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REPORT

ADSORPTION OF TRACE IONS
FROM INTERMEDIATE LEVEL RADIOACTIVE WASTES
BY ION EXCHANGE

B. W. MERCER

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BY ION EXCHANGE

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January, 1966

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INTRODUCTION

Cesium and strontium removal from waste solutions by ion exchange can usually be predicted theoretically. The simple solution chemistry of cesium and strontium permits a useful theoretical approach, but extension of this approach to rare earths, zirconium, niobium, and particularly ruthenium is limited. The ionic charges of these latter elements are often difficult to predict or measure in actual waste solutions, and without this information, distribution coefficients cannot be computed from selectivity coefficients. However, if the ion exchangers are selected with known capacities for removing cesium and strontium, the study of removing the remaining radionuclides from a particular waste can proceed.

Previous Hanford studies of radioactive condensate decontamination by ion exchange have been concerned with only a few ion exchangers^(1,2) and the effect of one competing cation on the uptake of trace cesium or strontium ions.⁽³⁾ This report discusses a more comprehensive study of 16 ion exchangers and the use of ion exchange theory to estimate adsorption and column breakthrough of trace cesium and strontium ions from solutions containing one or several competing cations. In addition, the results of pilot scale demonstration runs with actual plant wastes are also reported.

SUMMARY

Trace cesium and strontium selectivity coefficients were determined for 16 cation exchangers. Mass action equations were derived for determining the cesium and strontium equilibrium distribution coefficients for solutions containing several competing

cations. Good agreement was obtained between computed and experimental distribution coefficients. The computed 1% cesium breakthrough points were within 20% of the actual 1% cesium breakthrough points determined previously for two waste treatment pilot plant ion exchange columns with a plant condensate waste. The slopes of the computed breakthrough curves agreed well with the actual curves for the range covered.

A plant condensate waste was steam stripped, filtered, and decontaminated by ion exchange on a pilot plant scale. The inadvertent introduction of bacteria into the plant condensate retention tank complicated the decontamination of this condensate by increasing the filtration requirement. The steam stripped condensate waste containing bacterial residue was successfully filtered with a horizontal plate filter by using diatomaceous earth filter aid. The use of a fine particle zeolite as both a filtration and an ion exchange media for the horizontal plate filter was apparently unsatisfactory because only a fraction of the zeolite ion exchange capacity was used before the bed became plugged.

EXPERIMENTAL PROCEDURES

Laboratory Scale

Batch distribution experiments were performed by mixing 100 ml or 200 ml of solution containing a known concentration of Sr^{85} or Cs^{137} tracer with 0.4 g or 1.0 g of ion exchanger for 3 days. These solution to ion exchanger ratios were selected to minimize analytical errors. The mixtures were separated by centrifugation and aliquots of the supernate solution were analyzed for radionuclide concentration by gamma counting. The amount of Sr^{85} or Cs^{137} adsorbed was determined by the difference in Sr^{85} or Cs^{137} concentration in the solution equilibrated with the exchanger and in the same solution without the exchanger.

The ion exchangers were converted to the desired ionic form by contact with a fresh, saturated solution of the chloride salt of the appropriate cation at least five times during 24 hr. The ion exchangers were then washed thoroughly with distilled water and immersed in distilled water until the chloride ion was below the detection limit of AgNO_3 added to the rinse water. Undetectable chloride ion in the water was selected as proof that absorbed salt was removed.

The natural zeolite clinoptilolite was treated with 10% HNO_3 to remove calcite and clay impurities before conversion to the desired ionic form. All of the ion exchangers were air dried at 25°C before use. All experiments were conducted at $25 \pm 2^\circ\text{C}$.

The ion exchangers used in this work are listed in Appendix A with the names of the manufacturers or suppliers.

Pilot Plant Scale

Pilot-scale demonstration runs were undertaken to compare with laboratory studies. The pilot-plant process included steam stripping and filtration as treatment methods prior to ion exchange.

The filtration equipment consisted of a horizontal plate filter (Sparkler Model HRC-10)[†] with a maximum filter area of 6.48 ft^2 or a minimum of 0.9 ft^2 , depending on the number and size of the filter plates used in the filter tank. For this work, only the 0.9 ft^2 plate was used. The filter was leak tested with 20 psig air pressure to assure no bypassing of the filter plates. Diatomaceous earth filter aid^{††} or clinoptilolite slurries were circulated through the filter tank at 5 gal/min passed through the filter plate to apply the precoat. Filter

[†]Manufactured by the Sparkler Manufacturing Company, Conroe, Texas.

^{††}Dicalite Grade 4200, product of the Dicalite Company, Los Angeles, California.

aid and clinoptilolite were introduced from the top of the tank since the upward water flow velocity was insufficient to lift clinoptilolite particles larger than 0.074 mm up to the filter plates.

The steam stripping column was fabricated from stainless steel pipe 7 ft long by 8 in. in diameter and was filled with 1/4 in. SS Raschig rings. The reboiler was fabricated from 4 ft of 4 in. diam SS pipe fitted with steam coils.

The ion exchange columns were constructed of 6 in. diam glass pipe, 8 ft long. Amberlite IRA-900 (5.2 gal) was used in the anion column. A layer of Amberlite IR-200 (2.5 gal) on top of a layer of clinoptilolite (1.0 gal) constituted the cation exchange column. Both the resin and the zeolite were used in the cation column, the former for high strontium selectivity and the latter for high cesium selectivity.

The pilot plant flow diagram for the condensate waste decontamination process is shown in Figure 1.

RESULTS AND DISCUSSION

Ion Exchange Equilibria for Trace Ions

Single Competing Cation

Strontium and cesium ions are usually present in intermediate level waste solutions at a trace concentration. The theoretical treatment of the ion exchange equilibria of trace ion is relatively simple since the selectivity coefficient for the trace ion is a constant for practical purposes. The selectivity coefficients in this report were determined on solutions having total cation concentrations of 0.1 equivalents per liter or less to avoid using activity coefficients.

The equation for computing the selectivity coefficient K_{A^*B} for univalent trace ion A^* and competing ion B^+ is

[†]Letters with an asterisk (*) denote trace ions.

FIGURE 1
Flow Diagram

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$$K_{A^*B} = \left(\frac{\bar{c}_{A^*}}{c_{A^*}} \right) \left(\frac{c_B}{\bar{c}_B} \right) \quad (1)$$

where $\bar{c}_{A^*}$ and $\bar{c}_B$ are concentrations of A^* and B , respectively, in the ion exchanger (meq./g) and c_{A^*} and c_B are concentrations of A^* and B , respectively, in the solution (meq./ml).

The equilibrium distribution coefficient is

$$Kd_{A^*B} = \frac{\bar{c}_{A^*}}{c_{A^*}} \quad (2)$$

Substitution of Equation (2) into Equation (1) gives

$$K_{A^*B} = Kd_{A^*B} \left(\frac{c_B}{\bar{c}_B} \right) \quad (3)$$

Since $\bar{c}_B$ is essentially constant for the system ($\bar{c}_B = Q$, the total exchange capacity), $\bar{c}_B$ is set equal to one to yield

$$K'_{A^*B} = (Kd_{A^*B}) (c_B) \quad (4)$$

The coefficient K' is preferred over K for comparing different exchangers since K' is not influenced by the total exchange capacity. For example, K_{A^*B} may indicate high selectivity for A^* , but actually this desirable characteristic could be offset by a very low exchange capacity.

The general equation for K' is

$$K'_{X^*Y} = (Kd_{X^*Y})^x (c_Y)^y \quad (5)$$

where x and y are equal to the number of equivalents of X^* and Y represented in the chemical equation for the exchange equilibria of X^* and Y .

Letters with the bar above them indicate exchanger phase and those without the bar indicate solution phase.

The K_d values for Cs^+ and Sr^{+2} plotted versus c_{Na} and c_{Ca} are shown in Figures 2, 3, 4, and 5. The curves represent mass action law and were computed from average K' values for the experimental points shown. Good agreement with mass action law is generally observed for the K_d determinations. The K_d values for organic resins are usually more precise than for the inorganic exchangers. The variation in Cs^+ K_d values for clinoptilolite and Decalso in Figure 4 is partially caused by experimental error in determining very large distribution coefficients. The curve for clinoptilolite and Decalso in Figure 4 is approximately the same.

FIGURE 2
Cesium K_d Values as a Function of Na^+ Normality

FIGURE 3
Strontium K_d Values
as a Function of Na^+
Normality

FIGURE 4
Cesium K_d Values as
a Function of Ca^{+2}
Normality

FIGURE 5
Strontium K_d Values as a Function of Ca^{+2} Normality

Cesium and strontium K' values for 16 ion exchangers with competing ions are shown in Tables I and II. The K' values were computed by Equation (5) from at least two K_d values determined at different competing ion concentrations.

The inorganic exchangers listed in Tables I and II generally show greater cesium selectivity than the organic exchangers; whereas, the organic exchangers generally show greater strontium selectivity. Exceptions are noted for strontium K' values for Decalzo, AW 400, AW 500, and clinoptilolite in calcium systems; and 13 X and 4 AXW in sodium systems. Both Decalzo and AW 500 show quite high strontium selectivity in the presence of Ca^{+2} .

TABLE I
K' VALUES FOR TRACE Cs⁺

Exchanger	Exchanger Type	Exchanger Capacity meq/g Na ⁺	Cesium K' Values for the Indicated Competing Cation				
			H ⁺	NH ₄ ⁺	Na ⁺	K ⁺	Ca ⁺²
Amberlite IR-120	Sulfonated Polystyrene Resin	4.0	24	6.5	9.6	4.0	72
Amberlite IR-200	Sulfonated Polystyrene Resin	3.9	1.0 x 10 ²	6.9	20	4.4	1 x 10 ³
Dowex 50-X4	Sulfonated Polystyrene Resin	3.8	---	6.0	8.5	---	18
Dowex 50-X12	Sulfonated Polystyrene Resin	4.0	43	6.9	12	---	55
ZP-1	Zirconium Phosphate	1.2	2 x 10 ²	33	6 x 10 ²	25	2 x 10 ⁶
ZM-1	Zirconium Molybdate	0.9	---	11	9 x 10 ²	---	8 x 10 ⁴
ZT-1	Zirconium Tungstate	0.8	---	12	1 x 10 ²	---	1 x 10 ⁵
AMP-1	Ammonium Molybdo-phosphate	1.4	---	4.9 x 10 ²	4 x 10 ⁴	---	<10 ⁹
Zeodur	Processed Glauconite	0.18	--	3.1	1 x 10 ³	---	5 x 10 ⁶
Decalso	Alumino-Silicate Gel	3.0	---	22	5.6 x 10 ²	32	1 x 10 ⁸
AW 400	Synthetic Zeolite (Erionite)	2.0	---	29	1 x 10 ³	---	3 x 10 ⁷
AW 500	Synthetic Zeolite (Chabazite)	2.2	---	40	8 x 10 ²	41	1 x 10 ⁷
13X	Synthetic Zeolite (Faujasite)	3.5	---	2	31	2	2 x 10 ⁴
4AXW	Synthetic Zeolite (Type A)	3.9	---	---	26	---	2 x 10 ⁴
Zeolon	Synthetic Zeolite (Mordenite)	1.9	4 x 10 ³	35	1 x 10 ²	56	5 x 10 ⁶
Clinoptilolite	Natural Zeolite	1.7	8 x 10 ²	35	3.6 x 10 ²	32	1 x 10 ⁸

TABLE II								
K' VALUES FOR TRACE Sr^{+2}								
Exchanger	Exchanger Type	Exchanger Capacity meq/g Na^+	Strontium K' Values for the Indicated Competing Cation					
			H^+	NH_4^+	Na^+	K^+	Mg^{+2}	Ca^{+2}
Amberlite IR-120	Sulfonated Polystyrene Resin	4.0	1×10^2	45	44	44	8.2	5.4
Amberlite IR-200	Sulfonated Polystyrene Resin	3.9	8×10^2	1.3×10^2	1.2×10^2	87	---	6.4
Dowex 50-X4	Sulfonated Polystyrene Resin	3.8	---	24	31	---	---	5.0
Dowex 50-X12	Sulfonated Polystyrene Resin	4.1	---	82	57	---	---	5.7
ZP-1	Zirconium Phosphate	1.2	0.05	1	2	---	---	1.5
ZM-1	Zirconium Molybdate	0.9	---	0.6	1	---	---	2
ZT-1	Zirconium Tungstate	0.8	---	4.0	4	---	---	2
AMP-1	Ammonium Molybdo-phosphate	1.4	---	<0.1	1	---	---	0.3
Zeodur	Processed Glaucinite	0.18	---	0.2	1	---	---	0.4
Decalso	Alumino-Silicate Gel	3.0	---	12	38	---	1×10^3	23
AW 400	Synthetic Zeolite (Erionite)	2.0	---	5	6	---	---	6.2
AW 500	Synthetic Zeolite (Chabazite)	2.2	---	<0.1	4	0.67	---	21
13X	Synthetic Zeolite (Faujasite)	3.5	---	---	58	---	---	10
4AXW	Synthetic Zeolite (Type A)	3.9	---	---	56	---	---	10
Zeolon	Synthetic Zeolite (Mordenite)	1.9	0.01	<0.1	0.7	0.19	---	0.6
Clinoptilolite	Natural Zeolite	1.7	0.3	0.3	25	---	5×10^3	7.9

Multiple Competing Cations

Application of ion exchange theory to practical problems is often complicated by the presence of two or more competing ions. Mass action equations are derived for computing K_d values for systems containing two or more competing ions. The computations involve binary exchange coefficients determined in single competing ion systems. The derivation of these equations is based on the independence of the binary exchange equilibrium of one ion pair from other ion pairs in a multicomponent system.⁽⁴⁾ For the case of univalent ion A^* in equilibrium with univalent ions B and D, the sum of the $\bar{c}$ values is equal to the total exchange capacity Q. The exchange capacity is made equal to one to coincide with K' values, thus,

$$\bar{c}_{A^*} + \bar{c}_B + \bar{c}_D = 1 \quad (6)$$

Where A^* , B, and D are univalent ions the terms

$$\frac{(K_{d_{A^*B}})(c_B)}{K'_{A^*B}} \quad \text{and} \quad \frac{(K_{d_{A^*D}})(c_D)}{K'_{A^*D}}$$

are substituted for $\bar{c}_B$ and $\bar{c}_D$, respectively, in Equation (6) and $\bar{c}_{A^*}$ voided (it is negligible) to yield

$$\frac{(K_{d_{A^*B}})(c_B)}{K'_{A^*B}} + \frac{(K_{d_{A^*D}})(c_D)}{K'_{A^*D}} = 1 \quad (7)$$

Since $K_{d_{A^*B}}$ and $K_{d_{A^*D}}$ are equal in the same system, the term $K_{d_{A^*BD}}$ is substituted in place of them to give the final equation

$$\frac{1}{K_{d_{A^*BD}}} = \frac{c_B}{K'_{A^*B}} + \frac{c_D}{K'_{A^*D}} \quad (8)$$

The general equation is

$$\sum_{I=1}^{I=n} \left[\frac{(K_{d_{A^*D}})^a (c_I)^i}{K'_{A^*I}} \right]^{\frac{1}{i}} = 1 \quad (9)$$

Equations are given below for three specific systems:

Divalent A^* and univalent B and D,

$$\frac{1}{\sqrt{K_{d_{A^*BD}}}} = \sqrt{\frac{c_B^2}{K'_{A^*B}}} + \sqrt{\frac{c_D^2}{K'_{A^*D}}} \quad ; \quad (10)$$

Divalent A^* and B, and univalent D,

$$\frac{(K_{d_{A^*BD}})(c_B)}{K'_{A^*B}} + \sqrt{\frac{K_{d_{A^*BD}}(c_D)^2}{K'_{A^*D}}} = 1 \quad ; \quad (11)$$

Univalent A^* and B, and divalent D,

$$\frac{(K_{d_{A^*BD}})^2 (c_D)}{K'_{A^*D}} + \frac{(K_{d_{A^*BD}})(c_B)}{K'_{A^*B}} = 1 \quad (12)$$

Experimental K_d values for Cs^+ and Sr^{+2} are compared with K_d values computed by Equations (8), (10), (11), and (12) (Tables III and IV). Good agreement between computed and experimental K_d values is obtained in most cases. The computed cesium K_d for System 8 in Table III is believed to be high because of poor precision in the determination of K'_{Cs^*Ca} for clinoptilolite (Figure 4).

TABLE III
COMPARISON OF EXPERIMENTAL AND COMPUTED Kd VALUES FOR Cs⁺

System No.	Exchanger	Competing Cation Concentrations, meq/ml		Experimental Kd	Computed Kd
1	Amberlite IR-120	0.0515 H ⁺	0.0200 NH ₄ ⁺	193	191
2	Amberlite IR-120	0.0733 H ⁺	0.0252 NH ₄ ⁺	144	144
3	Amberlite IR-120	0.0732 H ⁺	0.0253 Na ⁺	160	176
4	Amberlite IR-200	0.0761 H ⁺	0.0224 NH ₄ ⁺	230	249
5	Amberlite IR-200	0.0187 Na ⁺	0.0900 Ca ⁺²	84	100
6	Amberlite IR-120	0.0187 Na ⁺	0.0850 Ca ⁺²	25	28
7	Decalso	0.0149 Na ⁺	0.0851 Ca ⁺²	21,700	22,000
8	Clinoptilolite	0.0162 Na ⁺	0.0838 Ca ⁺²	8,720	16,900

TABLE IV

COMPARISON OF EXPERIMENTAL AND COMPUTED Kd VALUES FOR Sr^{+2}

System No.	Exchanger	Competing Cation Concentrations, meq/ml		Computed Kd	Experimental Kd
1	Clinoptilolite	0.0104 NH_4^+	0.0891 Na^+	729	733
2	Decalso	0.0160 NH_4^+	0.0840 Na^+	3,010	4,360
3	Amberlite IR-120	0.0290 NH_4^+	0.0710 Na^+	4,450	4,530
4	Amberlite IR-120	0.076 H^+	0.024 Na^+	7,960	9,020
5	Amberlite IR-120	0.076 H^+	0.024 Na^+	7,990	8,080
6	Amberlite IR-200	0.0276 NH_4^+	0.0724 Na^+	12,300	10,900
7	Amberlite IR-200	0.022 Na^+	0.078 H^+	44,100	31,300
8	Clinoptilolite	0.0170 Na^+	0.0830 Ca^{+2}	113	160
9	Decalso	0.0164 Na^+	0.0836 Ca^{+2}	267	182
10	Amberlite IR-120	0.0193 Na^+	0.0807 Ca^{+2}	70	67
11	Amberlite IR-200	0.0187 Na^+	0.0813 Ca^{+2}	79	75

The exchange equilibria of trace Sr^{+2} in multiple competing cation systems with Dowex 50-X4 and montmorillonite clay has been studied by Baetsle, et al.⁽⁵⁾ Their general equation for a trace ion (A^*) Kd in a multiple competing ion system is

$$K_{A^*BDI} = \sum_{i=1}^{i=r} (K_{A^*I})^{\frac{1}{i}} \left(\frac{Q}{C_o}\right)^{\frac{\alpha}{i}} \frac{\left(\bar{x}_I\right)^{\frac{\alpha}{i}}}{\left(x_I\right)^{\frac{\alpha}{i}}} + 1 \quad (13)$$

where

- K_{A^*I} = selectivity coefficient for ions A^* and I
- C_o = total cation concentration in solution
- $\bar{x}_I$ = equivalent fraction of I on the exchanger
- x_I = equivalent fraction of I in solution
- i = valence of ion I
- α = valence of ion A^* .

Equation (13) is theoretically more accurate than Equation (9) because the actual distribution of competing ions is considered. However, Equation (13) is more difficult to use than Equation (9) because selectivity coefficients describing the distribution of competing ions are not generally constants. Therefore, the distribution of competing ions must either be determined experimentally or computed from known exchange isotherms.

Tables V and VI show experimental and computed Kd values for Dowex 50-X4 and montmorillonite clay in two competing cation systems⁽⁵⁾ compared with Kd values computed by Equations (8) or (11). Good agreement between both computed Kd values and experimental Kd values was usually obtained. The cause for the wide variance in experimental and computed Kd values for Solutions 1-4, Table V, is not known although selectivity coefficients calculated for K^+ and Mg^{+2} are much less than those for Solutions 5-8.

TABLE V
COMPARISON OF EXPERIMENTAL AND COMPUTED
STRONTIUM Kd VALUES FOR DOWEX 50-X4

Solution No.	C_K	C_{Mg}	C_{Ca}	Exp. Kd	Kd by Eq. (13)	Kd by Eq. (8) or (11)
1	0.0133	0.0799		229	---	131
2	0.0235	0.235		566	---	330
3	0.0052	0.0136		2,511	---	795
4	0.0070	0.0030		33,742	---	3,340
5	0.0442	0.0064		1,168	1,205	1,127
6	0.0185	0.0041		2,531	3,040	2,164
7	0.0075	0.0025		3,993	4,250	3,920
8	0.0037	0.0017		6,571	6,590	5,616
9		0.0114	0.0355	170	202	162
10		0.0102	0.0098	352	405	425
11		0.0084	0.0029	908	837	841
12		0.0044	0.0009	1,834	1,825	1,876
13	0.00452		0.0059	816	753	845
14	0.0177		0.0034	1,204	1,530	1,726
15	0.0077		0.0023	1,536	2,450	2,758
16	0.0043		0.0015	2,104	3,700	4,310
17		0.0892	0.0122	124	117	100
18		0.0279	0.0101	277	257	249
19		0.0116	0.0073	536	460	472
20		0.0043	0.0052	763	843	874

K' values computed from K values given by Baetsle, et al.⁽⁵⁾ for Dowex 50-X4 were: $K'_{Sr*K} = 21.8$, $K'_{Sr*Mg} = 10.9$, $K'_{Sr*Ca} = 6.95$.

TABLE VI

COMPARISON OF EXPERIMENTAL AND COMPUTED STRONTIUM

Solution No.	Kd VALUES FOR MONTMORILLONITE					
	C_K	C_{Mg}	C_{Ca}	Exp. Kd	Kd by Eq. (13)	Kd by Eq. (8) or (11)
1	0.0855	0.01382		24.8	21	10
2	0.0404	0.00962		59.5	41	33
3	0.0143	0.00604		135.5	102	102
4	0.00702	0.00412		207.0	177	191
5	0.00240	0.00282		369.7	368	352
6		0.0180	0.0769	12.17	12.1	11
7		0.0146	0.0348	20.6	21.3	21
8		0.0106	0.0096	56.9	53.2	53
9		0.0068	0.0032	114.3	106.8	109
10		0.0043	0.0009	193.5	221.8	212
11	0.0885		0.0124	18.0	22.0	10
12	0.0411		0.00850	50.0	48.0	33
13	0.0155		0.00520	116.0	111.0	102
14	0.00612		0.00360	193.0	203.0	206
15	0.00582		0.00248	336.0	300.0	285
16		0.0852	0.0128	12.3	14.5	11
17		0.0388	0.0114	25.8	24.5	22
18		0.0100	0.0074	58.6	55.0	62
19		0.0046	0.0056	100.6	107.0	104
20		0.0015	0.0036	244.1	209.0	206

K' values computed from K values given by Baetsle, et al.⁽⁵⁾ for Montmorillonite were: $K'_{Sr*K} = 0.104$, $K'_{Sr*Mg} = 1.12$, $K'_{Sr*Ca} = 1.02$.

Treatment of Plant Condensate Waste

Suspended Matter

Removal of trace radioactive ions from wastes by ion exchange is influenced not only by the concentration of competing ions but also by other substances such as suspended matter physically interfering with the operation of ion exchange columns. The waste treatment pilot plant effort was significantly concerned with pretreatment methods of removing dissolved and suspended organic materials from Purex tank farm condensate.⁽²⁾ Steam stripping was the most effective method found because both organic matter and ammonia were removed from the condensate. However, when pilot plant experiments were initiated to demonstrate a larger integrated treatment process, steam stripping was ineffective for clarifying the condensate. Subsequent investigation disclosed that bacteria were responsible for additional suspended matter not removed by steam stripping. The bacteria were probably introduced to the condensate retention tank via a temporary waste water line a few months prior to the startup of the waste treatment pilot plant.

Elimination of the bacteria in the condensate retention tank was attempted but was not completely successful. Treatment with hypochlorite was temporarily effective in eliminating viable cells from the condensate in the retention tank and aided in reducing the amount of suspended matter. However, the clarity of the condensate after steam stripping was not improved enough to demonstrate the integrated treatment process as originally intended. Since the practical value of demonstrating a process on a condensate containing bacteria or bacterial residue is questionable, only two pilot plant runs were carried to completion. The primary objective of these runs was to evaluate the effectiveness of diatomaceous earth filter aid or fine mesh clinoptilolite in a commercial filter for removing the suspended matter.

Pilot Plant Operation and Results

Purex tank farm condensate was treated with sodium hypochlorite in the condensate retention tank two days prior to removal of condensate for a run. The two day waiting period allowed most of the dead bacteria to be flushed out. Hypochlorite was also added to the tank trailer used to transport the condensate and again in the pilot plant storage tank. Because these latter hypochlorite additions caused a high chloride concentration, the condensate for the second run was stored outside during cool weather without hypochlorite addition.

The steam stripper was operated at a feed rate of 1 gal/min, with a boil off rate of 0.15 gal/min for both runs. The 15% boil off rate gave the lowest turbidity in the stripper bottoms. The concentrations of tributyl phosphate, hydrocarbon diluent, and ammonia were reduced to satisfactory levels in the stripper bottoms. Typical feed and stripper bottom concentrations of these substances are listed in Table VII.

TABLE VII

CONCENTRATIONS OF TRIBUTYL PHOSPHATE, HYDROCARBON DILUENT,
AND AMMONIA IN FEED AND STRIPPER BOTTOMS

	Concentration, mg/liter	
	<u>Feed</u>	<u>Stripper Bottoms</u>
Tributyl Phosphate	24-65	0.5 - 1.2
Hydrocarbon Diluent	5-23	1.0 - 2.2
Ammonia	16-22	0.1 - 0.8

The horizontal plate filter was operated with a precoat of 1/4 in. of diatomaceous earth filter aid in the first run. Stripper bottoms were fed to the filter at a flow rate of 0.85 gal/min. Filter aid was injected into the feed at a rate of 0.01% throughout the run to prevent an impermeable film forming on the precoat. The first run proceeded smoothly for 66 hr before the pressure

exceeded the feed pump limit. The differential pressure across the filter was 0.2 psig at the start of the run, and 13.4 psig at the end of the run. The filter removed essentially no Cs^{137} , about 10% of the Sr^{90} and Ru^{106} , and about half of the Ce^{144} and $\text{Zr}^{95}\text{-Nb}^{95}$.

The precoat used in the second run consisted of three layers: a 1/8 in. layer of diatomaceous earth filter aid on the filter plate, a 1/2 in. layer of 100 x 325 mesh clinoptilolite, and another 1/8 in. layer of diatomaceous earth filter aid on top of the clinoptilolite layer. Figure 6 is a picture of a precoat applied in this manner in a test run. The dark material on the top layer of filter aid is iron oxide that filtered out of the test feed. The clinoptilolite was used in combination with filter aid because high initial pressure differential across the filter occurred in tests when the clinoptilolite was applied directly to the filter plate.

Figure 7 shows differential pressure and $\text{Cs}^{137} \text{C}/\text{C}_0$ values plotted versus gallons put through the filter in the second run. Repair of the filter feed pump allowed a higher pressure differential than in the first run. Filter aid was injected in the feed at the same rate as the first run. The increasing $\text{Cs}^{137} \text{C}/\text{C}_0$ values indicate leakage rather than ion exchange breakthrough. With increasing pressure at twice the bed volumes of condensate a 2.4 cm² laboratory precoat bed showed no decrease in $\text{Cs}^{137} \text{C}/\text{C}_0$ values.

All radioisotopes were reduced below their respective MPC_w values except Ru^{106} in Run No. 1. The average feed and cation effluent radioisotope concentrations for the runs are shown in Table VII. Ruthenium removal in the anion column of Run No. 1 decreased to 75% within the first 100 gal, whereas, it remained at 85 to 90% through 1,300 gal in Run No. 2. High chloride ion concentration (151 ppm) in the feed of Run No. 1 is believed to have caused the lower Ru^{106} adsorption. Chloride breakthrough coincided with breakthrough of Ru^{106} to C/C_0 0.25 in the anion column of Run No. 1.

FIGURE 6

Interior of Sparkler Filter with Clinoptilolite
and Filter Aid Precoat

FIGURE 7
Differential Pressure and Cs¹³⁷ Breakthrough Across
the Filter for Run No. 2

TABLE VII
AVERAGE FEED AND CATION EFFLUENT RADIOISOTOPE
CONCENTRATIONS FOR RUNS NO. 1 AND 2

Radioisotope	Radioisotope Concentration in Run No. 1, C _i /ml		Radioisotope Concentration in Run No. 2, μ C _i /ml	
	Feed	Cation Effluent	Feed	Cation Effluent
Cs ¹³⁷	8.9×10^{-3}	6.9×10^{-5}	3.6×10^{-3}	9.4×10^{-6}
Sr ⁹⁰	2.7×10^{-4}	4×10^{-7}	1.7×10^{-4}	6×10^{-7}
Ru ¹⁰⁶	8.6×10^{-4}	1.5×10^{-4}	3.1×10^{-4}	7.4×10^{-6}
Zr ⁹⁵ -Nb ⁹⁵	1.7×10^{-3}	2×10^{-5}	4.6×10^{-4}	$< 2 \times 10^{-6}$
Ce ¹⁴⁴ -Pr ¹⁴⁴	2.2×10^{-3}	6×10^{-5}	1.0×10^{-3}	$< 3 \times 10^{-6}$

Application of Ion Exchange Theory to Column Operation

Application of ion exchange theory to column operation involves not only a suitable distribution coefficient but also some methods to estimate the breakthrough curve for the ions concerned. Several methods are available for estimating breakthrough curves based on various operating parameters such as flow rate, column size, etc. The method of Glueckauf^(6,7) is outlined below. The equation for the effective height of a theoretical plate (H) is

$$H = 1.64r + \frac{\delta}{(\delta + \beta)^2} \cdot \frac{(0.142)r^2v}{D_S} + \left(\frac{\delta}{\delta + \beta}\right)^2 \frac{(0.266r^2v)}{D_L(1 + 70rv)} + \frac{D_L \beta \sqrt{2}}{v} \quad (14)$$

where

r = average radius of the exchanger particle (cm)

δ = column distribution coefficient = (Kd) (packed bed density (g/cm³))

v = linear flow rate (feed volume per unit cross section of the column and unit time) (cm/sec)

D_S = particle diffusion coefficient for the trace ion (cm²/sec)

D_L = liquid diffusion coefficient for the trace ion (cm²/sec)

β = fractional void volume.

The third term on the right hand side of the equation above is the most important in low salt solutions because diffusion of the trace ion to the exchanger particle (film diffusion) is rate controlling. The last term of the equation can be neglected in normal column operations since longitudinal diffusion is significant only at very slow flow rates.

Figure 8 shows a comparison of experimental and computed breakthrough curves for Cs¹³⁷ for two waste treatment pilot plant

columns of IR-120 resin receiving steam stripped Purex tank farm condensate. Operating variables such as pH and NH_4^+ concentration were relatively constant for these two runs which simplifies the computations. The computations for MPP-16 are given in Appendix B.

FIGURE 8

Comparison of Experimental and Computed Cs^{137}
Breakthrough Curves for Amberlite IR-120 Columns

Conditions:

Flow Rate	4 gal/min/ft ²
Column Diameter	1 in.
Column Volume	250 cm ³
Temperature	25 °C
Exchanger Particle Size	16 x 50 mesh (USBS)
Packed Density of Resin	0.524 g/cm ³ (dry weight)
Competing Cation Concentra- tions, MPP-16	$2.4 \times 10^{-4} \text{ M NH}_4^+$, $7 \times 10^{-5} \text{ M Na}^+$
Competing Cation Concentra- tions, MPP-22	$1.1 \times 10^{-4} \text{ M NH}_4^+$, $7 \times 10^{-5} \text{ M Na}^+$

The slopes of the computed and experimental curves in Figure 8 agree quite well. The computed 1% cesium breakthrough points were within 20% of the experimental values. The main difference between the computed and experimental curve for MPP-22 is the computed Kd.

CONCLUSIONS

Equation (9) was useful for computing ion exchange distribution coefficients (Kd) for trace ions in solutions containing one or several competing ions. Equations involving only the selectivity coefficient for the trace ion and the concentrations of competing ions will give good estimates of Kd values in multi-competing ion systems.

A horizontal plate filter was found effective in removing suspended matter from steam stripped Purex tank farm condensate. The use of small particle zeolites for both filtration and adsorption of radioisotopes does not appear satisfactory for turbid waste solutions since the zeolite plugs well in advance of full utilization of the ion exchange capacity.

The addition of hypochlorite or other substances that contribute anions, such as Cl^- , to the waste solution should be avoided. The adsorption of ruthenium by the anion column is adversely affected by these anions.

Good agreement was obtained between experimental and computed Cs^{137} breakthrough curves for micro-pilot plant Amberlite IR-120 columns receiving steam stripped Purex tank farm condensate.

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APPENDIX A

LIST OF ION EXCHANGERS AND MANUFACTURERS OR SUPPLIERS

<u>Ion Exchanger</u>	<u>Manufacturer or Supplier</u>
Amberlite IR-120 Amberlite IR-200 Amberlite IRA-900	Rohm and Haas Company, Philadelphia, Pennsylvania
Dowex 50-X4 Dowex 50-X12	Dow Chemical Company, Midland, Michigan
Bio-Rad ZP-1 Bio-Rad ZM-1 Bio-Rad ZT-1 Bio-Rad AMP-1	Bio-Rad Laboratories, Richmond, California
Zeodur Decalso	Permutit Company, New York, New York
AW-400 AW-500 13X 4AXW	Linde Company, Tonawanda, New York
Zeolon	Norton Company, Worster, Massachusetts
Clinoptilolite	Baroid Division of the National Lead Company, Hector, California

BREAKTHROUGH CURVE COMPUTATION FOR MPP 16

Kd computation using Equation (8) is

$$\frac{1}{Kd_{Cs*NH_4,Na}} = \frac{c_{NH_4}}{K'_{Cs*NH_4}} + \frac{c_{Na}}{K'_{Cs*Na}}$$

where

$$K'_{Cs*NH_4} = 6.5$$

$$K'_{Cs*Na} = 9.6$$

$$c_{NH_4} = 2.4 \times 10^{-4} \text{ eq/liter}$$

$$c_{Na} = 7 \times 10^{-5} \text{ eq/liter}$$

$$\frac{1}{Kd_{Cs*NH_4,Na}} = \frac{2.4 \times 10^{-4}}{6.5} + \frac{7 \times 10^{-5}}{9.6}$$

$$Kd_{Cs*NH_4,Na} = 22,600$$

Computation of the height of a theoretical plate [Equation (14)]:

$$r \cong 0.04 \text{ cm}$$

$$\delta = (Kd_{Cs*NH_4,Na})(\text{packed resin density}) = (22,600)(0.524) = 11,800$$

$$\beta \cong 0.4$$

$$v = 0.27 \text{ cm/sec}$$

$$D_S \cong 1 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$$D_L \cong 2 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$H = (1.64)(0.04) + \frac{(0.142)(0.04)^2(0.27)}{(1.18 \times 10^4)(1 \times 10^{-6})} + \frac{(0.266)(0.04)^2(0.27)}{(2 \times 10^{-5})(1 + [70][0.04][0.27])}$$

$$H = 3.34 \text{ cm}$$

The number of theoretical plates (N) is

$$N = \text{Column Height}/H = 48 \text{ cm}/4.53 \text{ cm} = 14.4$$

Also

$$N = \frac{(V_{0.5})(V_{0.159})}{(V_{0.5} - V_{0.159})^2}$$

where

$V_{0.5}$ = number of column volumes to 50% breakthrough = 8

$V_{0.159}$ = number of column volumes is 15.9% breakthrough.

Therefore,

$$14.4 = \frac{(1.18 \times 10^4)(V_{0.159})}{(1.18 \times 10^4 - V_{0.159})^2}$$

$$V_{0.159} = 9060.$$

A straight line is drawn through the points $V_{0.5}$ and $V_{0.159}$ on logarithmic-probability paper.

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