

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES



3 4456 0287986 5

ORNL/TM-11891

ornl

**OAK RIDGE
NATIONAL
LABORATORY**

MARTIN MARIETTA

Low-Level Liquid Waste Decontamination by Ion Exchange

D. O. Campbell
D. D. Lee
T. A. Dillow

OAK RIDGE NATIONAL LABORATORY

CENTRAL RESEARCH LIBRARY

CIRCULATION SECTION

4500N ROOM 175

LIBRARY LOAN COPY

DO NOT TRANSFER TO ANOTHER PERSON

If you wish someone else to see this
report, send in name with report and
the library will arrange a loan.

UCN-7969 (3 9-77)

MANAGED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Chemical Technology Division

Low-Level Liquid Waste Decontamination by Ion Exchange

D. O. Campbell
D. D. Lee
T. A. Dillow

Date of Issue — December 1991

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES



3 4456 0287986 5

CONTENTS

LIST OF TABLES	v
LIST OF FIGURES	v
ACRONYMS AND INITIALISMS	vii
ABSTRACT	1
1. INTRODUCTION	1
2. LIQUID WASTE TREATMENT PROCESSES	3
3. CESIUM REMOVAL WITH HEXACYANOFERRATE(II) COMPOUNDS	4
4. PROCESS APPLICATION	8
5. CESIUM AND STRONTIUM REMOVAL WITH ORGANIC ION-EXCHANGE RESINS	9
5.1. BATCH K_d EXPERIMENTS	9
5.2. ION-EXCHANGE COLUMN TESTS	13
5.3. RESIN ELUTION	15
5.4. DATA ANALYSIS	16
SUMMARY	20
REFERENCES	23

1

2

3

LIST OF TABLES

	<u>Page</u>
1. Waste compositions	2
2. Cesium removal with KCoFCN	6
3. Effect of pH on cesium removal	7
4. Decontamination of LLLW supernate solution	7
5. ¹³⁷ Cs removal from process waste	8
6. Comparison of batch K _d data for SRS resin for various potassium, sodium, and pH conditions	12
7. Comparison of CS-100 and SRS resins	13
8. Data for SRS resin column runs	14
9. Data for SRS resin column runs	21

LIST OF FIGURES

	<u>Page</u>
1. Two-stage IX-UF process for LLLW	10
2. Effect of potassium on cesium breakthrough curves.	15
3. Effect of potassium on strontium breakthrough curves.	17
4. Cesium K _d s for column tests by graphical and breakthrough function methods. .	18
5. Elution of activity from SRS resin.	20
6. SRS resin breakthrough function curves	22

ACRONYMS AND INITIALISMS

AMFCN	Nonstoichiometric compound of formula $A_nM_{(2-n/2)}Fe(CN)_6$ where A is an Alkali metal; M is a metal such as Ni, Co, Cu, or Zn; and FC is ferrocyanide (i.e., NaNiFC for sodium nickel ferrocyanide)
CV	Volume of resin in IX column
DF	Decontamination factor (C_0/C)
FC	Transition metal hexacyanoferrate(II) compounds (ferrocyanide)
HTU	Height of a transfer unit
IX	Ion-exchange processes
K_a	Mass transfer coefficient
K_d	Distribution coefficient
K'_d	Volume-based distribution coefficient
LLLW	Low-level (radioactive) liquid waste
MVST	Melton Valley Storage Tanks
NaT	Sodium titanate
ORNL	Oak Ridge National Laboratory
PW	Process waste
SRS	Savannah River Site, DOE
TRU	Transuranic

LOW-LEVEL LIQUID WASTE DECONTAMINATION BY ION EXCHANGE

D. O. Campbell
D. D. Lee
T. A. Dillow

ABSTRACT

Improved processes are being developed to treat contaminated liquid wastes that have been and continue to be generated at Oak Ridge National Laboratory. Both inorganic and organic ion-exchange methods have given promising results. Nickel and cobalt hexacyanoferrate(II) compounds are extremely selective for cesium removal, with distribution coefficients in excess of 10^6 and remarkable insensitivity to competition from sodium and potassium. They tend to lose effectiveness at $\text{pH} > \sim 11$, but some formulations are useful for limited periods of time up to $\text{pH} \sim 13$. Sodium titanate is selective for strontium removal at high pH. The separations are so efficient that simple batch processes can yield large decontamination factors while generating small volumes of solid waste. A resorcinol-based resin developed at the Savannah River Site gave superior cesium removal, compared with other organic ion exchangers; the distribution coefficient was limited primarily by competition from potassium and was nearly independent of sodium. The optimum pH was ~ 12.5 . It was much less effective for strontium removal, which was limited by competition from sodium.

1. INTRODUCTION

A variety of contaminated liquid wastes are produced at Oak Ridge National Laboratory (ORNL), and nearly all of them are collected in one of two systems—the process waste (PW) or the low-level liquid waste (LLLW). Representative liquid waste compositions are shown in Table 1. The PW includes liquids with very low concentrations of radioactivity as well as water that is not normally contaminated but might be. It is generated at the rate of ~ 500 L/min and has a composition essentially that of ordinary tap water or groundwater in

Table 1. Waste compositions

Component	PW	LLLW	Simulant
pH	7.7	8-13	13.2
	<u>(mg/L)</u>	<u>(mg/L)</u>	<u>(mg/L)</u>
Sodium	20.	110,000.	104,000.
Potassium	2.	10,000.	9,800.
Cesium	-	0.34	
Calcium	40.	4.0	4.
Magnesium	10.	0.02	
Strontium	0.2	1.0	
Barium	-	1.0	
Aluminum	0.1	25.0	14.
Chromium	<0.02	2.5	
Lead	-	10.	
Zinc	-	50.	65.
Nitrate	4.	280,000.	258,000.
Carbonate	60.	8,000.	8,400.
Sulfate	18.	-	
Chloride	6.	3,500.	3,550.
	<u>(Bq/L)</u>	<u>(Bq/L)</u>	
Gross alpha	5.	2×10^3	
Gross beta	6000.	2×10^8	
^{60}Co	25.	5×10^5	
^{90}Sr	4000.	4×10^6	
^{137}Cs	400.	2×10^6	
^{134}Cs	10.	6×10^6	

the area; it contains small amounts of ^{137}Cs , ^{134}Cs , ^{90}Sr , very small amounts of ^{60}Co , and rarely other radioisotopes. The LLLW consists of waste concentrates from laboratories, radiochemical processing operations, and waste treatment facilities. The volume is small, 10 to 20 m³/year, but the liquid contains very high concentrations of dissolved solids.

The concept underlying the present work is that safety and economics would be improved if the wastes could be divided into three fractions:

1. The material, insoluble at high pH, contains the transuranic (TRU) constituents (if present) and other heavy metals and must be treated accordingly.
2. A non-TRU concentrate containing the major beta-gamma radionuclides (^{137}Cs , ^{134}Cs , and ^{90}Sr) that, because of its small volume, can be managed with great care is recovered from the supernate.
3. The bulk of the liquid waste is decontaminated from radioactivity sufficiently that it can be managed as a less hazardous material than it now is, thereby opening up much-needed capacity in the existing storage tanks.

The hazardous radioactivity in the wastes is dominated by actinides, ^{137}Cs , and ^{90}Sr . Because the actinides are insoluble in alkaline LLLW, the supernate is generally a non-TRU waste. Therefore, supernate decontamination requires the removal of ^{137}Cs and ^{90}Sr from very large amounts of sodium and potassium and smaller amounts of other elements, including alkaline earths and transition metals. Experimental studies have been undertaken to develop improved processes to decontaminate the wastes by removing nearly all of the cesium and strontium. Methods under study include scavenging precipitation and column separations with selective ion-exchange materials; both organic and inorganic exchangers are included. Most of the experiments were conducted with a synthetic solution that approximates the liquid in some existing waste tanks (LLLW simulant); the composition is 3.9 M NaNO₃, 0.25 M KNO₃, 0.24 M NaOH, 0.14 M Na₂CO₃, 0.10 M NaCl, 0.001 M Zn(NO₃)₂, 0.0005 M Al(NO₃)₃, and 0.0001 M CaCO₃. The pH was adjusted as necessary.

2. LIQUID WASTE TREATMENT PROCESSES

Until a few years ago, large volumes of LLLW were mixed with cement grout-forming chemicals and injected into a shale formation deep underground. Since shale hydrofracture was halted at ORNL, the LLLW has been accumulating in tanks that are now nearly full. This waste is a particular concern because no treatment process is immediately available for its disposal. Many options have been examined to relieve the short-term problem, which is

inadequate liquid waste storage capacity, and to properly deal with the material in the longer term.

As new regulations have been adopted, requiring ever-increasing decontamination factors (DFs) for discharge of PW, a series of flowsheets has been applied, based on different combinations of filtration, scavenging precipitation, water softening, and ion-exchange with either Duolite CS-100 or a strong-acid resin. These processes produced two liquid wastes: (1) the resin regenerant solution that was initially disposed of via shale hydrofracture and is presently concentrated and stored in LLLW tanks, and (2) a low-activity clarification sludge that is currently filtered and stored in drums. A simpler process has been developed for application in a few years, based on inorganic ion-exchangers (zeolites) that remove both strontium and cesium and can be disposed of directly without elution, thereby removing this source of liquid waste. In the meantime, simple modifications to improve the DF of the current process are under study.

In chemical separations processes for cesium, the primary interferences are usually other alkali metals, especially the heavier ones. In this case, sodium is in very high concentration and potassium is significant ($\sim 0.25 \text{ M}$). Therefore, depending on the particular process, sodium and potassium tend to control cesium removal. Good cesium separations have been accomplished with zeolites [notably at Three Mile Island],¹ phenolic ion-exchangers like Duolite CS-100, and tetraphenyl borate. The transition metal hexacyanoferrate(II) compounds (ferrocyanides) have been studied extensively and are used especially in Europe;² in addition, there are several other inorganic ion-exchangers that might be useful. This study focused on nickel and cobalt ferrocyanides and on organic ion-exchange resins based on phenol and resorcinol.

To a greater extent, alkaline earth elements interfere with strontium removal; therefore, the recovery of ^{90}Sr from waste solutions is more difficult because the alkaline earth metals are not easily separated. As a result, removal of trace ^{90}Sr generally requires removal of bulk calcium, which may require much more ion-exchange material and, thus, generate more solid waste. In some systems the high sodium concentration limits ^{90}Sr recovery, but several ion-exchangers are selective for the divalent alkaline earth elements over sodium. In this work, chelating resins and sodium titanate are being studied.

3. CESIUM REMOVAL WITH HEXACYANOFERRATE(II) COMPOUNDS

The ferrocyanides are readily prepared by mixing solutions of sodium or potassium ferrocyanide with a transition metal such as $\text{Co}(\text{NO}_3)_2$ or $\text{Ni}(\text{NO}_3)_2$.³ A precipitate forms

that often is nonstoichiometric, the composition depending on the method of preparation. The compound can be represented as $A_{2x}M_{2-x}Fe(CN)_6$, where A is an alkali metal (sodium, potassium), M is a transition metal (cobalt, nickel, zinc, etc.), and x can vary between 0 and 1; the abbreviation AMFCN will be used here. The precipitates tend to be very small crystals with pores containing water of hydration. They are remarkably stable chemically, withstanding even high concentrations of nitric acid and concentrated salt solutions but decomposing at pHs > -11 . Cesium will exchange into the crystal, replacing the alkali metal and part of the transition metal.

The ferrocyanides can be introduced as preformed slurries prepared by mixing solutions of the ferrocyanide and transition metal in the specified ratio, or the precipitate can be formed in situ by the addition of the two reagents to the waste solution, along with a pH adjustment or head-end pretreatment. The result may be different, depending on whether the ferrocyanide or metal is added first. Sedimentation characteristics and the ease of clarification vary greatly, depending on many factors, including the preparation method and aging. With some compositions, a hard, granular product can be prepared. This can have two advantages: (1) it is suitable for use in a column, and (2) it may be more resistant to high-pH solutions.

Typical results from tests with a waste simulant solution are shown in Table 2. The pH was adjusted to 6.5, and KCoFCN was precipitated in situ by adding potassium ferrocyanide followed by cobalt nitrate to give ~ 110 ppm of the compound. In the first test, $>99\%$ of the ^{137}Cs was removed at all mixing times from 11 min to 7 d. The distribution coefficient [$K_d = V(C_0 - C)/mC$, where V is the solution volume, m is the exchanger mass, and C_0 and C are the concentrations before and after mixing] was usually $>10^6$. The experiment was repeated, and ^{137}Cs removal was considerably smaller in the first three measurements. It was noted that crystals appeared in the bottom of some samples after they had been left standing for a day, so centrifugation had not removed all the solids. When the solution was clarified in a more effective manner, either by recentrifuging the sample or by filtering with a 0.2- μm filter, $>99\%$ ^{137}Cs removal was obtained.

Similar tests were performed under a range of conditions, and the initial data showed considerable scatter, as in Table 2, because of incomplete solids separation. As long as good clarification was achieved, ^{137}Cs decontamination was very large. Values of K_d were unusually large for an ion-exchange process, and in many cases, the measurements indicated the efficiency of solids removal instead of the selectivity of the ferrocyanide for cesium.

Table 2. Cesium removal with KCoFCN^a

Mix Time	Clarification Method ^b	Percentage of Cesium Removed	K _d
11 min	cent	99.2	1.19x10 ⁶
1 h	cent	99.7	2.57x10 ⁶
24 h	cent	99.1	9.87x10 ⁵
7 d	cent	99.7	3.39x10 ⁶
7 d	cent 2	99.85	6.05x10 ⁶
<u>Repeat Experiment</u>			
10 min	cent	76.8	3.00x10 ⁴
1 h	cent	70.0	2.13x10 ⁴
24 h	cent	82.9	4.41x10 ⁴
24 h	cent 2	99.34	1.38x10 ⁶
24 h	filt	99.97	2.80x10 ⁷

^a110 ppm KCoFCN in simulated LLLW; pH 6.5; Co/Fe = 1.7; add ferrocyanide, then cobalt.
^bcent: clarified by centrifuging 10 min.; cent 2: recentrifuged 1 d later; filt: filtered through 0.2- μ m filter.

At higher pH, > ~11, the ferrocyanides lost effectiveness. The removal of ¹³⁷Cs using dried, granular KNiFCN is shown in Table 3. Excellent results were obtained at pH values of 9 and 11, even after 2 weeks. At pH 12, however, ¹³⁷Cs was removed only for a short time. After 1 d, the removal decreased to 65%; after 4 d, it was essentially zero. A number of AMFCN preparations with various heat treatments were tested, and some — notably heat-treated KCoFCN — offered fairly good decontamination for a number of days at pH 12. However, all lost effectiveness with increasing time, probably because of decomposition of the metal ferrocyanide crystal to metal hydroxide at pH > ~11.

Results from a test made with actual supernate from one of the ORNL waste tanks are shown in Table 4. Several different ferrocyanides were used; and, in the first four cases, the solutions were adjusted to a lower pH, 9.6. NaCoFCN and NaNiFCN at 50 ppm were especially effective. Clarification problems caused some of the results for KCoFCN to be poor. The last column, for 21 d, is most significant because greater care was taken to remove solids that had caused poor ¹³⁷Cs decontamination in some cases.

At the higher pH of 11.5, good removal of ¹³⁷Cs was obtained with granular KCoFCN over a period up to ~1 d, but then it became less effective. At 100 ppm, it removed <10%

Table 3. Effect of pH on Cesium Removal^a

Mixing Time	Percentage of Cesium Removed at pH		
	9.0	11.0	12.0
1 h	96.63	93.18	89.9
24 h	99.60	99.22	65.8
24 h filt.	-	99.25	65.6
4 d	99.86	99.58	-0
7 d	99.80	99.50	-0
14 d	99.81	99.73	-0

^aSimulated LLLW adjusted to pH; +333 ppm dried KNiFCN, Ni/Fe = 1.7

Table 4. Decontamination of LLLW supernate solution^a

Sorbent PPM FCN ^b	LLLW pH	Mixing Time			
		15 m	4 h	24 h	21 d ^c
Percentage of Cesium Removed					
50 NaCo-S	9.60	83.8	96.7	99.0	99.5
50 NaNi-S	9.60	77.9	93.4	97.5	99.3
50 KCo-S	9.60	23.0	49.1	88.3	97.6
150 KCo-S	9.60	66.4	92.4	99.0	99.7
100 KCo-G	11.5	83.8	95.5	87.2	8.4
500 KCo-G	11.5	94.3	98.0	95.6	55.5
500 +NaT ^a					
Percentage of Strontium Removed					
500 KCo-G	11.5	58.2	92.2	97.3	99.5
500 +NaT					

^aFeed: 2.4×10^5 Bq/mL ¹³⁷Cs + 3.0×10^3 Bq/mL ⁸⁵Sr.

^bS = slurry; G = granular; NaT = sodium titanate.

^cSamples settled overnight, then filtered.

after 21 d; and at 500 ppm, ~50%. In the last case, 500 ppm of sodium titanate was also added, and ^{85}Sr was effectively removed. These experiments demonstrate that >99% of both ^{137}Cs and ^{85}Sr can be removed from this low-level waste with a single-stage batch separation.

These methods have also been applied to the process waste. The discharge limit for ^{137}Cs is currently being reduced, so that an additional DF of ~5 will be required to bring the large-volume PW stream into compliance. Some tests were made in which small quantities of ferrocyanides were added during the softening-clarification step of the present process (Table 5). Additions of NaNiFCN were most effective, with even 3 ppm giving an adequate DF. Nearly all the tests except the blanks gave useful DFs.

Table 5. ^{137}Cs removal from process waste^a

Sorbent		Conc. (Bq/L)		DF
PPM	FCN ^b	Feed	Supernate	
100	KCo-G	90.	3.1	61.
100	KCo-G	141.	1.6	88.
20	KCo-G	61.	2.9	21.
20	KCo-S ^c	141.	11.	13.
20	KNi-S	141.	2.8	50.
3	KNi-S	100.	1.9	54.
20	NaNi-S	100.	2.1	49.
3	NaNi-S	141.	8.	17.
20	NaCo-S	141.	19.	7.
0	Blank	141.	114.	1.2
0	Blank	190.	150.	1.3

^aAdd 2.5 ppm Fe^{3+} + 0.3 ppm Betz 1100 + NaOH to pH 11.5.

^bG = granular form; S = slurry form.

^cHeat-treated slurry.

4. PROCESS APPLICATION

Simple batch processes usually generate more solid waste (sludge) than multistage column operations and give smaller DFs, often in the vicinity of 10; therefore, multistage column processes are usually required to obtain large DFs. In this case, the ^{137}Cs K_d s are so large, 10^5 to 10^6 , that a batch process can provide DFs in the range of thousands while generating a reasonably small volume of solid waste. Two or three batch separation stages can yield a very efficient process. This opens the possibility of achieving large DFs using methods common to bulk water treatment, instead of multistage processes such as

ion-exchange columns. The very large theoretical column capacities, resulting from the large K_d s, generally cannot be realized in practice because of mechanical problems.

A single-stage process, such as a clarifier, in which a ferrocyanide and sodium titanate are added along with other chemicals for feed adjustment and clarification (i.e., ferric hydroxide scavenging precipitation), can effectively remove actinides, rare earths, ^{90}Sr , and ^{137}Cs . Depending on conditions, the clarified and decontaminated product water from such a process could be further treated (e.g., with ion-exchange columns), stored, solidified, or possibly discharged to the environment.

A more effective flowsheet, in which two stages of separation are obtained by adding the reagents to a second-stage mixer that feeds an ultrafilter, is shown in Fig. 1. The concentrate from the ultrafilter would be back-cycled to the first-stage clarifier, where the solid product is removed as a sludge. Such a process should give substantially better performance—a larger DF and a smaller reagent requirement. An ultrafilter is included because removal of colloidal material may be necessary to achieve the large DFs potentially available.

5. CESIUM AND STRONTIUM REMOVAL WITH ORGANIC ION-EXCHANGE RESINS

Approximately 1 L of resorcinol-based ion-exchange resin was provided by the Savannah River Site (designated as SRS resin),⁴ and a portion was washed and segregated into narrow size fractions. Duolite CS-100 was obtained previously from Rohm and Haas. The resins were prepared for column tests by washing twice with 10 resin volumes (CV) of 2 M formic acid, twice with 10 CV of distilled water, five times with 6 CV of 0.25 M NaOH, and, finally, three times with 10 CV of distilled water. The washed resin was dried by placing it on blotter paper at room temperature overnight. Weighed samples of this resin were used for batch K_d tests. For column tests, a volume of resin was measured, placed into the column, and rehydrated.

5.1. BATCH K_d EXPERIMENTS

Cation-exchange equilibria in systems containing ^{137}Cs and ^{85}Sr tracers in LLLW simulant composition were obtained using batch equilibration techniques at the conditions shown below. Combinations of the following variables were used:

1. simulant to water dilutions of 0, 3:1, 3:5, and 1:7;
2. initial feed pHs adjusted to 11, 12, 12.5, 13, and 13.3;

3. potassium concentrations of 0, 0.05, 0.1, 0.25, and 0.5 M; and
4. equilibration times of 1, 24, 48, and 90 or 96 h.

The experiments used 15 mL of solution (initial) along with 100 mg of dry 60-80 mesh sodium-form SRS resin. The pH of the liquid was measured before and after equilibrium contact, and it usually decreased by 0.1 to 0.3 pH units, with the greater decrease at the lower salt concentrations.

Some of the results are summarized in Table 6. For ^{137}Cs , the most favorable K_d s are obtained at pH ~12.5 in nearly all cases, and the sodium concentration had little effect when potassium was present. The K_d was approximately inversely proportional to the potassium concentration, varying from ~800 for 0.5 M potassium to 20,000 with no potassium at pH 12.5.

Strontium K_d s were primarily dependent on the sodium concentration and independent of the potassium concentration except when the sodium concentration was lowest; in that case, the dependence may be on the total alkali metal concentration. They were somewhat higher at the higher pH values. The ^{85}Sr K_d s ranged from ~175 for undiluted simulant to ~2000 for the highest dilution. In all cases except for the high potassium and lowest sodium concentrations, the K_d for ^{85}Sr was less than that for ^{137}Cs , confirming that ^{90}Sr should break through before ^{137}Cs , in many cases by as much as a factor of 10. As a general rule, the capacity of an ion-exchange column (liters processed per kilogram of resin) is somewhat less, at best, than the K_d value in the same units.

Measurements of the K_d values for ^{137}Cs and ^{85}Sr for CS-100 resin were made at a pH of 12.5 in LLLW simulant at sodium concentrations of 0.57, 1.82, 3.49, and 4.58 M and potassium concentrations of 0, 0.05, 0.1, 0.25, and 0.5 M for comparison with the SRS resin. These results are shown in Table 7. The K_d s for ^{85}Sr and ^{137}Cs ranged from ~200 and 28, respectively, at 4.58 M Na-0.5 M potassium to ~5100 and 490 at 0.57 M sodium. While potassium had little effect on the ^{85}Sr K_d , it had a substantial effect on the ^{137}Cs K_d . The CS-100 resin was generally comparable to the SRS resin for ^{85}Sr removal but was quite inferior for ^{137}Cs removal. The result for a column design is that ^{137}Cs removal limits the maximum throughput with CS-100, and ^{85}Sr removal limits the throughput with SRS resin. If both elements are present, the smaller K_d (lower breakthrough capacity) always occurs with CS-100.

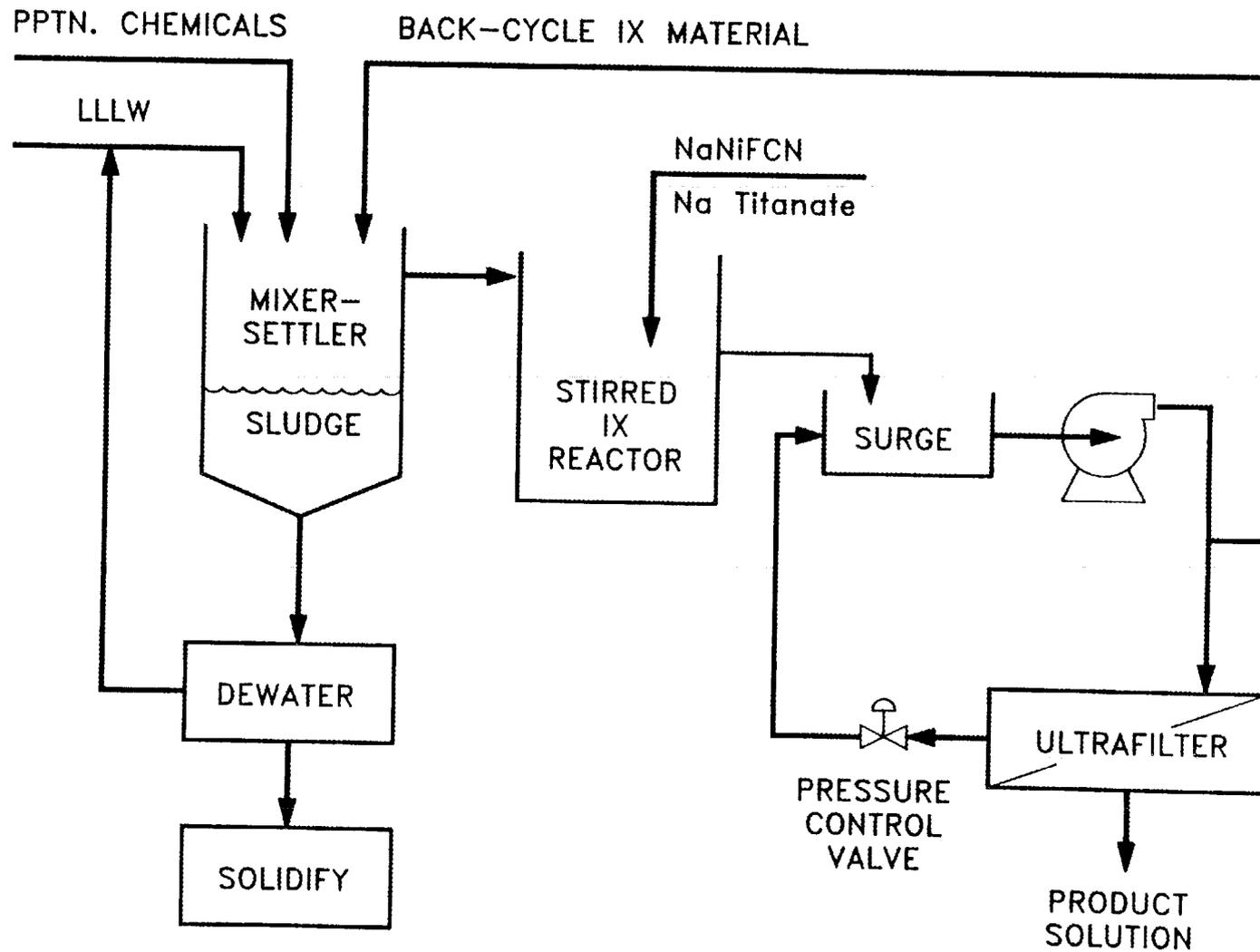


Fig. 1. Two-stage IX-UF process for LLLW

Table 6. Comparison of batch K_d data for SRS resin for various potassium, sodium, and pH conditions

pH	K (M)	Strontium K_{ds}				Cesium K_{ds}			
		sodium (M)				sodium (M)			
		4.58	3.44	1.72	0.57	4.58	3.44	1.72	0.57
11.0	0.5	50	75	175	587	356	352	332	272
12.0	0.5	64	87	218	666	588	623	662	594
12.5	0.5	167	229	395	660	797	851	923	638
13.0	0.5	176	240	531	1524	640	645	750	852
13.3	0.5	175	244	534	1436	562	599	689	756
11.0	0.25	47	74	202	824	502	538	523	435
12.0	0.25	67	104	258	996	955	987	1107	1047
12.5	0.25	178	223	462	1063	1212	1284	1634	1135
13.0	0.25	183	254	618	2164	990	1116	1342	1620
13.3	0.25	179	255	535	1784	993	1020	1263	1477
11.0	0.1	44	76	222	1106	775	898	929	822
12.0	0.1	69	104	283	1335	1649	1776	2068	2109
12.5	0.1	181	244	527	1378	2235	2524	3051	2283
13.0	0.1	187	269	608	2572	1830	1859	2866	3595
13.3	0.1	183	255	566	2050	1693	1970	2308	3333
11.0	0.05	48	70	232	1246	1053	954	1306	1241
12.0	0.05	71	106	293	1528	2141	2410	3170	3442
12.5	0.05	186	198	526	1481	3334	3857	4744	3366
13.0	0.05	188	279	597	2513	2445	2986	3642	5617
13.3	0.05	184	263	600	2049	2375	2886	3674	5315
11.0	0.0	47	79	209	1446	1963	2740	3771	5475
12.0	0.0	73	115	298	1723	4369	5607	8920	17425
12.5	0.0	175	244	519	1700	7532	9478	18300	20818
13.0	0.0	184	282	664	2723	5088	8078	11248	32408
13.3	0.0	188	271	620	2294	5008	6755	12688	25282

Table 7. Comparison of CS-100 and SRS resins

K (M)	Na (M)	CS-100 Resin				SRS Resin			
		1 h		90 h		1 h		90 h	
		⁸⁵ Sr	K _d	¹³⁷ Cs	K _d	⁸⁵ Sr	K _d	¹³⁷ Cs	K _d
0.50	4.58	62	198	20	28	112	167	161	797
0.25	4.58	75	208	25	38	113	178	192	1212
0.10	4.58	61	211	25	46	113	181	250	2235
0.05	4.58	66	202	31	55	115	186	283	3334
0	4.58	72	208	39	77	113	175	351	7532
0.50	3.49	113	291	26	32	173	229	259	851
0.25	3.49	103	298	30	42	153	223	297	1284
0.10	3.49	121	329	38	55	162	244	415	2524
0.05	3.49	121	311	47	68	123	198	322	3857
0	3.49	124	313	64	103	167	244	676	9478
0.50	1.82	313	700	37	42	342	395	438	923
0.25	1.82	344	777	56	66	363	462	643	1634
0.10	1.82	313	847	65	91	388	527	1032	3051
0.05	1.82	333	792	83	110	399	526	1244	4744
0	1.82	391	888	134	198	402	519	2009	18300
0.50	0.57	1053	2514	48	58	989	660	648	638
0.25	0.57	1346	3332	77	99	1298	1063	1091	1135
0.10	0.57	1625	3557	120	148	1664	1378	2066	2283
0.05	0.57	1872	4311	163	210	1811	1481	2776	3366
0	0.57	1682	5099	304	491	2046	1700	7864	20818

5.2. ION-EXCHANGE COLUMN TESTS

Several column tests were completed using LLLW simulant and 3 to 5 mL of SRS resin. Conditions for these runs are shown in Table 8. Preliminary ion-exchange column tests with SRS resin were unsuccessful because a precipitate coated the resin particles. The source of this problem is believed to be aluminum, which becomes less soluble as the pH is decreased. In some runs, the pH of the simulant decreased by 1 to 1.5 pH units upon contact with fresh resin. It is, therefore, necessary to maintain a high pH during column runs. A 1 M NaOH solution was passed through the column just before introducing the feed to prevent an initial decrease in pH. Using this procedure, almost no solids were observed in the columns or on the resin particles, and no significant increase in pressure drop was noted.

The ¹³⁷Cs breakthrough curves indicated rather slow kinetics, with 1% breakthrough at ~40 CV and a K_d' of ~750 (SRL1). Volumetric distribution coefficients (K_d's) were obtained from a probability-log graph of C/C₀ (%) vs the column throughput (CV).⁵ The CV at 50% C/C₀ is approximately the K_d'. When the feed pH was increased to 13.8 by

Table 8. Data for SRS resin column runs

Run	Sodium (M)	pH	Potassium (M)	Size (μm)	Flow (cm/min)
SRL1	4.58	13.3	0.25	210.	1.067
SRL2	5.06	13.8	0.25	210.	1.30
NaK1	4.70	13.2	0.25	210.	1.28
SRL3	4.58	12.8	0.25	210.	0.26
SRL4	4.58	13.2	0.25	115.	1.26
SRL5	4.58	13.2	0.50	115.	1.26
SRL6	4.58	13.2	0.10	115.	1.24
SRL7	0.95	12.65	0.052	115.	1.20
Na1	4.45	13.2	0.0	210.	1.28

adding NaOH to make the solution 0.7 M in NaOH (SRL2), the ^{137}Cs breakthrough occurred more rapidly. Test SRL3 using the LLLW simulant at 20% of the earlier flow rate through the column (0.26 cm/min vs 1.3-cm/min superficial velocity) resulted in a breakthrough curve that was much steeper, not beginning to rise until ~ 225 CV compared with the continuous rise in the earlier (SRL1 and SRL2) simulant tests. The 50% breakthrough occurred at 759 CV, as in the earlier tests. Run Na1 used feed consisting only of 4.45 M NaNO_3 plus a spike of LLLW supernate (no aluminum, calcium, zinc, potassium, or carbonate) and showed a high capacity ($K'_d \sim 7300$). Addition of 0.25 M KNO_3 to NaNO_3 in run NaK1 caused a decrease in K'_d to nearly that of the LLLW simulant containing all of the components ($K'_d \sim 690$ for NaK1 vs ~ 760 for SRL1 and SRL3). This relative behavior is about as expected. As with the batch K'_d measurements, competition from potassium is the key limitation in the cesium removal capacity of this resin.

The feeds for runs SRL4 through SRL7 had the same composition as LLLW simulant, except that the potassium concentration was varied to 0.1, 0.25, and 0.5 M. Also, a 3.8:1 dilution of the LLLW simulant (yielding 0.052 M potassium and 0.95 M sodium) was tested (SRL7). These runs used the same batch of 120 to 140 mesh resin (0.115-mm average diameter) and roughly the same flow-rate and resin-bed dimensions. The capacity of the resin bed for ^{137}Cs in runs SRL4 through SRL7 (Fig. 2) varied approximately inversely with the potassium concentration. The value of K'_d increased from 219 at 0.5 M potassium

Cesium Ion-Exchange Tests on SRS Resin

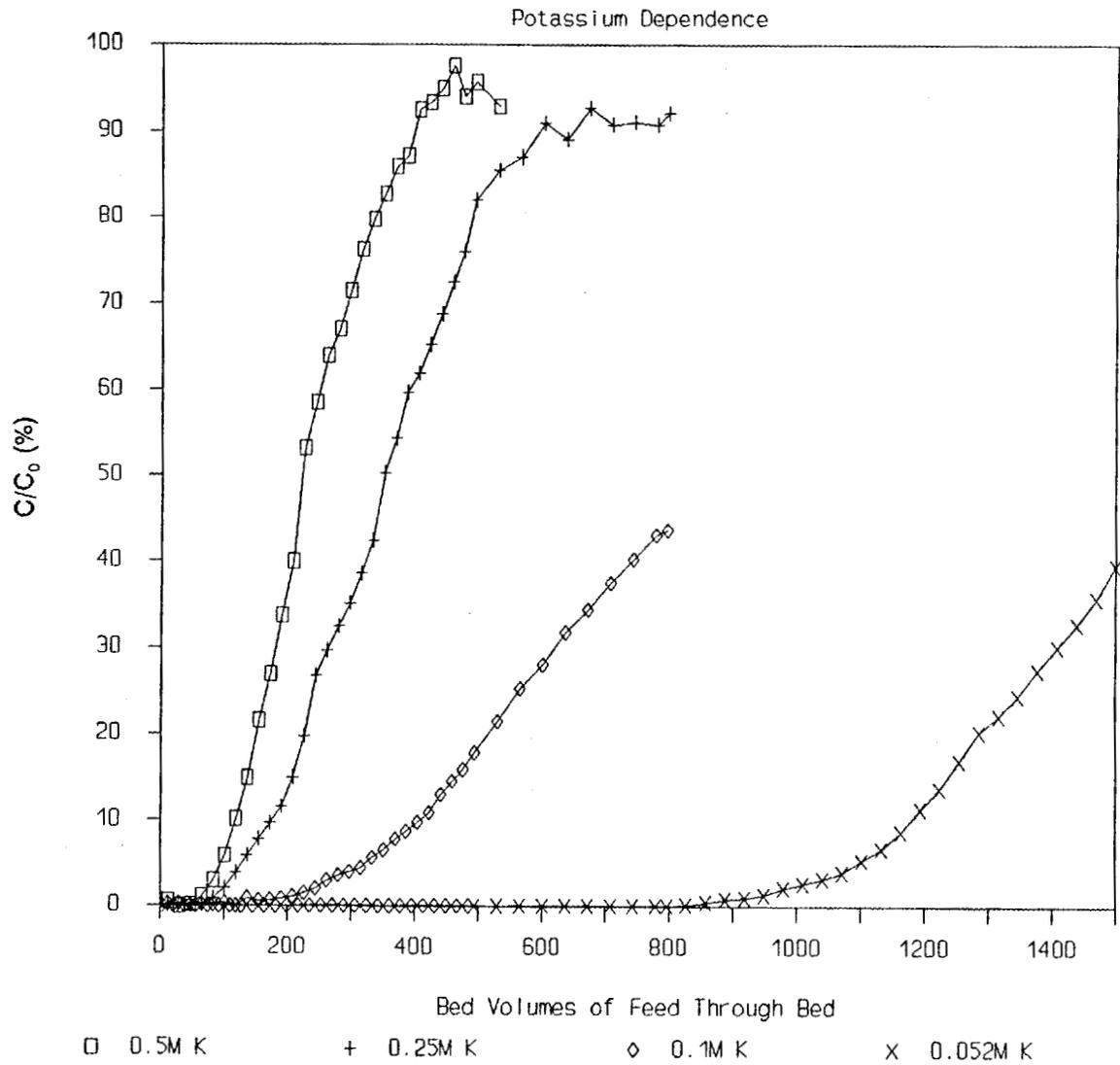


Fig. 2. Effect of potassium on cesium breakthrough curves

to 876 at 0.1 M potassium, and was 1587 with the dilute feed. Compared with SRL1, which used a larger particle size and a different batch of simulant than SRL4, the breakthrough curves were sharper but occurred earlier.

Strontium-85 was also used as a tracer in runs SRL4 through SRL7 to study the breakthrough and loading characteristics for strontium on SRS resin under LLLW conditions. The ^{85}Sr uptake remained almost constant with a K'_d of 94 to 102 over the range of 0.1 to 0.5 M potassium at 4.58 M sodium. The K'_d increased to 433 with the diluted simulant. Once ^{85}Sr broke through the column, its concentration rose to a value significantly above that of the feed (Fig. 3). It appears that some ion in the LLLW simulant selectively displaced ^{85}Sr from the resin.

5.3 RESIN ELUTION

The resins evaluated in the column tests were eluted with formic, hydrochloric, and nitric acids at various concentrations and using different procedures. Initially for ^{137}Cs removal, 2 M formic acid was used as the eluent, and 50 to 80 CV were required to elute all of the ^{137}Cs activity. In a second method, 3 CV of 4 M formic acid followed by 30 CV of 0.5 M nitric acid resulted in the elution of only 75% of the bound ^{137}Cs activity. In a third test, 12 CV of 4 M formic acid were followed by 8 CV of 0.5 M nitric acid, but only 56% of the ^{137}Cs activity was eluted. Elution with 4 M HCl resulted in ~100% ^{137}Cs activity removal in 11 CV, and counting of the eluted resin showed very little remaining activity. Examples of the elution curves for cesium and cesium and strontium are shown in Fig. 4. It was possible to account for only about 70% of the ^{85}Sr that had apparently loaded. However, because of the increase in the ^{85}Sr content of the exit stream above the feed concentration during later stages in the run, the total ^{85}Sr on the resin at the end of the run is subject to some uncertainty.

5.4 DATA ANALYSIS

The data were analyzed in two different ways for computing the K'_d values. In the first method, K'_d was determined graphically, as described previously.

The second method was one used by Doulah and Jafar⁶ in which the relationship between the concentration C at time Θ is expressed by a breakthrough function given by

$$C/C_0 = \exp[-((\Theta - \Theta_0)/\Theta_m)^b], \quad (1)$$

where

Θ = time (proportional to volume fed),

Θ_0 = time to breakpoint (when C/C_0 becomes greater than 0.05),

Strontium Ion-Exchange on SRS Resin

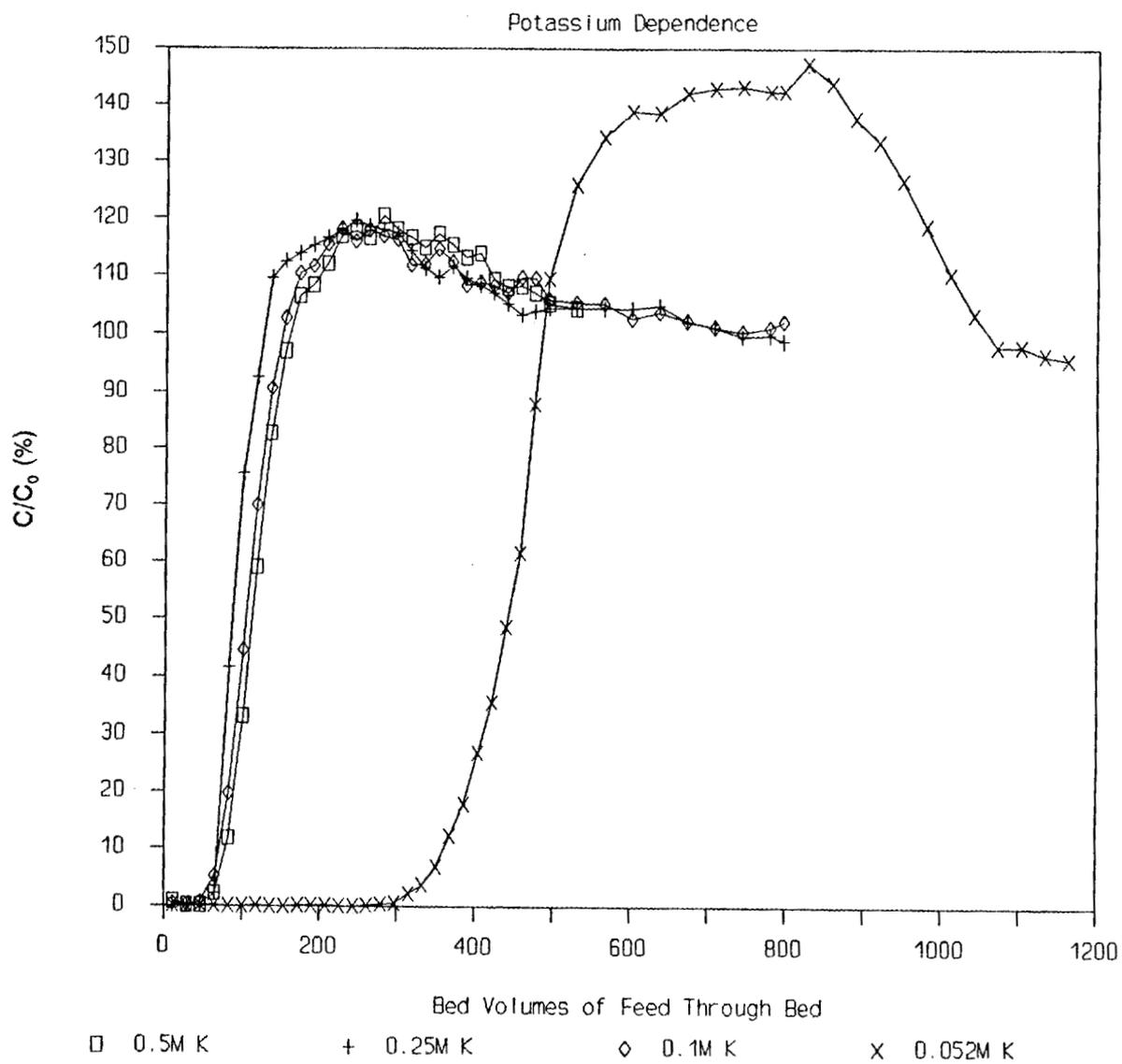
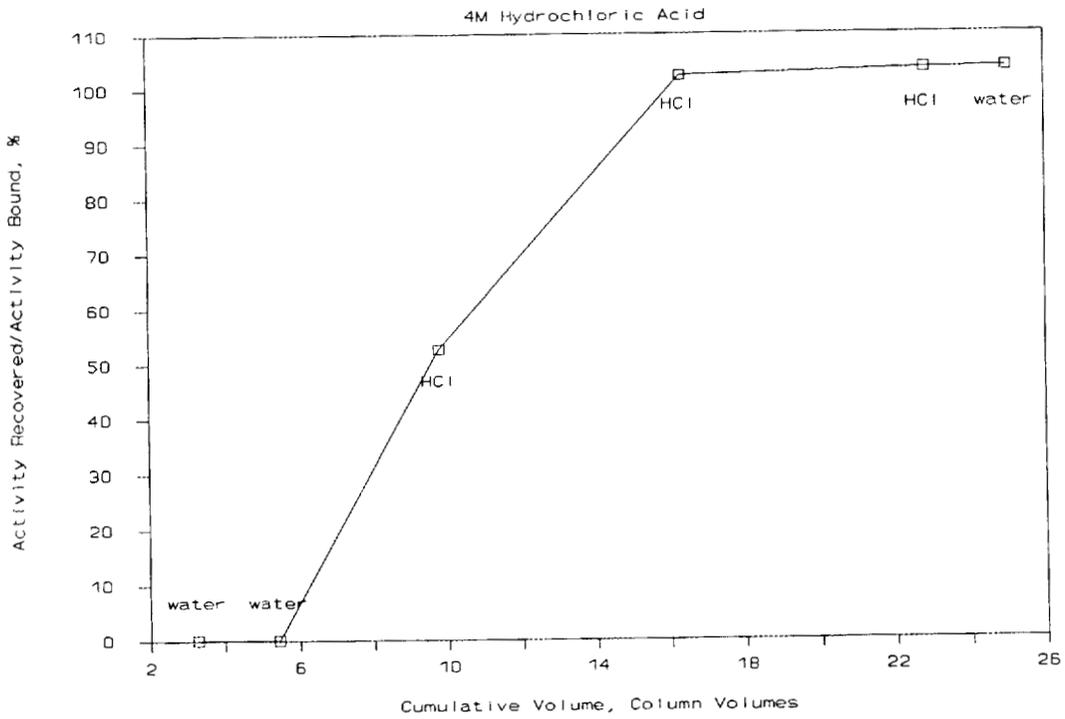


Fig. 3. Effect of potassium on strontium breakthrough curves

Run SRL3, Elution of Cesium Activity



Run SIMSRL5, Resin Elution

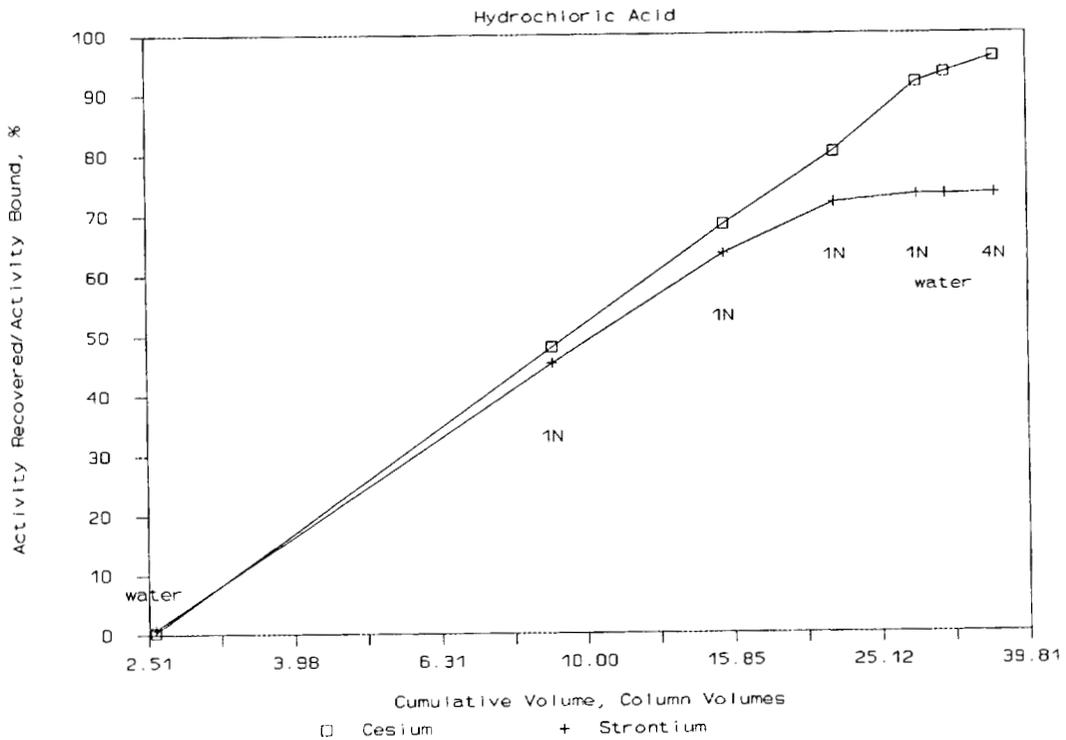


Fig. 4. Elution of activity from SRS resin

Θ_m = mean time of the function ($\Theta - \Theta_0$ at $C/C_0 = 0.63$), and
 β = shape factor for the curve (slope, if curve is straight line).

Analysis consists of plotting the $\log\{\ln(1/(1 - C/C_0))\}$ vs $\log(\Theta - \Theta_0)$. If a straight line emerges, the slope is β , and Θ_m is the value of $(\Theta - \Theta_0)$ at $\ln(1/(1 - C/C_0)) = 1$, as shown in Fig. 5. Other parameters can be calculated once the breakthrough function is determined, including the mass transfer coefficient (K_{fa} , s^{-1}), height of a transfer unit (HTU, cm), the distribution coefficient (K'_dJ), the time of bed saturation (Θ_s), and the resin capacity (q_0).

Parameters obtained from the column runs using the method of Doulah and Jafar are shown in Table 9. Values of K'_d 's obtained by both the graphical method (K'_d) and calculations using the breakthrough function method (K'_dJ) are given. The comparison is also shown in Fig. 6 for the cesium K'_d 's and shows that the calculation method gives consistently larger values. Comparison of K_{fa} to K_{pa} , the liquid film mass transfer coefficient based on the system hydrodynamics⁷ shows that the system is limited by the mass transfer inside the resin particle. Indeed, the intraparticle diffusion coefficients that have been measured for organic ion-exchange resin systems are generally lower by two orders of magnitude compared with the fluid-phase diffusion.⁸

SUMMARY

Several inorganic ion exchangers provide extremely large distribution coefficients for ^{137}Cs and ^{90}Sr , even in the presence of high concentrations of sodium and moderate amounts of potassium. This unusually high selectivity allows more flexibility in application than do the more familiar processes.

The most valuable characteristic of the ferrocyanides is their extreme selectivity for cesium. With high-salt waste concentrates, which generally present the greatest problem, these reagents are remarkably effective. In many cases, they can be used in a head-end clarification step that is often automatically required, and this may provide an adequate process by itself.

Both the batch and the column results verify that SRS resin has excellent properties for cesium removal but shows much poorer results for strontium. It is effective in high-pH, high-salt solutions, particularly for cesium. Cesium removal is strongly dependent on the potassium concentration, while strontium removal is dependent on the sodium or total alkali metal content. This will allow relatively small ion-exchange columns to be used for ^{137}Cs removal if very little ^{90}Sr is present. In cases of high strontium concentrations, another resin column or a mixture of resins may be required to remove both of the contaminants.

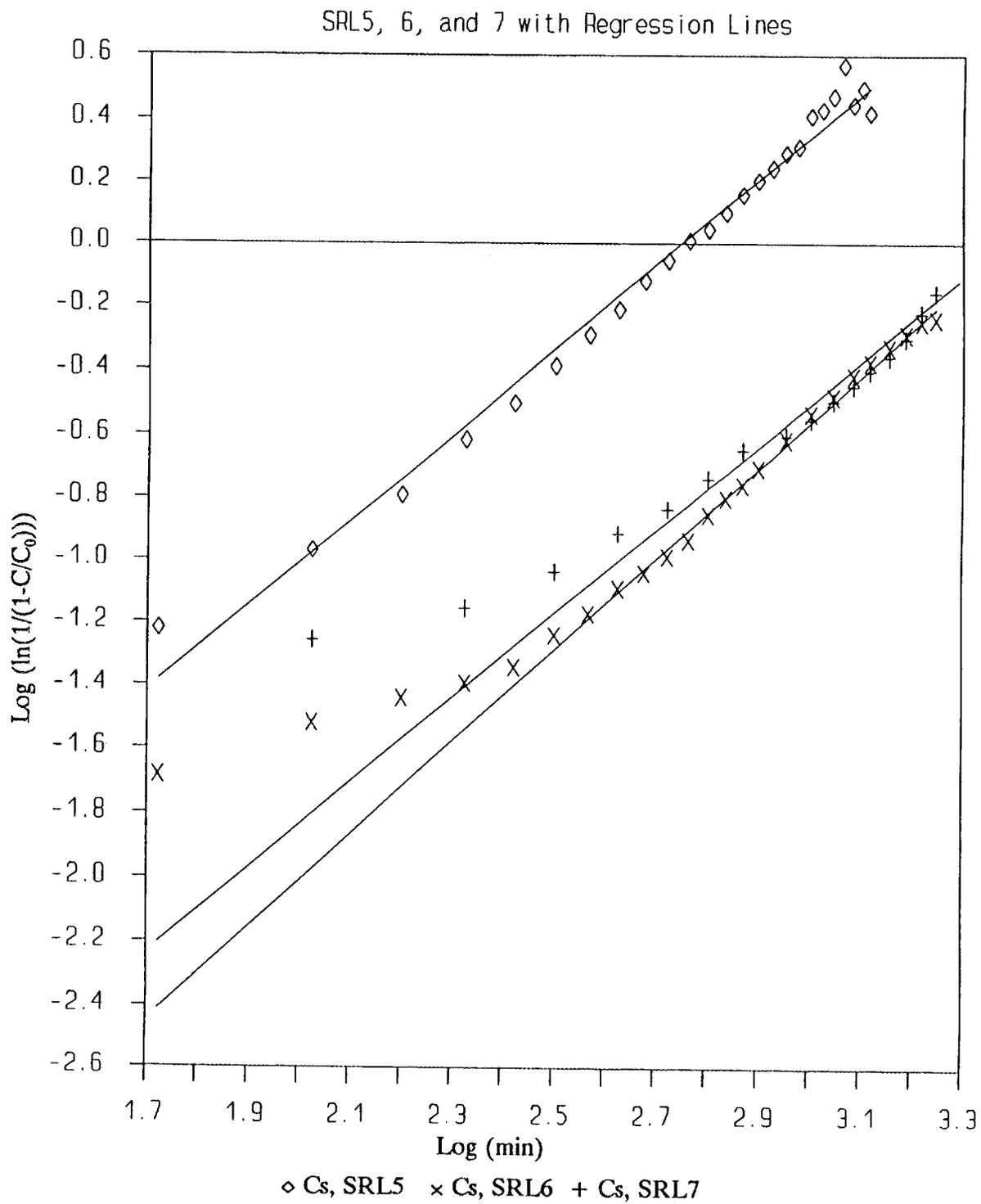


Fig. 5. SRS resin breakthrough function curves

Table 9. Data for SRS resin column runs

A. Cesium									
	SRL1	SRL2	NaK1	SRL3	SRL4	SRL5	SRL6	SRL7	Na1
K'_d	= 755	546	692	759	348	219	876	1587	7293
K'_dJ	= 1000	815	954	1054	421	258	1045	1703	8619
K_{fa}	= 5E-6	5E-6	4E-6	1E-6	2.4E-5	4E-5	9E-6	9E-6	.6E-9
$^aK_{1a}$	= 0.0296	0.0327	0.0325	0.0146	0.0795	0.0795	0.0789	0.0789	0.0325
Htu	= 4655	5437	6111	3901	1094	663	2671	2849	19540
θ_s	= 4965	3260	3615	18642	1304	799	3120	6174	31827
β	= 1.405	0.934	0.894	1.033	1.475	1.350	1.447	1.330	1.478
Int	= -5.175	-3.256	-3.151	-4.219	-4.427	-3.706	-4.903	-4.494	-5.424
θ_m	= 4815	3067	3351	12168	1005	557	2447	2398	22213
θ_0	= 150	193	264	6473	298	241	672	3775	9614
q_0	= 2.3E6	2.1E6	2.4E6	2.6E6	1.1E6	6.3E5	2.6E6	5.9E6	1.8E7
H	= 5.3	5.2	4.85	4.6	3.9	3.9	3.7	4.35	4.75
a	= 10.77	10.77	10.77	10.77	19.67	19.67	19.67	19.67	10.77

B. Strontium

	SRL4	SRL5	SRL6	SRL7
K'_d	= 94	102	99	433
K'_dJ	= 145	130	112	436
K_{fa}	= 2.6E-4	2.2E-4	2.0E-4	7.8E-5
K_{1a}	= 0.0795	0.0795	0.0789	0.0789
Htu	= 103	122	131	337
θ_s	= 451	403	334	1581
β	= 4.04	2.82	2.34	2.07
Int	= -9.75	-6.57	-5.35	-5.47
θ_m	= 260	214	194	441
θ_0	= 190	188	140	1140
q_0	= 3.0E5	3.2E5	2.7E5	1.5E6

^aCarberry's Correlation = $K_1 = 1.15(\rho D_p U_s / \mu_l \epsilon)^{-1/4} (\mu_l / \rho_l D)^{-2/3} (U_s / \epsilon)$

Col diameter, d = 1.12838 cm

Resin bulk dry density = 0.848

μ_l = viscosity ~ 0.01 g/cm·s

H = bed height (cm)

ϵ = Void fraction = 0.4

D = Diffusion coefficient ~ 2×10^{-5} cm²/s

a = $\epsilon^{1.5} / D_p$ (cm⁻¹)

ρ_l = liquid density ~ 1.24 g/cm³

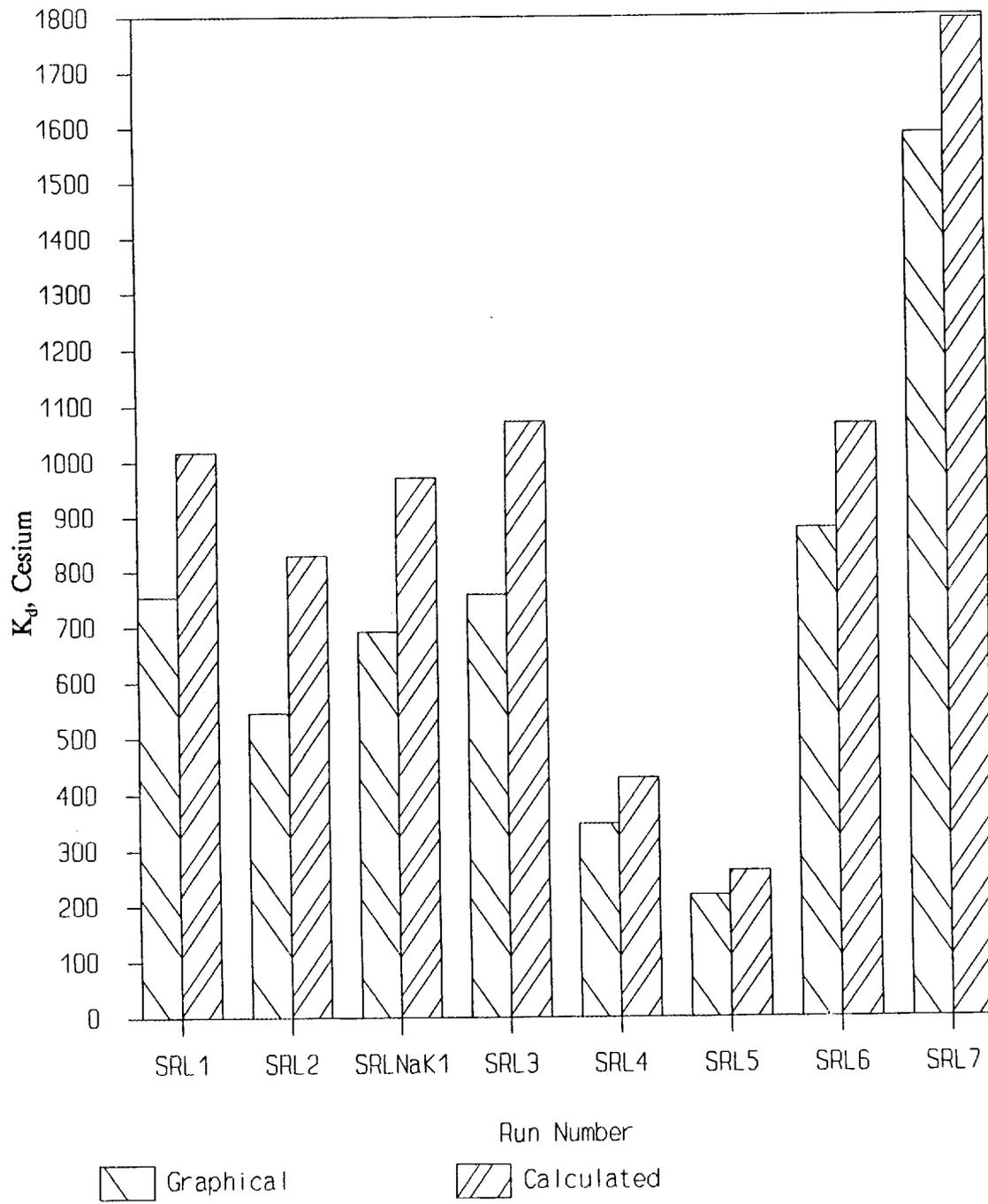


Fig. 6. Cesium K_d s for column tests by graphical and breakthrough function methods

REFERENCES

1. D. O. Campbell, E. D. Collins, L. J. King, and J. B. Knauer, "Evaluation of the Submerged Demineralizer System (SDS) Flowsheet for Decontamination of High-Activity-Level Water at the Three Mile Island Unit 2 Nuclear Power Station," ORNL/TM-7448, Oak Ridge National Laboratory (July 1980).
2. V. Kourim, J. Rais, and B. Million, "Exchange Properties of Complex Cyanides — I; Ion Exchange of Cesium Ferrocyanides," *J. Inorg. Nucl. Chem.*, 26, 1111 (1964).
3. W. E. Prout, E. R. Russell, and H. J. Groh, "Ion-Exchange Absorption of Cesium by Potassium Hexacyanocobalt(II)ferrate(II)," *J. Inorg. Nucl. Chem.*, 27, 473 (1965).
4. J. P. Bibler, R. M. Wallace, and L. A. Bray, "Testing a New Cesium-Specific Ion-exchange Resin for Decontamination of Alkaline-High Activity Waste," presented at Waste Management '90, Tucson, Arizona, February 25 - March 1, 1990.
5. E. D. Collins, D. O. Campbell, L. J. King, J. B. Knauer, and R. M. Wallace, Evaluation of zeolite mixtures for decontaminating high-activity-level water at the Three Mile Island Unit 2 Nuclear Power Station, p.43 in "Inorganic Ion Exchangers and Adsorbents for Chemical Processing in the Nuclear Fuel Cycle," IAEA-TECDOC-337 (1984).
6. M. S. Doulah and S. A. Jafar, "A method for the prediction of mass transfer parameters in an ion exchange process," pp. 293-305 in Ion Exchange for Industry, Michael Streat, ed., Ellis Horwood, Limited, Chichester, England (1988).
7. J. J. Carberry, "A Boundary Layer Model of Fluid-Particle Mass Transfer in Fixed Beds," *AIChEJ*, 6(3), 460 (1960).
8. Chemical Engineers' Handbook, Fifth ed., 16-19 (J. H. Perry et al., eds.) McGraw-Hill, New York (1973).

1

2

3

INTERNAL DISTRIBUTION

1. H. L. Adair
2. J. M. Begovich
3. J. T. Bell
4. J. B. Berry
5. W. D. Bond
6. C. H. Brown, Jr.
7. C. O. Campbell
8. R. M. Canon
9. E. D. Collins
10. K. W. Cook
11. A. G. Croff
12. T. A. Dillow
13. S. M. DePaoli
14. C. P. East
15. B. Z. Egan
16. W. Fulkerson
17. R. K. Genung
18. J. R. Hightower
19. V. T. Hinkel
20. L. Holder
21. E. K. Johnson
22. C. M. Kendrick
23. T. E. Kent
24. J. R. Lawson
- 25-26. D. D. Lee
27. J. J. Maddox
28. R. C. Mason
29. A. J. Mattus
30. L. E. McNeese
31. L. J. Mezga
32. J. J. Perona
33. D. J. Peterson
34. S. M. Robinson
35. T. F. Scanlan
36. C. B. Scott
37. M. G. Stewart
38. P. A. Taylor
39. J. R. Trabalka
40. D. W. Turner
41. E. L. Youngblood
42. Cen. Res. Library
43. Doc. Ref. Section
44. Lab Records
45. Lab Records. R.C.
46. ORNL Pat. Sect.

EXTERNAL DISTRIBUTION

47. Office of Assistant Manager, Energy Research and Development, DOE-OR, P. O. Box 2001, Oak Ridge, TN 37831-8600
- 48-57. Office of Scientific and Technical Information, P. O. Box 62, Oak Ridge, TN 37831