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TESTING A NEW CESIUM-SPECIFIC ION EXCHANGE RESIN FOR DECONTAMINATION OF ALKALINE HIGH-ACTIVITY WASTE (U)*

by

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Richard M. Wallace

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ABSTRACT

Radioactive Cs-137 is a fission product found in wastes produced by reprocessing fuels from nuclear reactors. The highest concentrations of this isotope in wastes from the reprocessing of defense production reactors are found in the alkaline high-activity waste, a mixture primarily of sodium nitrate and sodium hydroxide called the supernate. In recent years, much research has been directed at methods for the selective removal and concentration of Cs-137 during waste processing.

The approach to the ultimate management of high-activity waste at the Savannah River Site (SRS) is to remove cesium from the supernate, combine it with insoluble sludge formed on neutralization of acidic waste, and convert them both to glass by vitrification in a joule heater melter. A cesium-specific ion exchange resin that will adequately decontaminate the supernate but will not introduce excessive amounts of organic material into the melter has been developed at SRS. The resin has been tested with simulated, both at SRS and at Battelle's Pacific Northwest Lab, and with actual supernate at SRS. It has consistently shown reliable performance and higher selectivity than other organic ion exchangers for cesium ion in those solutions. Repeated cycles on 200 mL. columns using simulated supernate feed and formic acid eluent have established operation parameters for the resin.

INTRODUCTION

Liquid radioactive wastes from the separations plants at the Savannah River Site (SRS) are neutralized prior to storage in mild steel tanks. On standing, the waste separates into a water insoluble component, called sludge, and a water soluble component, called supernate. The bulk of the fission products are contained in the sludge. However, Cs-137, a gamma emitter with a 30-year half life, remains in the supernate as the principal radioactive

constituent. Current plans for waste treatment at SRS involves separation of the sludge from the supernate and removal of the cesium from the supernate. The decontaminated supernate will be solidified with grout and stored in concrete vaults. The cesium will be combined with the sludge and converted to glass in a joule heated melter.

The reference process for cesium removal involves precipitation, along with potassium, as the tetraphenylborate salt. Ion exchange, using the resin described in this report, is being considered as a backup for the precipitation process. This resin is a resorcinol-formaldehyde condensation polymer that is highly specific for cesium. Its development is a continuation of initial studies by Ebra et al.¹ and by Walker².

DISCUSSION

Properties of the Resin

The resin is prepared by condensing the potassium salt of resorcinol with formaldehyde in an aqueous solution. The resulting gel is then dried at about 100°C. Gram quantities of the resin were prepared at SRL; kilogram quantities were prepared by Boulder Scientific Co. using a similar procedure. Samples of the resin were converted to the hydrogen form by passing a dilute nitric acid solution through a column containing the potassium form resin. A mixed sodium-potassium (Na/K) form was prepared by passing a 2 M NaOH solution through a similar column. The composition of the various forms of the resin are shown in Table 1. The ion exchange capacity and the bulk density of the (Na/K) form are found there also.

TABLE 1

ELEMENTAL ANALYSES FOR Na/K-, H-, AND K-FORMS OF THE RESIN

<u>ELEMENT</u>	<u>Na/K-FORM</u>	<u>H-FORM</u>	<u>K-FORM</u>
% C	45.90	59.46	42.20
% H	5.35	5.67	5.37
% Na	2.01	<0.5	0.015
% K	7.68	<0.5	8.94
% O	38.13	33.82	41.33
Total	99.07	98.95	97.86

Capacity: 2.85 milliequivalents per gram of air dried resin

Bulk density: 0.36 (grams of dry resin)/(ml of swollen resin)

Distribution Coefficients

Distribution coefficients (Kd) were measured in solutions containing 4.5 M NaNO₃ and 1.0 M NaOH with varying amounts of cesium. Coefficients were also measured in simulated supernate whose composition is given in Table 2. The distribution coefficients are seen to vary with cesium concentration in a sensitive manner, a behavior characteristic of phenolic resins. Table 3 shows results with resins prepared by SRL and Boulder Scientific. Kd values for Duolite™ CS-100, a commercially available phenolic resin, are also shown for comparison.

TABLE 2.
COMPONENTS OF SIMULATED SUPERNATE

<u>CHEMICAL</u>	<u>grams/Liter</u>	<u>Molarity</u>
NaOH	116.0	2.9
Al(NO ₃) ₃ ·9 H ₂ O	142.6	0.38
NaNO ₃	101.2	1.2
NaNO ₂	49.0	0.71
Na ₂ CO ₃ ·H ₂ O	24.8	0.20
Na ₂ SO ₄	24.0	0.17
KNO ₃	1.52	0.015
CsNO ₃	0.049	2.4E-4
Cs-137		trace

Total [Na⁺] = 5.6 M

TABLE 3.

DISTRIBUTION COEFFICIENTS FOR CESIUM BETWEEN RESIN AND
4.5 M NaNO₃-1.5M NaOH

Initial Cs Molarity	<u>Resorcinol Resin</u>		
	SRL Kd, ml/g	Boulder Kd, ml/g	CS-100 ** Kd, ml/g
Trace	5450	4600	317
2.00E-04	3570	2630	150
2.00E-03	325	319	57
2.50E-04 *	4400	3220	

* Simulated Supernate

** CS-100 values determined at half the Cs⁺ concentrations shown

Column Tests

Two column tests were run using resin prepared at SRL. One test involved simulated supernate while a second was performed in a high-level cell (HLC) with actual supernate. In both cases, the ratio of the cesium concentration in the effluent to that in the feed (C/C₀) was determined as a function of the the number of column volumes (CV) passed through the column.

The breakthrough curves were described by means of the J function:

$$C/C_0 = J(N, NT)$$

where

$$N = K_d \rho_B K_a / (f/v)$$

$$T = CV / K_d \rho_B$$

K_d = the distribution coefficient (ml/g)

ρ_B = bulk density of the resin (g/ml)

K_a = mass transfer coefficient for the system (hr⁻¹)

f = flow rate of feed solution (ml/hr)

v = volume of resin in the column (ml)

The J function can be represented over the region of interest by:

$$J(s,t) = 1/2 \left[\operatorname{Erfc}(\sqrt{s} - \sqrt{t}) + \frac{\operatorname{Exp}(-(\sqrt{t} - \sqrt{s})^2)}{\sqrt{\pi}(\sqrt{t} + \sqrt{st})} \right]$$

Erfc refers to the complementary error function.

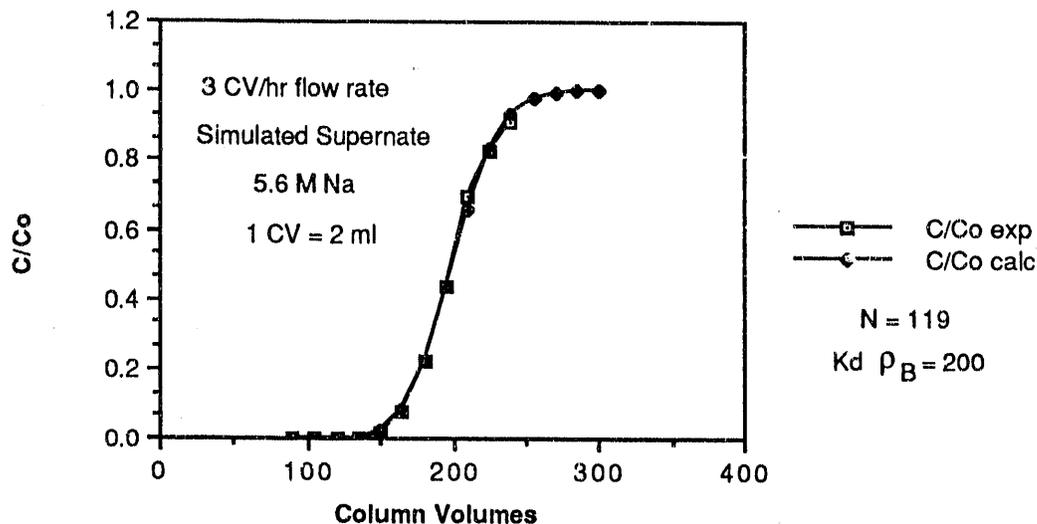
The breakthrough curves were fit by a nonlinear regression procedure. Values of N and $K_d \rho_B$ were varied to obtain the best fit.

Column Test with Simulated Supernate:

Simulated supernate containing cesium tracer was passed, at a rate of 3 column volumes (CV) per hour, through a column containing 2 ml of resorcinol resin in the Na/K form. The results of this test are shown in Figure 1 below in which experimental values of C/C_0 are given together with values calculated from the best fit of the J function. Values of N and $K_d \rho_B$ were 119 and 200 respectively.

Figure 1.

LABORATORY COLUMN SYSTEM Cs-137 BREAKTHROUGH

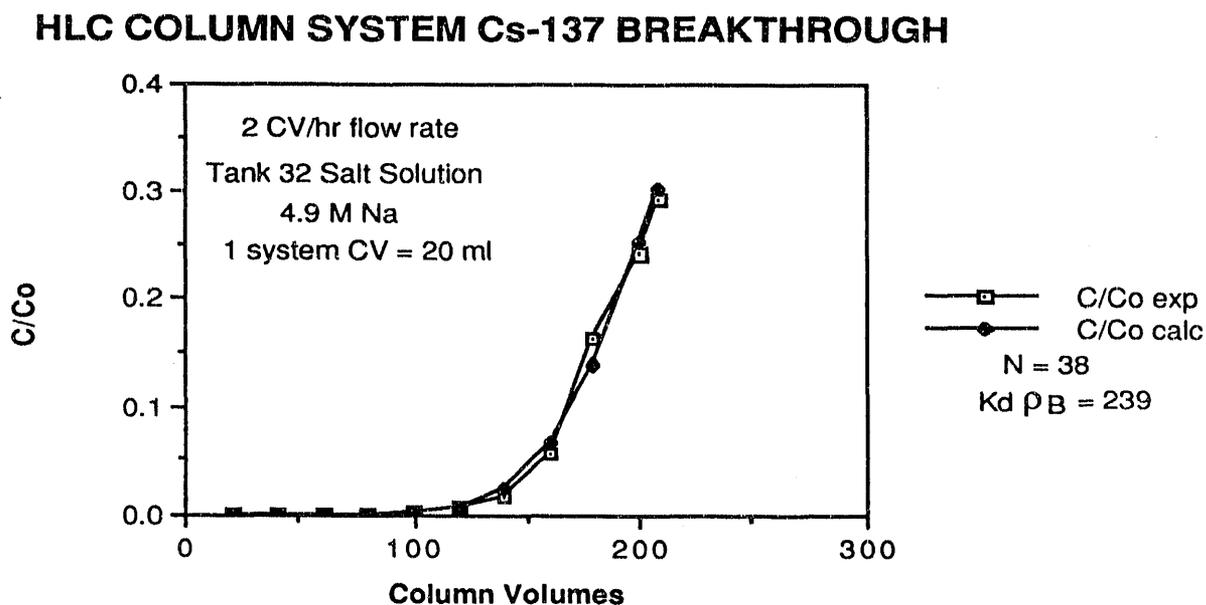


Column Test with Actual Supernate

Actual waste supernate was passed through two columns arranged in series, each of which contained 10 ml of resorcinol resin... The test was carried out in the HLC to provide shielding from the high concentrations of Cs-137 in the feed. The columns were arranged in series to simulate the manner in which they might be arranged in plant operation. The flow rate through the columns was 40 ml/hr (2 CV/hr for the whole system).

The results of the test are shown in Figure 2, where data are presented in the same manner as in the previous test. Values of N and $K_d \rho_B$ were found to be 38 and 239 respectively. The smaller value of N in this test relative to the N value determined in the laboratory test indicates that the mass transfer kinetics were somewhat slower in this case; this may have been caused by precipitation of aluminum hydroxide on the surface of the resin. The larger value of $K_d \rho_B$ in the present test is attributed to the slightly smaller sodium ion concentration in the actual feed than in the simulated feed.

Figure 1



Radiolytic Stability

Samples of resin were subjected to gamma radiation at levels up to $4.5 \text{ E}+08$ rad. Distribution coefficients were measured for samples of the irradiated resin with a solution containing 4.5 M NaNO_3 , 1.5 M NaOH , $2.0 \text{ E}-4$ M CsNO_3 , and a trace of Cs-137 . The results, given in Table 4, show no significant loss in capacity below $1 \text{ E}+07$ rad.

The maximum dose rate estimated for the fully loaded resin is $5.50\text{E}+5$ rad/hr. The dose rate was estimated assuming the liquid high level waste contained 6 Ci/gal of Cs-137 and that it was concentrated by a factor of 200 in the resin. It was further conservatively assumed that all of the radiation was absorbed by the resin and associated water. A column system using this resin could be designed such that a spent column would be changed before any significant radiolytic damage could occur. Long-term radiation effects on the resin for doses in a Co-60 source of up to $4.53 \text{ E}+8$

rad, or approximately two years' storage of spent resin in supernate, have been studied. Analyses of the simulated supernate solution above the irradiated resin and in the vapor space above the solution found no molecular organic products. Presumably, only soluble salts of organic materials are formed on radiolysis.

TABLE 4

THE CHANGE IN K_d WITH INCREASED RADIATION EXPOSURE

<u>DOSE, rad</u>	<u>K_d, ml/g</u>
0	3.46 E+3
2.0 E+6	2.17 E+3
8.6 E+6	2.78 E+3
1.4 E+7	7.38 E+2
2.4 E+7	4.68 E+2
1.4 E+8	6.81 E+1
4.5 E+8	1.15 E+1

MODES OF OPERATION WITH THE RESIN

Two modes of operation are being considered for decontamination of Savannah River Site (SRS) waste supernate with the resorcinol resin. The first method consists of discharging cesium loaded resin directly to the glass melter. The second method involves elution of the cesium from the resin with formic or nitric acid and discharging the eluate to the melter. In either case, the design would require three resin columns arranged in carousel fashion. The feed would enter the first column while the second and third columns would act as guard columns. When saturated, the first column is removed from the train and is either discharged or eluted. The second column then becomes the first, the third becomes the second, and the regenerated first column becomes the third.

Two questions arise concerning these procedures: (1) Will operation in this carousel fashion lead to adequate decontamination, when carried out over several cycles? and (2) If the elution mode is adopted, will continued elution seriously affect the resin behavior?

Column Tests at Pacific Northwest Laboratory (PNL)

A series of column tests was run at PNL to answer these questions. The tests were divided into two phases. Both Phase 1 and Phase 2 involved operation of a system for removing cesium from simulated SRS supernate containing ^{137}Cs tracer (Table 2).

Phase 1.- Carousel Configuration

The system consisted of three ion exchange columns A, B, and, C arranged in carousel configuration, and designed to be sequenced, as described in Table 5, during the completion of six loading tests.

Table 5.

COLUMN CONFIGURATIONS IN PNL TESTS; PHASE 1

<u>Test #</u>	<u>Column Sequence</u>
1	A, B, C
2	B, C, A
3	C, A, B
4	A, B, C
5	B, C, A
6	C, A, B

Three columns were connected in series. Each column contained 72 grams of 30-60 mesh resin prepared by Boulder Scientific Company (BSC). The resin received from BSC was treated with 2 M NaOH prior to loading and occupied 200 ml in each column. The columns were loaded downflow with simulated supernate, at 2 CV/hour. When the first column was loaded to about 50% cesium breakthrough at about 200 CV, the system was washed with 3 CV of 2 M NaOH followed by 6 CV of water. The sodium hydroxide was used to prevent precipitation of aluminum hydroxide. The first column was then detached and eluted with 5 to 15 CV of 1 M formic acid at flow rates between 0.5 and 2 CV/hr and reattached to the third position. Before loading again, 3 CV of 2 M NaOH was fed through the first column to prevent aluminum precipitation at the start of the next loading cycle. All operations were carried out at 35°C. During the loading cycles, samples were taken after each of the columns in the series.

Phase 2 - Single Column Configuration

At the end of Phase 1, each of the three columns had been loaded and eluted twice. No decrease in capacity was observed. To obtain additional information, Phase 2 was initiated using only column C which was loaded five additional times under the same conditions

outlined for Phase 1.

Results of PNL Column Tests

The breakthrough curve for the first column in all of the tests were fit to the J Function and values of the parameters N and $Kd\rho_B$ determined. Table 6 contains these values for both Phase 1 and Phase 2 tests together with values of the mass transfer coefficients, Ka , calculated from these parameters.

Table 6
PARAMETERS DERIVED FROM PNL TESTS

<u>Test #</u>	<u>Column</u>	<u>$Kd\rho_B$</u>	<u>N</u>	<u>Ka</u>
Phase 1				
1	A	261	4.68	0.036
2	B	208	18.2	0.175
3	C	194	312	3.22
4	A	233	365	3.13
5	B	238	744	6.25
6	C	236	664	5.63
Phase 2				
7	C	235	813	6.92
8	C	203	468	4.61
9	C	188	408	4.34
10	C	194	220	2.37
11	C	185	321	3.47

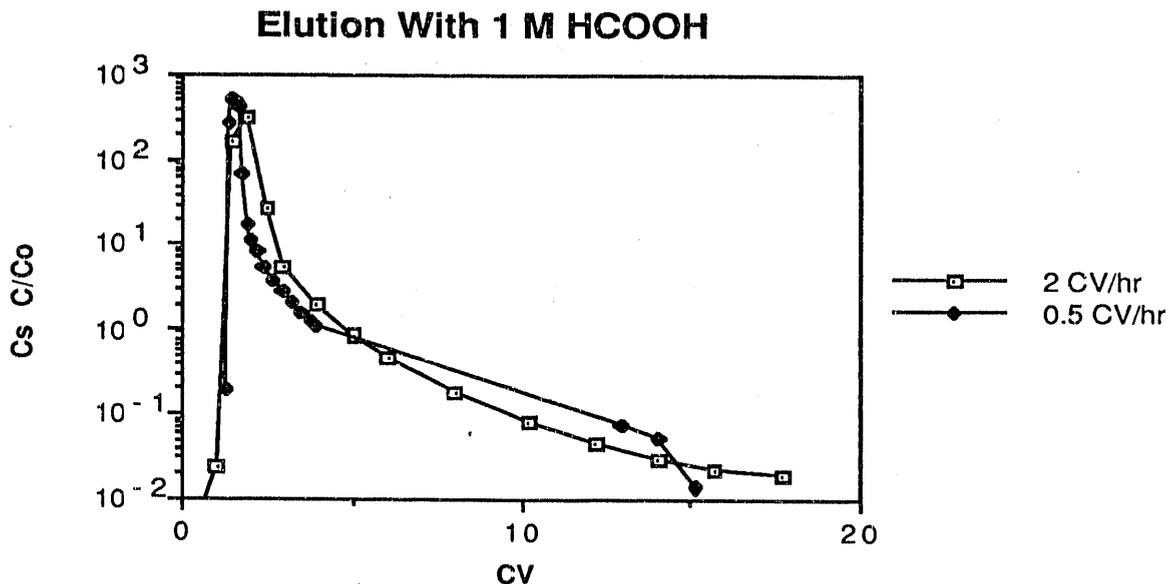
The first two Phase 1 tests were anomalous in that the kinetics were poor, as indicated by the small values of N and Ka . This was probably due to channelling in the resin beds. After that, the breakthrough curves were very sharp as shown by the large values of these parameters. Values of $Kd\rho_B$ were all near or above 200 in Phase 1 which shows that about 200 CV of feed can be processed initially in each cycle before discharge of the first column is necessary. The results from Phase 2 show that the resin does lose capacity on repeated elution. It is not known whether this is due to physical attrition or some chemical change in the resin. A minimum of six feed-elute cycles on one resin bed appears possible without recharging.

The activity of the effluent from the third column was at or near the detection limit in all tests of Phase 1. This made an exact cesium DF impossible to calculate but it can be approximated as $1.0 \text{ E}+4$. This is at least as good as the cesium DF ($4.4 \text{ E}+3$) demonstrated in the reference precipitation process.

Elution With 1 M FORMIC ACID

Approximately 99% of the cesium was eluted efficiently in about 10 CV of 1 M formic acid at 35°C and flow rates of 0.5 to 2 CV/Hr. The results, summarized in Figure 3, compare favorably with those obtained at SRL by downflow elution of a 2 mL. column with 1 M HCOOH.

Figure 3



Small column tests indicate that an equally efficient elution can be accomplished with the same number of column volumes (about 10) of 0.1 M HNO₃.

CONCLUSION

The resorcinol-formaldehyde ion exchange polymer developed at SRL is extremely selective for the cesium ion in SRS high-activity supernate. The cesium capacity of the resin is ten times that of any similar available resin and supports a throughput of about 200 column volumes of feed. Elution with about 10 column volumes of either 1 M formic acid or 0.1 M nitric acid removes 99% of the sorbed cesium, allowing the resin to be returned to service. After six feed-elute cycles have been completed, approximately 20% of the capacity of the resin is lost, requiring either partial reconstitution or replacement of the resin in the column. The resin can probably be used for other waste streams where cesium

decontamination is necessary.

REFERENCES

1. EBRA, M. A., WALLACE, R. M., WALKER, D. D. and WILLE, R. A., "Tailored Ion Exchange Resins for Combined Cesium and Strontium Removal from Soluble SRP High-Level Waste", The Scientific Basis for Nuclear Waste Management p 633 (1982), S. V. Topp, ed., Elsevier.
2. KACZVINSKY, J. Jr., FRITZ, J. S., WALKER, D. D., and EBRA, M. A., "Synthesis and Development of Porous Chelating Polymers for the Decontamination of Nuclear Waste", J. Radioanalytical and Nuclear Chem., Articles, 91/2, (1985) 349-360.

Slides

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Capacity: 2.85 milliequivalents per gram of air dried resin

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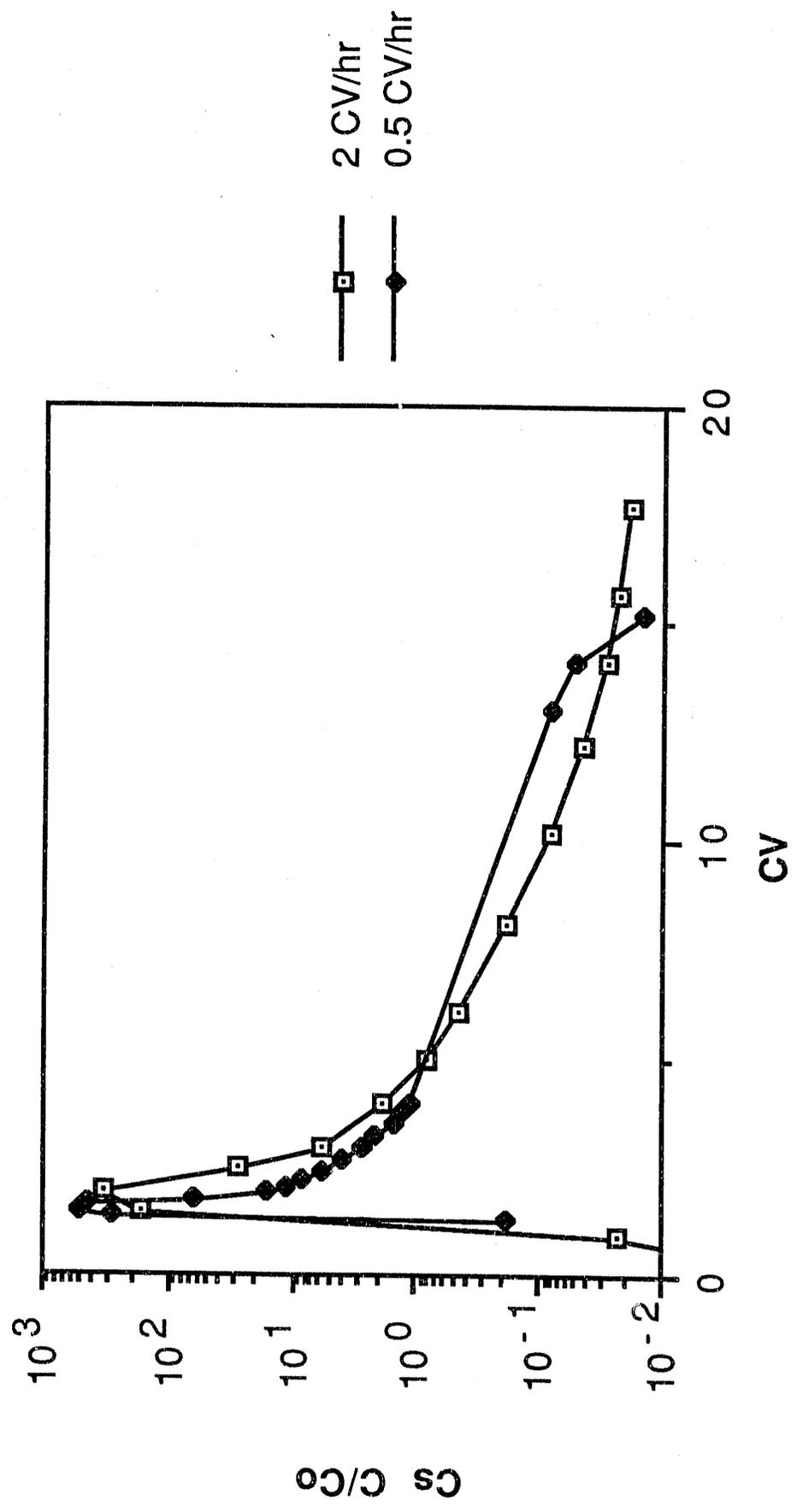
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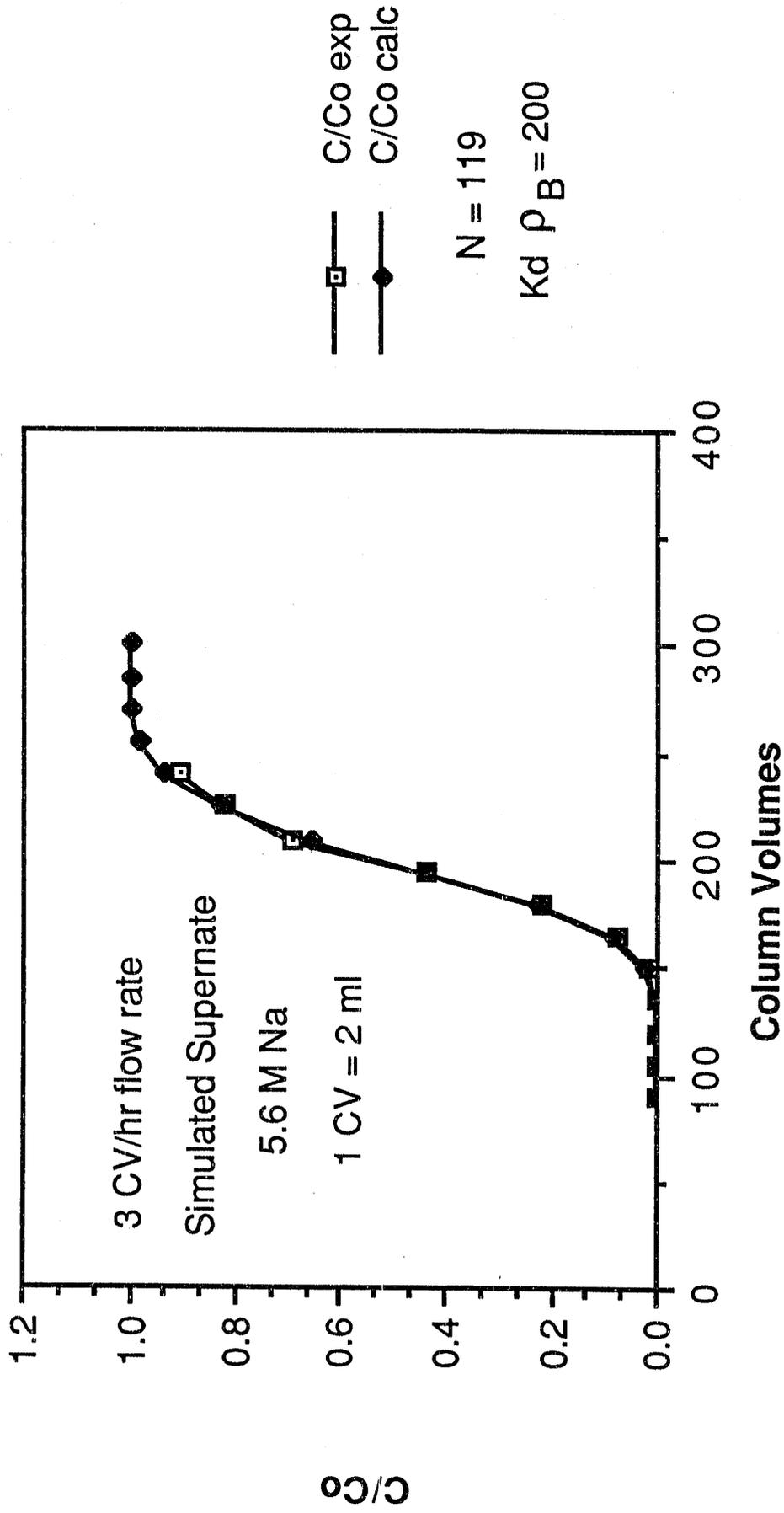
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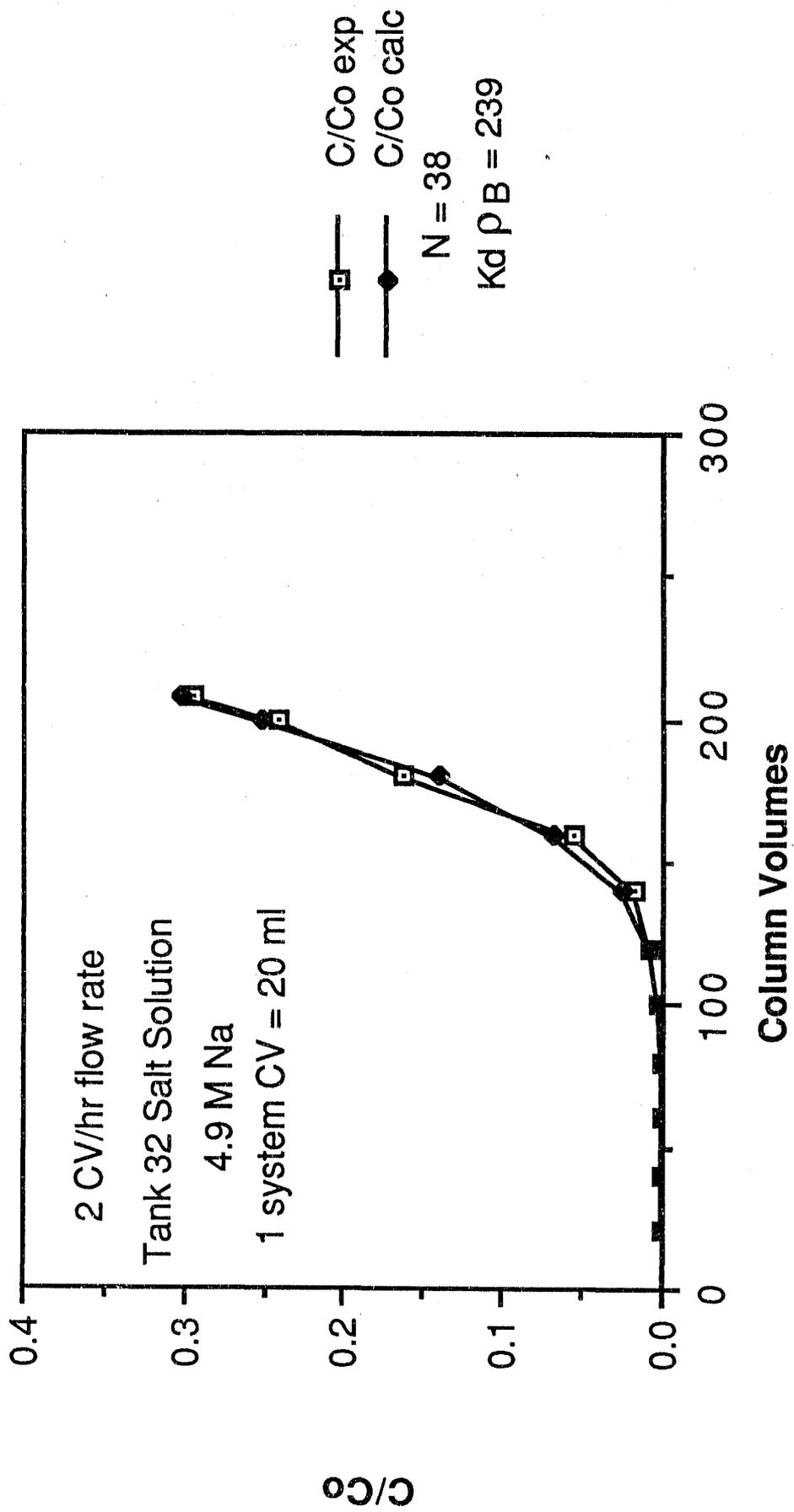
Elution With 1 M HCCOH



LABORATORY COLUMN SYSTEM CS-137 BREAKTHROUGH



HLC COLUMN SYSTEM Cs-137 BREAKTHROUGH



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