.

(a) HDEHP: di-(2-ethylhexyl)phosphoric acid.
(b) POPOP: p-bis(2-[phenyloxazolyl])benzene.

APPENDIX B

WASHING PROCEDURES FOR WEST VALLEY SIMULATED ALKALINE WASTE SLUDGE

APPENDIX B

WASHING PROCEDURES FOR WEST VALLEY ALKALINE SIMULATED WASTE SLUDGE

The current process approach for treatment of the alkaline PUREX waste stored at West Valley involves separation of the sludge and supernatant, and washing of the resultant sludge to remove soluble salts. The objective of this work is to develop chemical and radiochemical data for the various chemical and radiochemical species distribution between the sludge and supernatant during the sludge-washing process. Two scenarios were investigated: 1) the case of the waste as it exists, and 2) the case in which Na-TiA has been added to the waste to remove Pu and Sr.

Simulated waste representing the West Valley HLW was prepared by the neutralization and precipitation of simulated acidic PUREX waste (see Appendix A). The simulated waste was spiked with ^{85}Sr, ^{137}Cs, ^{99}Tc, $^{152-154}Eu$, ^{237}Np, ^{241}Am, or ^{238}Pu. The simulated sludge was washed to a sulfate concentration equivalent to 1 wt% Na_2SO_4 in the waste glass. The chemical species of interest in the washing study are NO_3^-, NO_2^-, $SO_4^=$, and Na^+. Wastes of pH ~10 and pH ~13 were prepared, and the effect of the additive Na-TiA was investigated. Radiochemical data were developed for the pH ~10 case only.

SLUDGE WASHING WITHOUT PRECIPITANTS

The simulated waste was separated into sludge and supernatant phases with an International Equipment Co. centrifuge, Size 1, Type SB. In some instances it was not possible to decant off as much supernatant as desired because the simulated sludge was not as well settled as actual West Valley sludge. In these cases, as much supernatant was decanted as possible. Below is the general procedure used for 1 L batches.

The supernatant is decanted from the sludge and then 375 mL of distilled water is added to the sludge. The mixture is agitated for 24 hours and then centrifuged, and the 375 mL wash solution is

decanted. The procedure is repeated three times, adding and decanting 230, 200, and 180 mL of supernatant for the second, third, and fourth wash steps, respectively. After the final decant step, the sludge is dissolved in HCl for analytical purposes and diluted to 5000 mL. Samples are taken of the supernatant and the wash solutions at each step, and of the final dissolved sludge. Sludge samples containing tracers will be dissolved in HNO_3.

SLUDGE WASHING WITH Na-TiA

The procedure used for the sludge washing with Na-TiA ($Na_2Ti_3O_7$) is virtually the same as that for the sludge without additives. The simulated waste, however, is first contacted with 62 g of Na-TiA/L and agitated at 25°C for 24 h. The addition of 62 g of Na-TiA/L was based on the assumption that the supernatant was 2.74×10^{-8} M Sr, and that a Na-TiA to Sr mole ratio of 2.45×10^{6} was required. It was assumed that there was 1.05×10^{-3} moles/g of Na-TiA of centrifuged slurry. The Na-TiA is not allowed to dry during use, but is weighed for each sample after being centrifuged to a wet paste.

After the Na-TiA is agitated with simulated waste, the mixture is centrifuged and the washing process is initiated as in the no-additive case.

CALCULATION OF Na-TiA WET PASTE MOLARITY

The Na-TiA slurry purchased from AFF Inc., Marietta, Georgia, contained 7.2% Na-TiA; 67.4% isopropyl alcohol; 7.8% sodium salts of nitrate, nitrite aluminate, and sulfate; and 17.6% H_2O. The slurry settled easily. A centrifuged sample of slurry had a specific gravity of 1.07 g/mL. A 1 mL centrifuged sample was dried at 110°C for 16 hours and its weight assumed to be that of $Na_2Ti_3O_7$ (molecular weight = 301.7) was 0.317 g. From these factors it was calculated that there was:

$$\frac{0.317 \text{ g } Na_2Ti_3O_7/\text{g wet paste}}{301.7 \text{ g } Na_2Ti_3O_7/\text{mole } Na_2Ti_3O_7} = 1.05 \times 10^{-3} \text{ mole } Na_2Ti_3O_7/\text{g wet paste.}$$

This was the value we assumed in this study.

SAMPLE ANALYSES

Chemical analyses for cations are obtained by use of inductively coupled argon plasma spectrography (ICP) using a Jarrell-Ash Model 975 spectrometer. The anion results are obtained by ion chromatography (IC) using a Dionex Model-14 ion chromatograph.

Radiochemical trace analyses of ^{85}Sr, $^{152-154}Eu$, and ^{137}Cs are obtained by counting samples with a Canberra Model 40 multichannel gamma analyzer, which has a 7.6-cm-dia well NaI crystal detector. The ^{238}Pu tracer solution is contacted by HDEHP-PCS extraction; the ^{99}Tc, ^{237}Np, and ^{241}Am tracers by the use of PCS; and both are counted by liquid scintillation.

APPENDIX C

PROCEDURE TO TEST ADDITIVES THAT PRECIPITATE RADIONUCLIDES FROM ALKALINE SUPERNATANT

APPENDIX C

PROCEDURE TO TEST ADDITIVES THAT PRECIPITATE RADIONUCLIDES FROM ALKALINE SUPERNATANT

Laboratory-scale experiments were conducted to study the performance of a Na-TPB precipitation process for recovery of Cs and a Na-TiA recovery process for Sr and Pu from simulated West Valley alkaline supernatant. The effect of the following process variables were examined: temperature (25 and 50°C), pH (10.4 and 13.7), contact time (1 to 14 days), and quantity of precipitant chemical added.

The experimental procedure involved the use of simulated supernatants. The stock supernatant was spiked with ^{137}Cs, ^{89}Sr, or ^{238}Pu, and the solution filtered through 0.2 μm filter paper. The precipitant chemicals added were either Na-TPB for Cs studies or Na-TiA for Sr and Pu studies. Sealed bottles of the test solutions were prepared and placed in a constant-temperature shaker oven maintained at 50°C or a room-temperature shaker table maintained at 25°C. At defined time intervals, samples were withdrawn from the test bottles, poured through 0.2 μm filter paper, and analyzed for the recovery fractions of ^{137}Cs, ^{85}Sr (determined by gamma energy analysis); and ^{238}Pu (determined by extraction and scintillation counting).

TEST PROCEDURE FOR Na-TiA

Methods used to examine Sr and Pu recovery from simulated supernatants by the use of Na-TiA ($Na_2Ti_3O_7$) are described below.

Initially, a slurry of the alcohol-H_2O-$Na_2Ti_3O_7$ precipitate is added to weighed sample bottles. The alcohol-water is separated from the $Na_2Ti_3O_7$ by centrifugation and decantation, and the bottles reweighed. The Na-TiA paste should vary from 0.4 to 4.0 g. To each sample bottle 50 mL of simulated supernatant (pH 10.4 to 13.7) is added. The resultant solutions are capped and placed in a

constant-temperature (50°C) oven, or directly on the shaker table (25°C) and agitated. After agitation for a predetermined time period (from 1 to 14 days), a test bottle is removed, and a 5-mL sample is taken. The sample is filtered through a Gelman #4192 Acrodisc® filter disc (pore size 0.2 μm). About 4 mL of the resultant filtrate is sampled and counted for ^{85}Sr using gamma energy analysis to determine the Sr remaining in solution. The 4 mL sample is then returned to the test bottle, which is returned to the shaker table. The remaining 1 mL sample is extracted with 10 mL of organic HDEHP-PCS to recover the Pu. The extraction procedure does not remove traces of ^{85}Sr associated with the aqueous phase. However, the organic is scrubbed with 10 mL of 2M HNO_3 to remove traces of the aqueous phase containing ^{85}Sr. Organic samples of 5 mL each that contain Pu are analyzed using liquid scintillation counting. The 1 mL sample used for Pu analysis is not returned to the bottle. Samples of the original stock supernatant serving as standards are filtered and counted as above.

The Na-TiA slurry purchased from AFF Inc. contained 7.2% Na-TiA; 67.4% isopropyl alcohol; 7.8% sodium salts of nitrate, nitrite, aluminate, and sulfate; and 17.6% H_2O. This slurry settled easily. A centrifuged sample of slurry should be analyzed for specific gravity. The centrifuged sample is dried at 110°C for 16 hours and its weight assumed to be that of $Na_2Ti_3O_7$/g (molecular weight = 301.7). From these factors, a value for the moles of $Na_2Ti_3O_7$ per gram of centrifuged slurry is assumed. The Na-TiA slurry should not be allowed to dry out during use, but should be weighed out for each sample after being centrifuged in the test bottle.

TEST PROCEDURE FOR Na-TPB

Methods used to examine Cs precipitation using a sodium tetraphenylboron are described below.

Stock supernatant solutions of 25 mL each spiked with ^{137}Cs are blended with 0.4M Na-TPB. The final alkaline supernatant Na^+ ion

concentration (not including the Na^+ ion concentration with the Na-TPB) is held at a constant Na^+ ion concentration by adjusting the final volume with H_2O. To determine the effect of varying the Na^+ ion concentration on the precipitation of Cs^+, 25 mL of supernatant was placed in shaker bottles with 1.5 g of solid Na-TPB. The Na^+ ion concentration in the final solution of this series of tests varies from 3 to 6M Na^+ by the addition of 4 to 34 mL of H_2O. The resultant solutions/precipitates are placed in test bottles, capped, and placed in a constant-temperature oven (50°C), or placed directly on the shaker table (25°C) and agitated. After agitation for a predetermined time period, a test bottle is removed, and a 5 mL sample is taken and filtered through a Gelman #4192 Acrodisc filter disc (pore size of 0.2 μm). The resultant filtrate is sampled (4 mL) and counted using gamma energy analysis to determine the Cs concentration remaining in solution. The 5 mL sample is then placed back in the test bottle and the bottle returned to the shaker table. Samples of the original stock supernatant are filtered and counted as above for the standards.

Stock solutions of Na-TPB ($Na[C_6H_5]_4B$) were prepared. The Na-TPB was purchased from AFF Inc. with 95% purity. A formula weight of 360.2 g was used in preparation.

The following test parameters were examined for the Cs precipitation process:

- mole ratio Na-TPB/Cs+K+Rb (0.007 to 2.3)
- pH (10 and 12)
- contact time (1 to 14 days)
- temperature (25 and 50°C)
- Na concentration in the alkaline supernatant (3 to 6M).

APPENDIX D

PROCEDURE TO MEASURE BATCH SORPTION RATIOS FOR ION-EXCHANGE MATERIALS USING RADIONUCLIDE TRACER TECHNIQUES

APPENDIX D

PROCEDURE TO MEASURE BATCH SORPTION RATIOS FOR ION-EXCHANGE MATERIALS USING RADIONUCLIDE TRACER TECHNIQUES

This procedure describes a method to determine the relative distribution ratio for the batch ion-exchange method for specific radionuclides. The laboratory batch methodology provides a rapid and cost-effective method of comparing a wide variety of ion-exchange materials for their selectivity of specific radionuclides. Batch ion-exchange experiments involve contacting a sample of supernatant that contains the radionuclide under investigation with a small, weighed sample of ion-exchange material. After steady state is approached, the distribution ratio R_d is determined:

$$R_d = \frac{C_s}{C_l}, \ cm^3/g$$

where

C_s = the concentration of radionuclide exchanged in or on the solid phase (g/g of solid)

C_l = the concentration of radionuclide remaining in the liquid phase (g/cm^3 of solution).

The R_d generated by these batch selectivity experiments is a measure of the overall ability of the solid phase to remove the radionuclide from solution. The data are reported as distribution ratios (R_d) rather than distribution coefficients (K_d) because more than one mechanism may be involved and reversibility has not been demonstrated. In addition, contact temperature, contact time, and pH contribute to the value obtained.

RADIOTRACERS

Radiotracers used in this experiment include ^{137}Cs, ^{99}Tc, ^{131}I, ^{85}Sr, ^{237}Np, ^{238}Pu, and ^{241}Am. These radiotracers may be obtained either through commercial companies (e.g., New England Nuclear, Boston Massachusetts; or

Amersham, Arlington, Illinois), or from stock solutions already available. Technical data sheets accompanying the commercial shipments list the assay of the isotope (i.e., chemical form, purity, assay date, specific activity, concentration, and volume). This data, combined with calibrated known radiostandards, is used to determine the final concentration of the radiotracer as it is added to the supernatant.

Special precautions are taken when adding the actinides to synthetic supernatant to ensure that the tracer is in solution and not precipitated. A known aliquot of radiotracer is added to the supernatant solution and equilibrated. The stock solution is then filtered prior to use in batch tests.

COUNTING EQUIPMENT

Gamma counting is performed by a multichannel analyzer and suitable detector; Tc, I, Np, Pu, and Am are counted by mixing 1 mL of sample with 15 mL of scintillation cocktail such as PCS and counting the sample using a liquid scintillation system.

PREPARATION OF CANDIDATE ION-EXCHANGE RESIN

A sample (0.1 g) of material is weighed out on a 4- or 5-place analytical balance for each test. A 1 g sample of similar material is dried at 105 ±10°C for 24 hours and cooled in a desiccator before being reweighed to determine the correction factor (F).[a] One or two samples are weighed for each test and placed in 25 mL polyethylene bottles. Five to 20 mL of radionuclide spiked supernatant is added to each bottle. The bottle is sealed with a piece of Parafilm M (American Can Company, Greenwich, Connecticut) and then tightly capped and placed on an Eberbach mechanical shaker for continuous agitation. The agitation rate is set at ~1 stroke/ min.

STANDARD SOLUTION

A standard solution is prepared and placed in a similar 25 mL polyethylene bottle and treated as a normal sample. Each standard contains 5 to 20 mL of

(a) $F = \frac{\text{Weight of Material After Drying @ 105°C for 24 h}}{\text{Weight of Material (~1 g)}}$

radionuclide-spiked supernatant. The sample is agitated, sampled, filtered, and counted with the other samples. The standard represents the supernatant prior to contact with the solid sample.

FILTERING AND ANALYSIS PROCEDURE

The samples and standard are removed from the shaker and allowed to settle for 24 hours. Approximately 5 mL of each sample is filtered using a Gelman 4192, 0.2-μm pore size disposable filter. After filtration, 3 to 4 mL of solution is transferred to standard gamma-counting tubes, or a 1-mL sample is added to 15 mL of scintillation solution and stirred. The samples are gamma counted for 2 to 20 minutes, depending on the count rate, and the liquid scintillation samples are counted for 200 minutes or until the sample has reached the 2σ confidence level.

REPORTING METHOD

$$R_d = \frac{\text{Filtered standard (c/m/mL)} - \text{Filtered sample (c/m/mL)}}{\text{Filtered Sample (c/m/mL)}} \times \frac{\text{Sample volume (cm}^3\text{)}}{\text{Weight of material (g)} \times F} = \text{cm}^3/\text{g}$$

pH DETERMINATION

Each sample used for gamma counting is saved for pH determination. Since the liquid scintillation sample is a mixture of organic and aqueous material, it is not used for pH determination. Instead, the 2 mL of sample not required for analysis is removed from the centrifuge cone and placed in a bottle for later pH determination. The pH is determined for each sample using an Orion Research Microprocessor, Ionalyzer/901, and a Corning Combination electrode. The pH meter is standardized before and during the analysis of a number of samples using standard Beckman buffers covering the range of 7 to 10.

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