HW-71374

UC-70, Waste Disposal and Processing
(TID-4500, 16th Ed.)

QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
FIXATION OF RADIOACTIVE RESIDUES
JULY - SEPTEMBER, 1961

By

Members of the Staff
Chemical Research and Development
Hanford Laboratories Operation

Edited By

E. R. Irish

October 13, 1961

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Work performed under Contract No. AT(45-1)-1350 between the
Atomic Energy Commission and General Electric Company

Printed by/for the U. S. Atomic Energy Commission

Printed in USA. Price $1.00. Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

DISCLAIMER

TABLE OF CONTENTS

QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
FIXATION OF RADIOACTIVE RESIDUES
JULY-SEPTEMBER, 1961

INTRODUCTION

This progress report is the eleventh in a series presenting research and development activities in the field of fixation of radioactive wastes.

Research and development work continued in the study of pot calcination and radiant-heat spray calcination of synthetic Purex high-level wastes. A prototype radiant-heat spray calciner unit is being constructed for large-scale studies with nonradioactive solutions. Equipment is being fabricated and assembled for small-scale studies with actual Purex wastes in calciners to be located in the High-Level Radiochemistry Facility.

Sorption studies using natural minerals in waste fixation processes have been expanded to include synthetic minerals and resins. The place of various sorption phenomena in the over-all waste fixation process is being explored. In addition to providing a fixation technique for low-level wastes, sorption reactions may be utilized for treatment (e. g., recovery of heat-producing, long-lived radionuclides Cs^{137} and Sr^{90}) of high-level wastes prior to solidification or calcination of the bulk salts. Such a procedure may simplify management of the bulk salts and improve the form of Cs^{137} and Sr^{90} for fixation and possibly future use.

Some experimental work charged to programs other than those of the Division of Reactor Development is included for general interest and completeness; such work is identified in the headings.

The previous report in the series is HW-70517, April - June, 1961.

RESEARCH AND DEVELOPMENT PROGRESS

A. CALCINATION STUDIES (R. L. Moore, A. M. Platt)

Batch calcination studies with simulated Purex high-level waste solutions were continued. The items investigated included solution foaming and internal pressurization. A heated thermocouple was tested for potential use as a liquid-level detection element.

A prototype radiant-heat spray calciner or flame denitration unit is being constructed for large-scale studies with nonradioactive solutions.

Design and construction of the calciners for the High-Level Radiochemistry Facility are proceeding on schedule. Most of the equipment to be used has been built. As soon as all components are available, the calciner will be assembled in a "cold" area and thoroughly tested with operations being conducted through a "dummy" wall with spare manipulators. Plans for installation in A-Cell are targeted for March, 1962.

Batch Calcination

(J. J. Shefcik)

(Not charged to Division of Reactor Development)

Solution foaming, internal pressurization and liquid-level control were the major items investigated during recent studies of the batch calcination of simulated Purex high-level wastes. The pot sizes ranged from 4 inches in diameter and 15 inches high to 8 inches in diameter and 5-1/2 feet high.

The behavior of a simulated Purex high-acid (6.2$\underline{M}$ HNO_3) waste during batch calcination was the objective of one study. The annular calciner pot used was fabricated from 6-inch and 3-inch pipe and was 15 inches high. Extensive foaming occurred during the boil-down step, and a reduction in power input was necessary to prevent boil-over. An air sparge was partially effective in reducing the foaming problem.

The effect of two specific chemical compounds on foaming was investigated. Lead acetate and sodium acetate were individually added in two runs to simulated **Purex** low-acid (0.5$\underline{M}$ HNO_3) waste solution that had previously demonstrated little tendency to foam. The presence of either acetate salt did not cause foaming or affect calcination.

As reported previously,(1, 2) internal pressures can develop within the solids during the calcination step if only partial calcine melting occurs and if the sulfate molarity in the waste solution is in excess of the stoichiometric sodium equivalent. In a recent study internal pressurization occurred in a 4-inch diameter by 15-inch high pot. The waste solution used met the above criteria. A 2-inch thick layer of solids rose approximately 6 inches to the top of the pot. Later inspection revealed a 7-inch long void between two layers of solids. A run with the same waste in a 6-inch diameter by 15-inch high annular pot failed to give any indication of internal pressurization. This was a rerun of a previously reported(2) study, and the results of the two runs were similar. Evidently, the geometry of the calcination vessel has an effect on the generation of internal pressures during the calcination step.

A pilot plant run was made using a pot 8 inches in diameter and 5-1/2 feet high. A 16-inch diameter by 2-foot high disengaging section surmounted the pot and extended out of the furnace. A translucent lid permitted visual inspection. Feed addition to the unit was continued until nitrate decomposition gases obscured vision. The furnace temperature was maintained at 500 C. Observations made during the run include:

1. The boil-off rate was a uniform 1.9 l/(hr)(sq ft of heated surface).

---

(1) Pearce, D. W. Quarterly Progress Report - Research and Development Activities - Fixation of Radioactive Residues, October - December, 1960. HW-68193. January 15, 1961.

(2) Irish, E. R. Quarterly Progress Report - Research and Development Activities - Fixation of Radioactive Residues, April - June, 1961. HW-70517. July 15, 1961.

2. Splashing and bumping became worse as the run progressed and the liquid increased in solids content. The pot wall 1 to 1-1/2 feet above the liquid level became coated with a 1-inch thick layer of solids. Some of the liquid splashed up to the lid which was 3 to 3-1/2 feet above the liquid.
3. After the liquid was siphoned from the pot, a continuous 1/2-inch thick coating of solids was observed on the pot wall below the operating liquid level.
4. There was an 8- to 10-inch layer of solids on the bottom of the pot. Most of these solids were fine crystals.

A reliable and practical means of detecting the liquid level and/or foam in a calciner pot during the boil-down step is required for plant application of the batch calcination technique. The standard air-purged dip tube became plugged with solids and required frequent clean out during the boil-down step; a steam bleed reduced the plugging frequency but may still not be adequate to prevent it. Conductivity probes proved to be unsuccessful because bumping and splashing of the boiling liquid coated the probes with salts and thus provided an electrical short circuit. The temperature differential between the boiling liquid and the vapor can be used as a basis for a liquid-level control system. However, such a system requires a relatively large number of temperature detection elements and is, therefore, costly and not readily adaptable to a remotely-maintained installation.

A liquid-level detection device which operates on the principle that the heat dissipation rate from a heated element to a liquid is greater than that to a vapor was designed and fabricated. This liquid-level probe is a stainless steel-sheathed thermocouple heated by an alternating current flowing through the thermocouple wire. The thermocouple d-c millivolt output is greater when the probe is in the vapor than when it is submerged in the liquid. The probe was used in the previously described pilot plant run with an 8-inch diameter by 5-1/2-foot high pot.

During the early stages of the feed addition step, the probe functioned satisfactorily although splashing of the boiling solution caused the probe to react as if it were submerged in the liquid. Positioning of the probe 6 to 8 inches above the liquid level was necessary to overcome this effect. As the run progressed, splashing of the liquid deposited solids along the length of the probe. As a result the probe sensitivity decreased markedly. Shortening the thermocouple or pointing the junction up rather than down may reduce or eliminate the problem of solids deposition.

Melting of Pot Calcination Products

(G. B. Barton)

Investigation of Phosphate Addition to Purex-Type Wastes

The work described in the last Quarterly Report(1) was completed. The only significant additional information learned was that an excess of sulfuric acid in a mixed phosphate-borate system leads to difficulties with foaming of the melt at temperatures in the neighborhood of 800 C. Apparently, this foaming is due to the sulfate being decomposed in a viscous melt; unless this is done slowly (by gradual temperature change), the melt will foam excessively.

A few qualitative experiments on crucible materials indicated silicon nitride to be very promising. A magnesia-titania crucible was also resistant to attack by the melt but did not have sufficient thermal shock resistance.

Glasses Containing High Concentrations of Strontium and Cesium

One more type of strontium-containing glass was examined. This was based on beryllium fluoride as the glass former. Two compositions were melted, containing 67 and 50 per cent strontium fluoride with the balance being a mixture of beryllium fluoride and aluminum fluoride. The higher strontium fluoride content mixture melted below 900 C to give a glass that

---

(1) Ibid.

partially crystallized on cooling. The other mixture melted below 925 C, but, when poured, it crystallized and fractured badly. The glass had a density of 3.1 g/ml. About 2 per cent dissolved in the four-hour boiling-water test. This type of material might be of interest as a low-melting, moderately insoluble glass of medium strontium content (1.45 g/ml).

A few additional experiments on the cesium-aluminum phosphate system indicated that the solubility could be reduced considerably by the presence of lanthanum or zirconium to the extent of 5 mole per cent. (The melt contained 40 per cent cesium.). This gave a meltable system that appeared like an opaque white glass. The solubility was about 0.6 per cent on the first four-hour boiling-water test period but increased to 2 per cent in the next test period.

Spray Calcination

(H. T. Blaine, R. T. Allemann)

(In part charged to Division of Reactor Development)

Cold Semi-Works Spray Calciner

Construction of the prototype spray calciner is underway. The 18-inch diameter, 10-foot long reactor will have a nominal capacity of 20 gallons of simulated waste per hour.

During the initial phases of the experimental program, the unit will be operated to study techniques for waste fixation by both radiant-wall heating and flame heating. A second phase test program will determine scale-up factors for the calciner.

High-Level Radiochemistry Facility Equipment(1)

Much of the equipment which will be used for the in-cell calciners has been built. The melt pots and their covers and the spray calciner are on hand. The insulation cans for the spray calciner are being made, and

---

(1) Ibid.

the calciner should be cold-tested during the next quarter. A surplus induction heater motor-generator will be used to heat the melt pots. Coaxial cable will be used to transmit the energy from the generator through the cell wall. Cell height limitations will require that the spray calciner be moved vertically in order to change spray nozzles. Therefore, the column-supporting framework is to be set on jacks. Also, a relatively short manipulator is required for nozzle changing, but an on-hand Model-8 manipulator can be modified to do the job. As soon as all components of the calciner are available, it will be assembled in a "cold" area and thoroughly tested with synthetic feed (all operations being conducted with a spare pair of manipulators through a "dummy" wall) prior to moving into the High-Level Cell. Exact date of installation in A-Cell of the High-Level Radiochemistry Facility is dependent on successful cold testing and completion of present in-cell programs and cell decontamination, but plans are targeted for March, 1962.

Off-Gas Treatment

(R. T. Allemann, G. B. Barton)

Scrubber and Filter Tests

The proposed method of sampling the off-gases from the in-cell calciners is to use membrane filters in disposable plastic holders. After the radioactivity on the filters is counted with an in-cell gamma spectrometer, the filters can be thrown away or removed from the cell for further analysis. Use of the plastic holder will greatly simplify filter handling with manipulators. A series of runs in the 8-inch (cold) demonstration unit were accordingly made to prove the effectiveness of this sampling scheme for the very small particles which pass through the off-gas clean-up system associated with the calciner.

Much of the previous off-gas clean-up experimentation was done with membrane filters as off-gas samplers, and further tests showed their use to be the best method. Most of the powders produced in the spray calciner have a surface-area mean particle diameter of 2 - 5 microns. However, there are smaller particles which pass through the primary filter and the condenser. Their total mass is very small since decontamination factors (DF's) of 10^5 were measured between the feed and off-gas coming from the condenser. Several methods of off-gas sampling were tried (including a thermal precipitator and cascade impactors), but none appears to be as simple or as accurate as the membrane filter.

Electron photomicrographs (Figure 1a and 1b) of the powder caught on a membrane filter show the extremely small size of particles passed through the condenser. The particles range from 0.01 to 0.1 micron. However, membrane filters are available which collect 99 per cent of 0.01 micron particles. The sphericity of the particles in Figure 1a and 1b is believed to result from high relative humidity in the condenser, causing some particle dissolution with a tendency to round off particle corners. The rounding-off could also result from traces of moisture in the acetone used to dissolve the membrane filter during preparation of the electron microscope screen. The tendency of some particles to agglomerate on the microscope screen, and a very small (< 1 per cent) weight loss of powder in acetone, is evidence of the latter effect.

Off-gas clean-up experiments utilized the 8-inch spray calciner as a dust generator. A run was made in which steam was added to off-gas from the condenser and condensation carried out a second time. This gave an additional DF of about two. This improvement is about the same as with an impingement plate scrubber on a Raschig-ring packed scrubber of the same length.(1) Further tests are being made with new models of the electrostatic bubble scrubber.(1)

Removal of Ruthenium Tetroxide from Gas Streams

Studies were continued to determine the effect of elevated temperatures on the removal of ruthenium tetroxide from a gas stream by a

---

(1) Ibid.

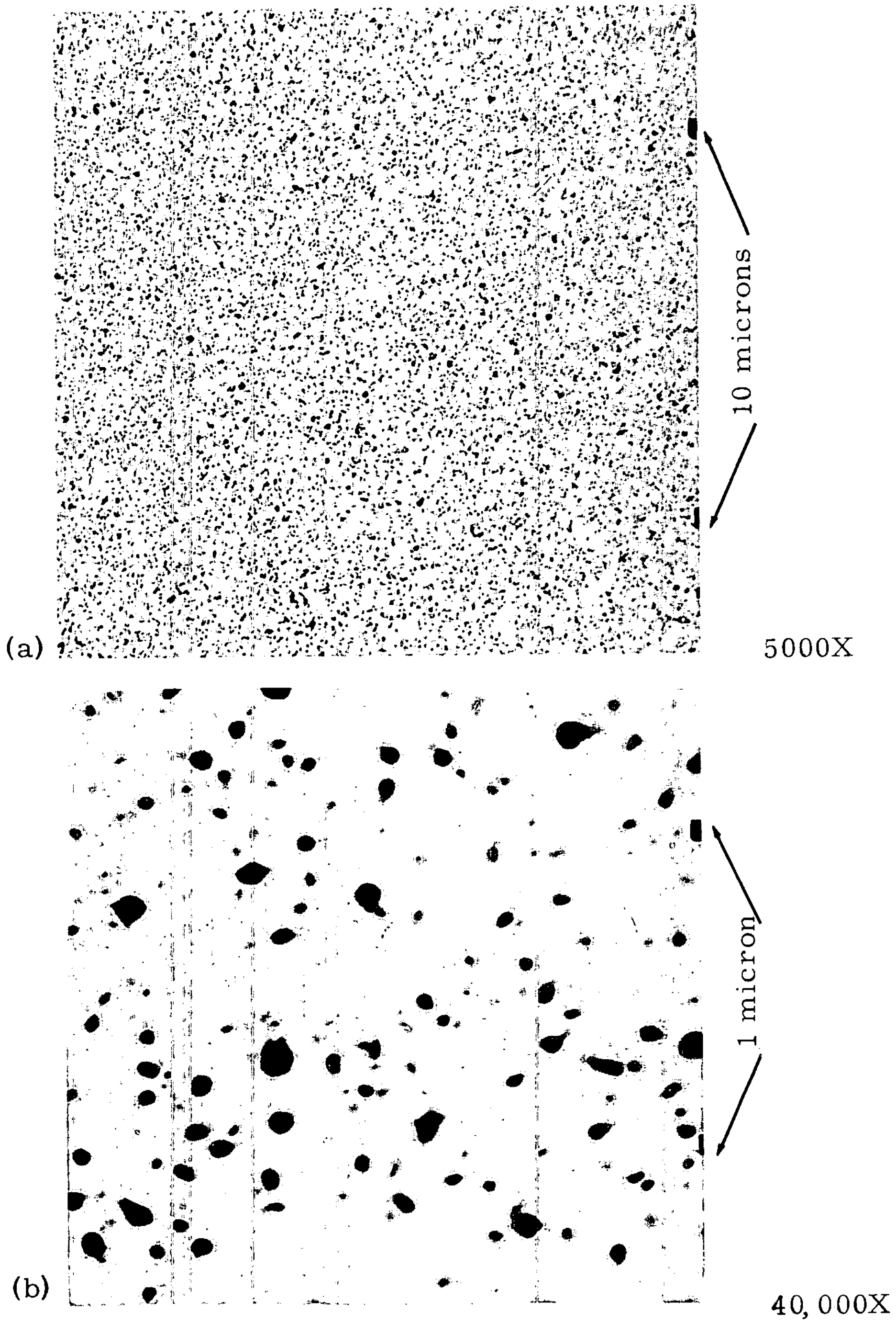

FIGURE 1

Dust Removed from Off-Gases of Spray Calciner
Processing Simulated Purex Waste
(Subsequent to Primary Filtration and Condensation)

silica gel bed. In short term tests no measurable effect was observed when the temperature of the silica gel was varied from 25 to 80 C. The measured decontamination factors were greater than 10^4, higher than some previously reported.(1) The silica gel was not as intensely colored by the ruthenium tetroxide at the higher temperatures; perhaps an extended test would show lower decontamination factors or reduced capacity.

Measurements were also made at various gas temperatures up to 156 C with the silica gel bed being held at room temperature. The primary objective of these measurements was to see if ruthenium decontamination would be adversely affected by holding the ruthenium-containing gases at elevated temperatures for a period of time before passing them through the silica gel bed. The amounts of ruthenium passing the bed and collected in the downstream caustic scrubber were very small (30 - 100 c/m out of approximately 10^6 c/m in the gaseous feed), so the analytical uncertainty is large. However, if the data are correct, an increase in decontamination by the system was indicated as the inlet gas chamber temperature was raised from 80 to 156 C. This effect is attributed to the deposition of ruthenium (possibly as the dioxide) on the walls of the heated glass chamber prior to passage through the silica gel.

Experiments were then made so that the ruthenium tetroxide-air stream was passed through the heated chamber and directly to the downstream absorber, by-passing the silica gel bed. The amounts of ruthenium collected in the absorber and apparently deposited in the chamber are indicated in Table I, the data listed in order of consecutive experiments.

The extent of deposition on the chamber walls is shown in Figure 2. It is evident that the bulk of the deposition occurs near the inlet to the chamber. Close visual inspection fails to show any deposit on the exit half of the chamber. Apparently, the decomposition occurs on the ruthenium oxide surface and continues to build up there. The variable results listed in Table I are interpreted as arising from the build-up of this surface. This

---

(1) Ibid.

TABLE I

DEPOSITION OF RUTHENIUM FROM THE GAS STREAM BY PASSAGE THROUGH A HEATED GLASS CHAMBER

(Residence Time - 30 Minutes)

Chamber Temperature, C	Per Cent Ruthenium Collected in Absorber	Apparent Per Cent Ruthenium Deposited
150	80-85	15-20
143-161	80	20
147	6	94
152-155	75-96	4-25
188-196	1.3	>98
170	0.7	>99
155	0.45	> 99

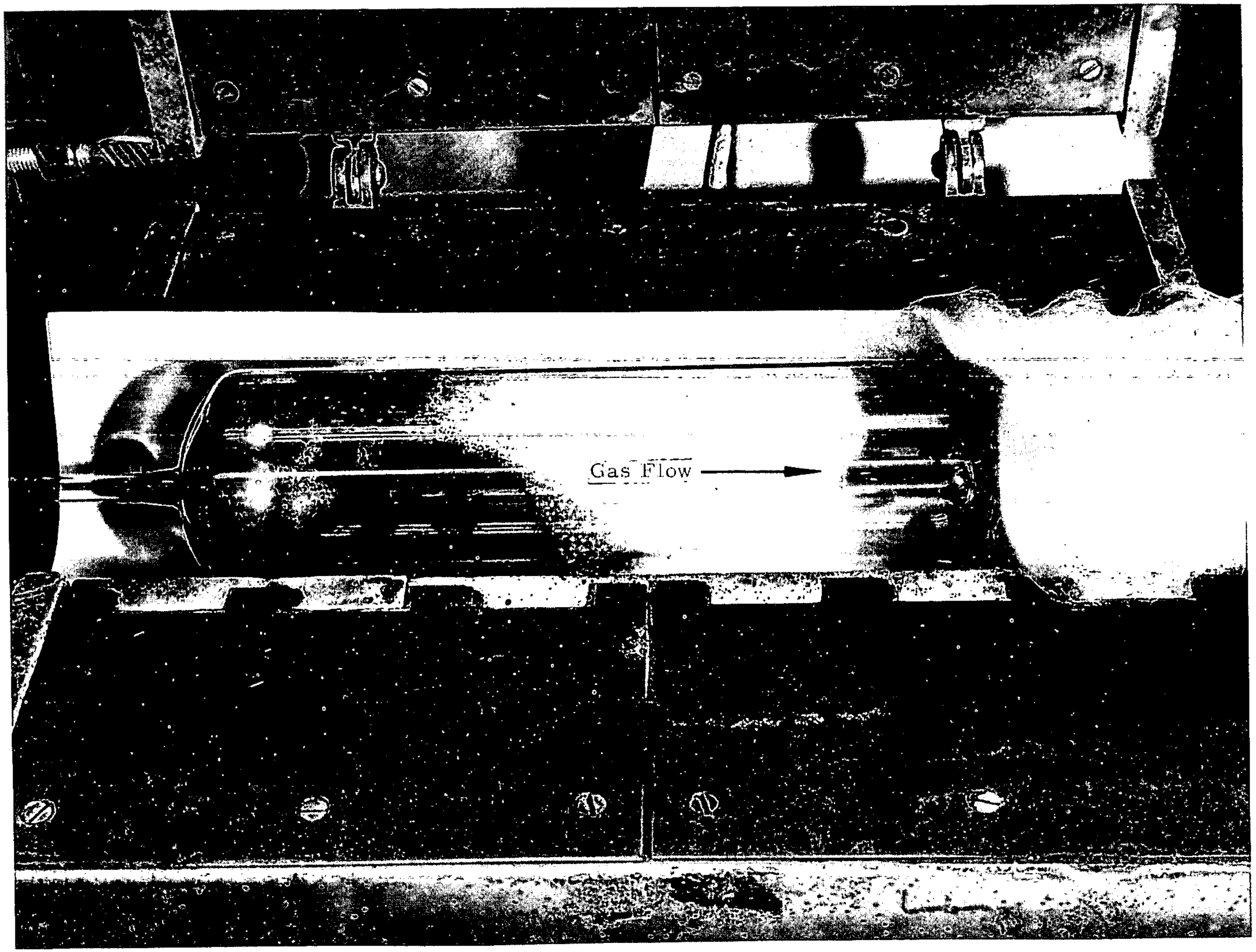

FIGURE 2

Deposition of Ruthenium Dioxide
on the Walls of a Heated Glass Chamber

is in agreement with the results reported by investigators at Vitro Laboratories(1) who report that ruthenium dioxide reduces or eliminates the induction period for decomposition of ruthenium tetroxide.

An additional observation that may be of significance was that the ruthenium compounds deposited on the glass surfaces at low temperatures readily dissolved in sodium hypochlorite, whereas, those deposited at the higher temperatures were nearly insoluble. This implies clean-up of equipment and piping may be difficult.

Measurements were also made on the vapor pressure of ruthenium tetroxide over 6M sulfuric acid up to a concentration of 0.05M. This information is needed because the dilute ruthenium tetroxide streams used in the above studies are prepared by volatilization from 6M sulfuric acid containing periodic acid. The method used was not precise enough to eliminate considerable scatter in the data; however, a linear variation was observed, indicating ideal behavior up to at least 0.05M. New apparatus was assembled to make more precise measurements.

B. SORPTION STUDIES (J. F. Honstead, C. E. Linderoth)

A statistical design to minimize experimental requirements for chemical research involving multiple variables was utilized for obtaining data in mineral research. For correlation of these data a quadratic expression was found more representative than a linear regression equation. The column residence time variable was probably responsible for the poor correlation of the data by the linear regression equation. Thorough studies of the influence of sodium concentration on the cesium capacity of zeolites confirmed the selectivity data obtained in statistically-designed experiments.

Laboratory research was continued in studies of Hanford high-level neutralized waste. In particular, the application of Duolite C-3 (a sulfonated

---

(1) Ortner, M. H., C. J. Anderson and P. F. Campbell. Research and Development Studies on Waste Storage Process, V-2138-13-0. August 31, 1959.

phenol resin) for removing radioisotopes from the high-sodium waste appears interesting. An experiment with a column of the resin was conducted in a High-Level Cell with actual Purex waste. Supporting experiments in the laboratory indicate the desirability for a higher caustic concentration in the wastes used in future experiments. The influence of temperature and resin grain size was also evaluated in small-scale laboratory columns.

The removal of radiocerium from condensate wastes by adsorption was found to be much more effective at pH 3 than at pH 9. This is ascribed to the formation of a colloidal precipitate at the higher pH. A sulfonated polystyrene resin appeared to have a higher capacity for adsorbing radiocerium than did clinoptilolite. Experiments with dilute nitric acid solutions indicated that beds of clinoptilolite and sulfonated polystyrene resin in series can satisfactorily decontaminate such waste solutions with respect to cesium, strontium, and cerium.

In the Micro Pilot Plant, extended experiments were continued to study the application of laboratory findings to the decontamination of fuel processing plant condensate streams. A pretreatment operation to remove organic and ammonia by steam stripping was successfully carried out over a period of 3000 hours. Ruthenium continues to be the major radiocontaminant which is not effectively removed by any of the adsorbent materials tested.

Mineral Reactions

(L. L. Ames, K. C. Knoll)

(In part charged to Division of Reactor Development)

Laboratory work was continued on the problem of strontium removal from wastes by adsorption on natural and synthetic zeolites. A method was studied for evaluating adsorption performance from the C/C_0 value attained at a fixed throughput through a column. Attempts to fit these C/C_0 values to a linear regression equation were only modestly successful. A better fit was obtained when a quadratic relationship was assumed. A multiple correlation coefficient of 0.87 was obtained for the linear equation and 0.97

for the quadratic equation. To clarify the relationship between column residence time and column capacity (meq Sr^{+2}/100g zeolite), complete breakthrough curves were measured for several experimental systems, as shown in Figure 3. These results pointed to column residence time as the factor responsible for the poor correlation of the data by a linear regression equation. The statistical technique remains as an excellent means of ascertaining and defining the adsorption selectivities and capacities of zeolites.

Experiments were conducted to confirm selectivity data obtained from a statistically designed research program that indicated the superiority of clinoptilolite for cesium adsorption. The effect of increasing sodium concentration on the cesium adsorption capacities of clinoptilolite, Linde 4A (a Type A zeolite) and Decalso (a silica gel; SiO_2/Al_2O_3: 6/1) were investigated. As shown in Figure 4, the cesium capacity of Linde 4A is limited, even with no competing sodium present. Figure 5 compares the cesium capacity of a column of clinoptilolite with that of Decalso with increasing concentrations of sodium in the influent. The cesium capacity of Decalso is initially greater than that of clinoptilolite, but rapidly diminishes in the presence of increasing sodium concentration.

Analysis of the strontium selectivity data indicated that Linde 4A was the most strontium-selective of the zeolites tested. The effect of competing sodium and calcium on the strontium capacities (as determined by the 50 per cent column breakthrough volume) of clinoptilolite, Decalso, and Linde 4A are given in Figures 6 and 7. At neutral to alkaline pH, Linde 4A was the most strontium-selective zeolite, as was also indicated by the statistical studies. However, acidic conditions cause the physical deterioration of Linde 4A and Decalso as is shown in Figure 8. Clinoptilolite showed the greatest acid resistivity, and hence, the greatest strontium capacity of these three zeolites at low pH.

Influent solution - 0.008$\underline{N}$ Sr^{+2}, 120,000 Sr^{85} d/m/ml, 0.1$\underline{N}$ $Mg(C_2H_3O_2)_2$
Influent pH - 7.0
Temperature - 25 C
Column - 10 g of 1.0 to 0.25 mm, Na-based Decalso and clinoptilolite; 1/16-inch, Na-based, pelletized Linde 4A
Flow rate - 285 ml/hr and 57 ml/hr
Column residence time - as indicated

Curve Designation	Zeolite	Residence Time, min	Strontium Capacity, meq/100 g
a	Clinoptilolite	1.01	58.4
a'	Clinoptilolite	5.05	58.4
b	Decalso	1.05	128.0
b'	Decalso	5.25	128.0
c	Linde 4A	1.18	72.7
c'	Linde 4A	5.90	72.7

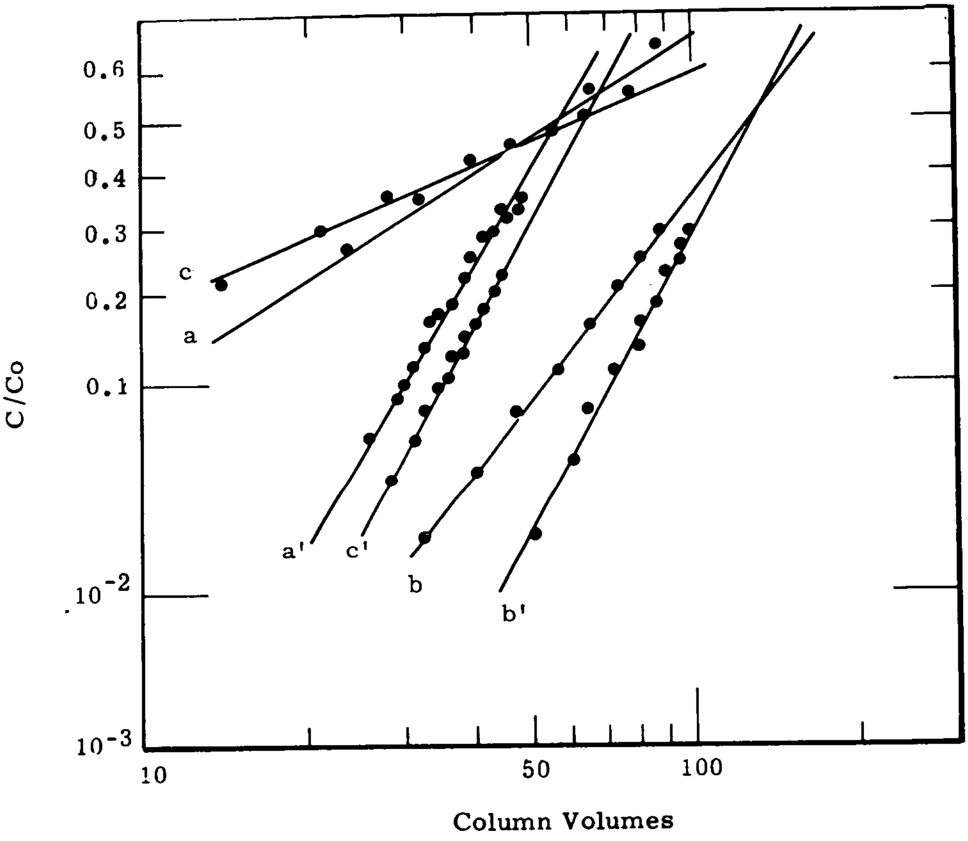

FIGURE 3

Effect of Column Residence Time on the Slope of Sr^{+2} Breakthrough Curves of Clinoptilolite, Decalso and Linde 4A (Error Function C/C_o vs Log Column Volumes)

Influent solution - 0.01$\underline{N}$ CsCl, 100,000 Cs^{137} d/m/ml
Influent pH - 6.6
Temperature - 25 C
Column - 10g of 1.0 to 0.25 mm, Na-based Decalso and clinoptilolite; 1/16-inch, Na-based, pelletized Linde 4A
Column flow rate - 835 ml/hr

Curve Designation	Zeolite	Column Residence Time, min	Cesium Capacity, meq/100g
a	Clinoptilolite	0.37	135.2
b	Decalso	0.36	250.0
c	Linde 4A	0.39	49.7

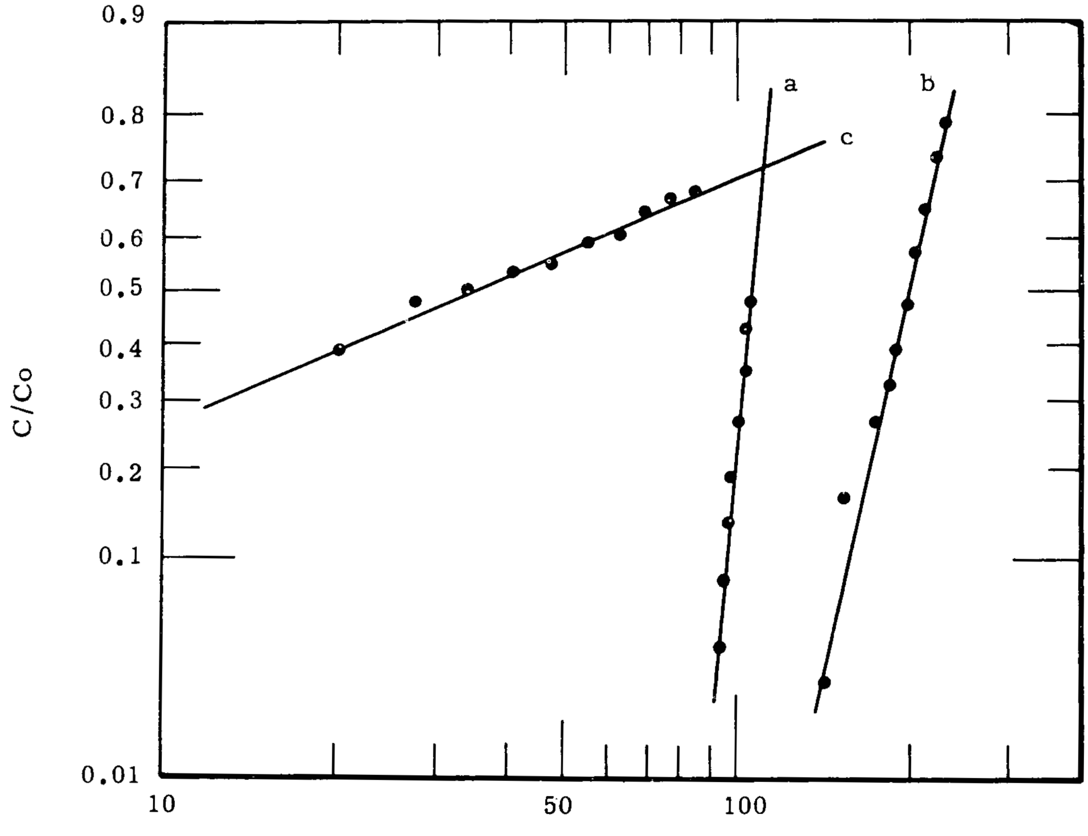

FIGURE 4

Comparative Cesium Capacities of Clinoptilolite, Decalso and Linde 4A in the Absence of Competing Cations (Error Function C/C_o vs Log Column Volumes)

Influent solution - 0.01N CsCl, 100,000 Cs^{137} d/m/ml, Na^+ as indicated
Influent pH - 6.0
Temperature - 25 C
Column - 10g, 1.0 to 0.25 mm, Na-based zeolite
Column flow rate - 835 ml/hr
Column residence time - Decalso, 0.36 min and clinoptilolite, 0.37 min

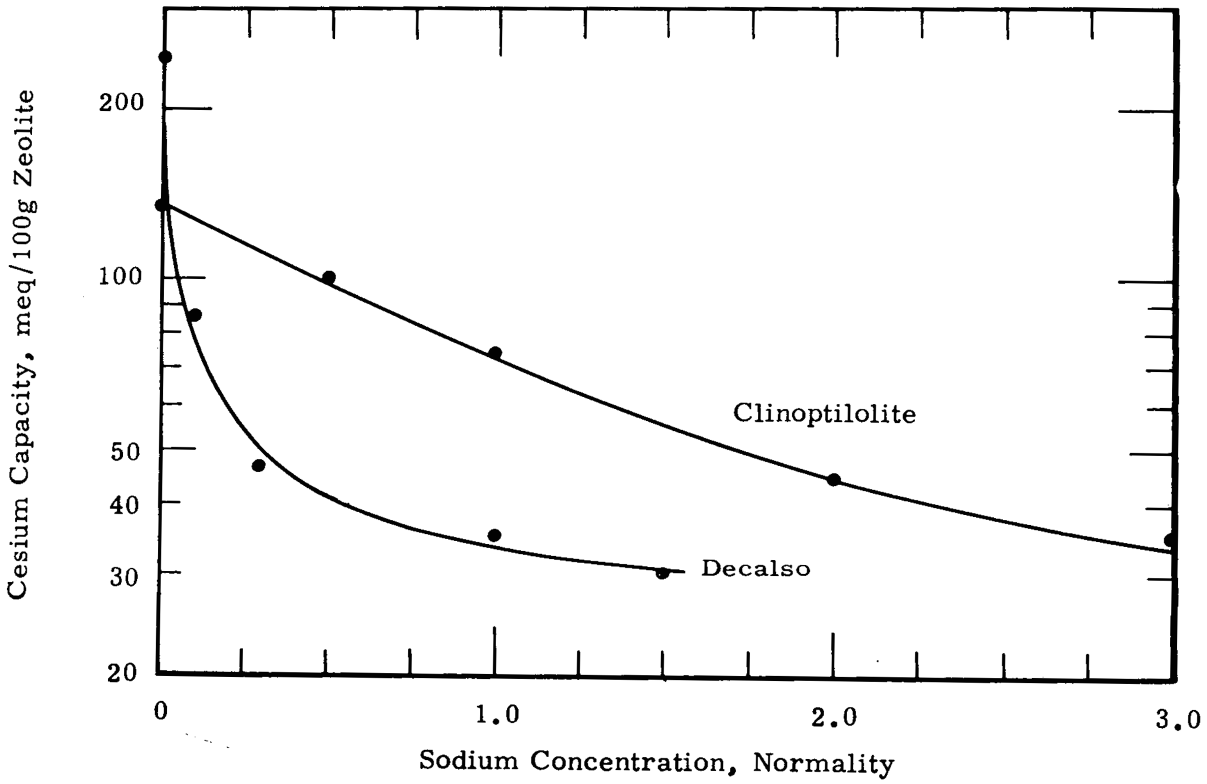

FIGURE 5

Effect of Competing Na^+ on the Cs^+ Capacity of Clinoptilolite and Decalso

Influent solution - 1.0$\underline{N}$ Na^+, 0.008$\underline{N}$ Sr^{+2}, 120,000 Sr^{85} d/m/ml, 0.1$\underline{N}$ $Mg(C_2H_3O_2)_2$
Influent pH - 7.0
Temperature - 25 C
Column - 10g of 1.0 to 0.25 mm, Na-based Decalso and clinoptilolite; 1/16-inch, Na-based, pelletized Linde 4A
Flow rate - 285 ml/hr
Column residence time - same as lesser values given in Figure 3

Curve Designation	Zeolite	Sr^{+2} Capacity meq/100g	Index of Strontium Selectivity
a	Clinoptilolite	0.03	0.001
b	Decalso	1.71	0.013
c	Linde 4A	12.50	0.172

The breakthrough curves of Figures 6, 7, and 8 are directly comparable to their shorter residence-time counterparts in Figure 3. Strontium selectivity indices were calculated by dividing the strontium capacity in meq/100g zeolite for the systems containing the competing cation by the strontium capacity of the same systems without competing cations present.

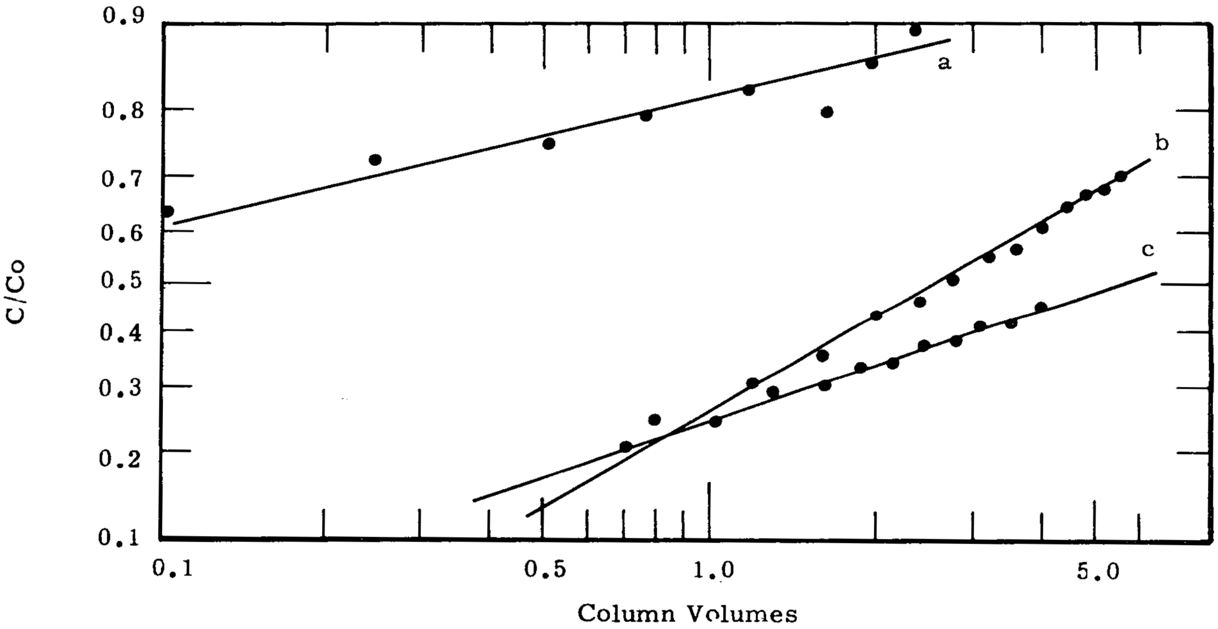

FIGURE 6

Effect of Competing Na^+ on the Sr^{+2} Capacity of Clinoptilolite, Decalso, and Linde 4A (Error Function C/C_o vs Log Column Volumes)

Influent solution - 0.4N Ca^{+2}, 0.008N Sr^{+2}, 120,000 Sr^{85} d/m/ml, 0.1N $Mg(C_2H_3O_2)_2$
Influent pH - 7.0
Temperature - 25 C
Column - 10g of 1.0 to 0.25 mm, Na-based Decalso and clinoptilolite; 1/16-inch, Na-based, pelletized Linde 4A
Flow rate - 285 ml/hr
Column residence time - same as lesser values given in Figure 3

Curve Designation	Zeolite	Sr^{+2} Capacity, meq/100g	Index of Strontium Selectivity
a	Clinoptilolite	1.7	0.029
b	Decalso	8.0	0.063
c	Linde 4A	7.2	0.099

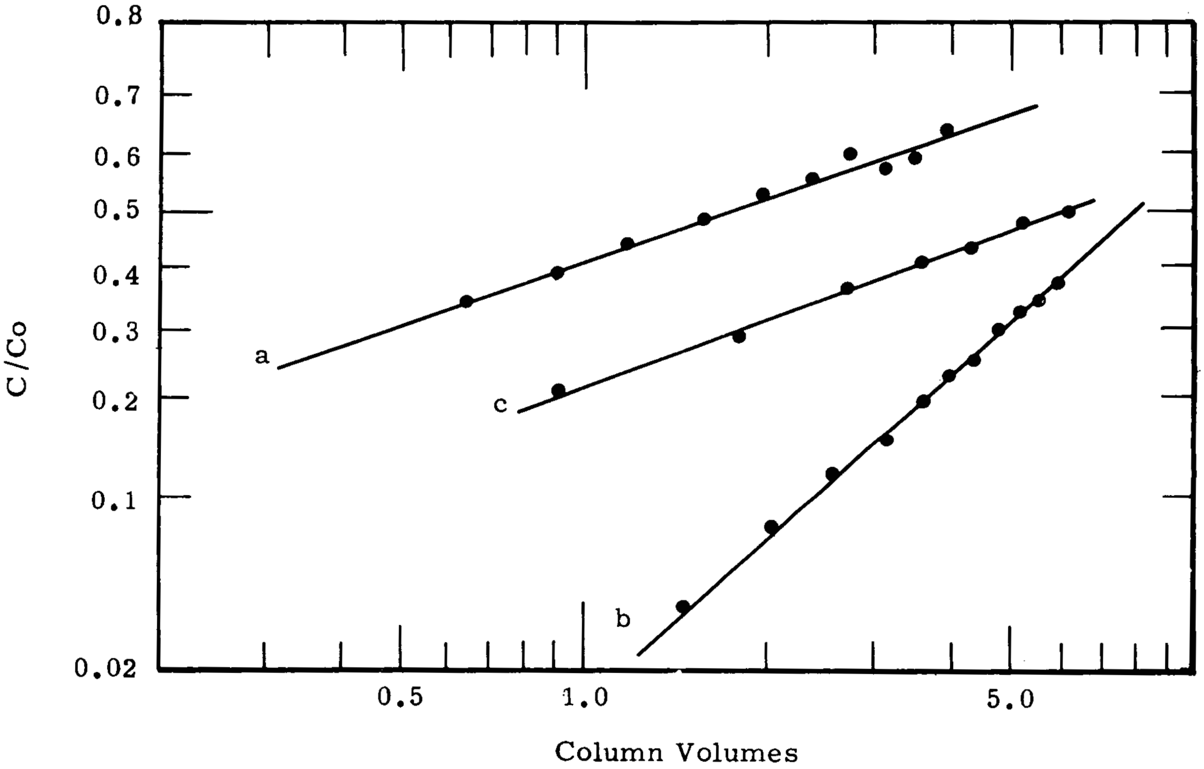

FIGURE 7

Effect of Competing Ca^{+2} on the Sr^{+2} Capacity of Clinoptilolite, Decalso, and Linde 4A (Error Function C/C_o vs Log Column Volumes)

Influent solution - 0.008N Sr^{+2}, 120,000 Sr^{85} d/m/ml, 0.1N CH_3COOH
Influent pH - 3.0
Temperature - 25 C
Column - 10g of 1.0 to 0.25 mm, Na-based Decalso and clinoptilolite
Flow rate - 57 ml/hr
Column residence time - same as lesser values given in Figure 3

Curve Designation	Zeolite	Strontium Capacity, meq/100g	Index of Strontium Selectivity
a	Clinoptilolite	55.3	0.947
b	Decalso	16.0	0.125

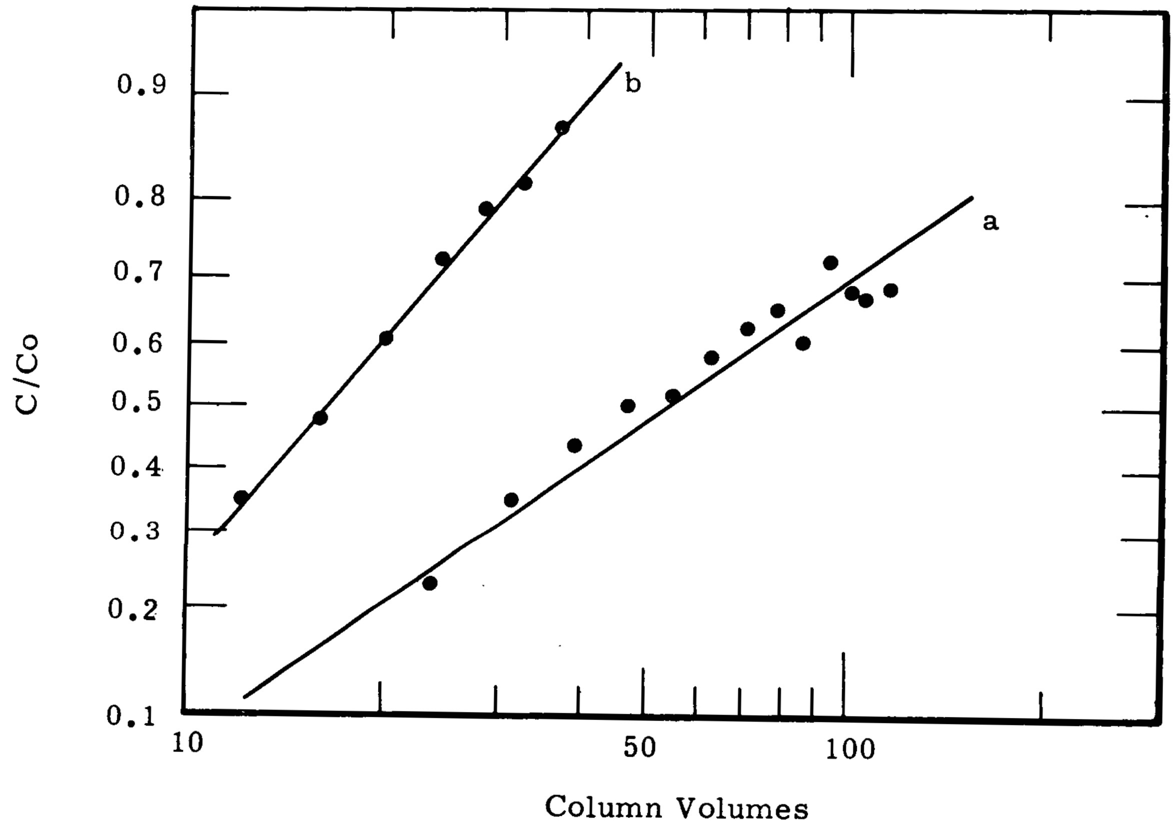

FIGURE 8

Effect of Competing H^+ on the Sr^{+2} Capacity of Decalso and Clinoptilolite (Error Function C/C_o vs Log Column Volumes)

Previous research(1) showed that, following a two-hour heat treatment at 400 C, clinoptilolite was capable of adsorbing twice as much cesium from 1M sodium solutions as that which was not heat treated. Further experiments confirmed evidence that heat treatment did not increase the total ion exchange capacity of the mineral but did improve its selectivity for cesium in the presence of high sodium concentrations. The effect of heating is shown in the data of Table II.

TABLE II

EFFECT OF HEAT TREATMENT ON CLINOPTILOLITE

4-hour Treatment, C	K_d for Cs^+ in 1M Na^+	Cation Exchange Capacity (Sodium Acetate Method) meq/100g
100	230	180
200	300	170
400	450	150
1000	1	0

$$K_d = \frac{\text{c/m/g exchanger}}{\text{c/m/ml solution}}$$

Fixation Chemistry

(J. L. Nelson, R. Fullerton, K. C. Knoll,
L. A. Bray, E. J. Wheelwright)

Further laboratory research was conducted in the application of Duolite C-3 to the adsorption of radioisotopes from the supernatant solution of neutralized Purex high-level waste. In the case of high-pH solutions that

---

(1) Irish, E. R. *op. cit.*

produced the best cesium adsorption on Duolite C-3 resin, very little strontium adsorption was obtained. Strontium breakthrough from resin columns was complete after passage of only three or four column volumes of waste, compared with at least thirty column volumes for cesium. The major radioactive isotope in aged, neutralized Purex waste supernatant solution is Cs^{137}, and very little strontium is present.

Laboratory column studies of the effect of alkalinity on cesium adsorption by Duolite C-3 resin corroborated the equilibrium experiments performed earlier.(1) Cesium selectivity of the resin is greatly improved by very high alkalinity. Solutions having a pH of 9.9 were found to reach 50 per cent column breakthrough after 6 column volumes. When caustic was added to the solution to give 3.1M hydroxyl ion, the 50 per cent column breakthrough volume was increased to 190 column volumes.

Further studies were also made of the elution of cesium from Duolite C-3 resin. Several acid-salt mixtures were tried and compared with acid alone. The acid makes the resin less selective for cesium, but also metal cations displace cesium more effectively than do hydrogen ions. The experimental results are reported in Table III.

TABLE III

ELUTION OF CESIUM FROM DUOLITE C-3 RESIN

Eluting Agent	Elution Volume (Bed Volumes) 50 Per Cent Elution	 98 Per Cent Elution
2N H_2SO_4	7	20
1N $Al_2(SO_4)_3$ + 1N H_2SO_4	7	18
1N Na_2SO_4 + 1N H_2SO_4	5	14
1N K_2SO_4 + 1N H_2SO_4	3	7
1N $(NH_4)_2SO_4$ + 1N H_2SO_4	3	6

---

(1) Irish, E. R. *op. cit.*

Table III indicates that the elution volume can be reduced by use of ammonium ion from that required by acid alone. This would be advantageous if the eluate were to be later calcined, because the ammonium ion would not contribute to the volume of calcined product.

A High-Level Cell experiment was initiated, using Duolite C-3 resin and actual neutralized Purex high-level waste solution. The resin column used was two inches in diameter and eight feet long. About 100 liters of waste supernatant solution were passed through the column. In the initial run no caustic was added to the solution, and column influent had a pH of 9.9. Early effluent from the column showed a cesium decontamination factor of 500. Cesium breakthrough reached 50 per cent after passage of 13 column volumes of solution and reached 75 per cent after passage of 15 column volumes. The bed was washed with water and then with 3.6 column volumes of 0.25M nitric acid. These washings removed about 4 per cent of the Cs^{137} and most of the sodium from the bed. The remaining Cs^{137} was then eluted with 20 column volumes of 1M nitric acid, giving 96 per cent recovery. Following elution, wash water was started through the bed, at which point gassing was observed and flow through the bed was blocked. The resin had to be removed from the column. An experiment is planned for processing waste with excess caustic added and eluting with sulfuric acid.

Experiments were performed to study the effects of temperature and grain size of Duolite C-3 resin on cesium adsorption curves. The column adsorption capacity, as indicated by the 50 per cent breakthrough volumes, decreased as the temperature increased in the range of 20 to 80 C. Experiments with synthetic, formaldehyde-treated, neutralized Purex waste, diluted 1:1, gave 50 per cent cesium breakthrough after 74 column volumes at 20 C, 57 column volumes at 40 C, 43 column volumes at 60 C, and 31 column volumes at 80 C. Cesium breakthrough became more abrupt with increasing temperature, as is reflected in the slope of the cesium breakthrough curves in Figure 9.. Similar experiments showed the relationship between resin grain size and the mean residence time (inversely proportional to flow rate) required to give optimum adsorption performance. It was found possible to attain comparable adsorption performance at a reduced residence time by use of a smaller resin particle size; the pressure drop across the column was not excessively increased with the sizes tested. This adsorption performance is reflected in the number of theoretical plates calculated from the data obtained for a standard laboratory column and listed in Table IV.

TABLE IV

CESIUM ADSORPTION BY DUOLITE C-3 RESIN AS AFFECTED BY GRAIN SIZE AND FLOW RATE

	Residence Time, min		
Grain Size mm	12	6	3
	Number of Theoretical Plates		
>0.833	3.50	1.84	1.47
0.420-0.833	13.2	18.7	3.50
0.246-0.420	73.5	32.6	5.97
0.147-0.246	73.5	- -	31.9
<0.104	103	121	127

Laboratory scouting experiments were performed to study reported reactions between salts and metals as a possible waste fixation mechanism for high-temperature separations processes. Attempts were made to produce reactions between 1:1 molar ratios of tungstic oxide and antimony, lead, tin, and zinc. At atmospheric pressures no reactions were observed when oxide-metal mixtures were heated to 500 C for four days. For study of

Influent solution - synthetic neutralized Purex waste (1WW), diluted 1:1, 2$\underline{M}$ NaOH (after dilution), 0.001$\underline{M}$ Cs^+, 30,000 Cs^{137} d/m/ml
Column - 2 g Na-based Duolite C-3 resin; 5 ml
Column flow rate - 25 ml/hr
Column residence time - 5.2 min

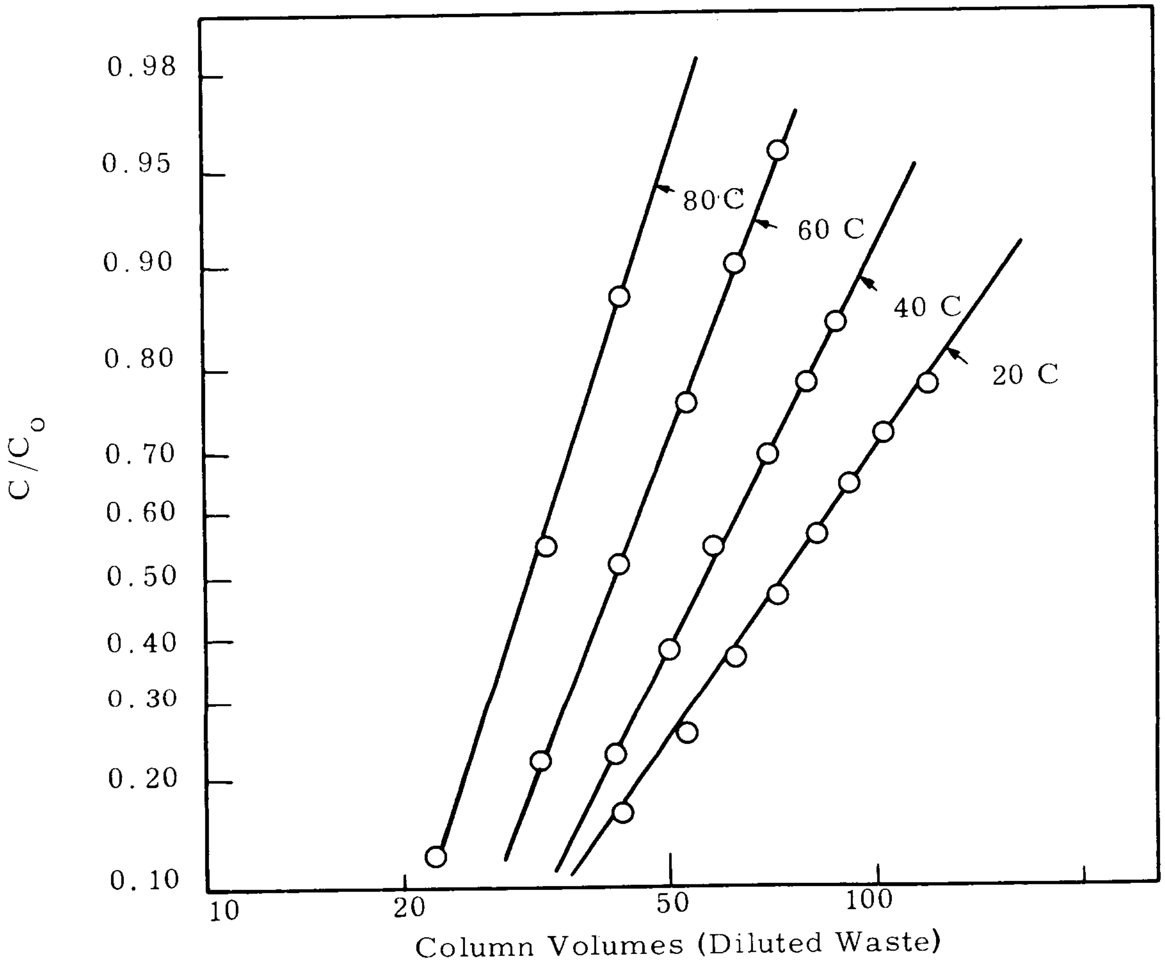

FIGURE 9

Effect of Temperature on Adsorption of Cesium by Duolite C-3 Resin (Error Function C/C_o vs Log Column Volumes) possible reactions at low pressures, the tungstic oxide and metals were dried at 105 C for three hours and placed in heavy-walled tubes which were heated, evacuated, sealed and annealed. After being heated to 500 C in these tubes for periods ranging up to five days, the products were examined by X-ray diffraction. These experiments gave no evidence of reactions. Similar experiments were also conducted with aluminum oxide in place of tungstic oxide and again no reactions were detected. No further experiments of this nature are planned.

Condensate Wastes

(B. W. Mercer, J. M. Skarpelos)

Laboratory experiments with Purex Tank Farm condensate indicated improved removal of radiocerium when the pH of the condensate was reduced from 9 to 3. The condensate, as produced, contains a small concentration of ammonia, resulting in the higher pH solution. At pH 9 less than half of the radiocerium content was usually removed by a bed of clinoptilolite. At pH3 both clinoptilolite and a sulfonated polystyrene resin gave cerium decontamination factors ranging from 8 to 200 for condensate wastes. Cerium tends to precipitate in solutions having a pH above 3 and would form a peptized colloid in these low-ion systems. This colloid is apparently not efficiently removed by adsorption. The resin had a higher capacity for cerium than did clinoptilolite in these experiments. A resin bed removed radiocerium from more than 20,000 bed volumes of treated condensate waste containing 0.012$\underline{M}$ ammonia without cerium breakthrough. Radiostrontium was removed from the waste with a decontamination factor greater than 1000 in the same experiment without breakthrough. On the other hand, a bed of clinoptilolite showed 50 per cent radiocerium breakthrough after passage of 18,000 bed volumes of condensate.

Equilibrium experiments were conducted with Decalso and clinoptilolite and solutions containing 1-12 ppm Na^+ and trace Cs^{137}. The concentrations of Na^+ in these experiments are representative of the Na^+

concentrations found in condensate wastes resulting from the evaporation of high-sodium process solutions. These experiments show that a bed of Decalso should remove the trace Cs^{137} from over 100,000 bed volumes of these solutions before reaching 50 per cent cesium breakthrough. Actually, 150,000 bed volumes of a solution containing 12 ppm Na^+ and trace Cs^{137} were passed through a small laboratory bed of Decalso to 50 per cent Cs^{137} breakthrough. The use of Decalso for either very high or low pH solutions is not recommended because of its chemical instability. Considerable difficulty was experienced in performing equilibrium experiments with clinoptilolite involving low-salt solutions. During mixing a fine suspension forms in the solution which is not readily removed by either filtration or centrifugation. Therefore, the equilibrium distribution coefficients measured for clinoptilolite in low-salt systems were probably low. However, a small bed of clinoptilolite removed trace Cs^{137} from over 200,000 bed volumes of a 12 ppm Na^+ solution -- the same solution as used for the Decalso bed -- without reaching breakthrough of the Cs^{137}.

Table V shows Cs^{137} and Sr^{85} equilibrium distribution coefficients, K_d, and column equilibrium distribution coefficients, δ*, calculated from the K_d values, for clinoptilolite, a sulfonated polystyrene resin, and a sulfonated phenol-base resin for dilute nitric acid systems containing trace Cs^{137} and Sr^{85}.

Values of δ above 100 are essentially equal to the number of bed volumes to 50 per cent breakthrough of the radioisotopes. Decontamination of dilute nitric acid wastes could best be accomplished by a bed of clinoptilolite in series with a bed of sulfonated polystyrene resin.

---

* $\delta = \rho K_d$ where ρ is packed-bed density, $\frac{\text{g exchanger}}{\text{ml bed}}$; $\delta = \frac{\text{c/m/ml bed}}{\text{c/m/ml solution}}$

TABLE V

EFFECT OF NITRIC ACID CONCENTRATION ON Cs^{137} AND Sr^{85}

K_d OR δ

Exchanger	H^+ M	Cs^{137} K_d	Cs^{137} δ	Sr^{85} K_d	Sr^{85} δ
Clinoptilolite	0.113	7.7×10^3	5.7×10^3	11	8
	0.0410	2.1×10^4	1.5×10^4	93	68
	0.0134	6.3×10^4	4.6×10^4	1200	860
	0.00465	6.3×10^4	4.6×10^4	1.5×10^4	1.1×10^4
Sulfonated Polystyrene Resin	0.113	150	77	4.0×10^3	2.0×10^3
	0.0410	480	250	4.5×10^4	2.4×10^4
	0.0134	1.6×10^3	820	4.3×10^5	2.2×10^5
	0.00465	4.4×10^3	2.3×10^3	4.0×10^6	2.1×10^6
Sulfonated Phenol Resin	0.113	490	200	2.1×10^3	830
	0.0410	1.5×10^3	600	2.2×10^4	8.6×10^3
	0.0134	5.0×10^3	2.0×10^3	2.4×10^5	9.5×10^4
	0.00415	1.3×10^4	5.3×10^3	9.7×10^5	3.9×10^5

Temperature - 25 C
Mixing time - 72 hours
Packed-bed densities - Clinoptilolite - 0.736 g/ml
- Sulfonated polystyrene resin - 0.524 g/ml
- Sulfonated phenol resin - 0.400 g/ml

The data in Table V fits the mass action law reasonably well for the following equilibria:

$$H^+ \text{ (Resin)} + Cs^+ \text{ (aq)} \rightleftharpoons Cs^+ \text{ (Resin)} + H^+ \text{ (aq)}$$

and

$$2H^+ \text{ (Resin)} + Sr^{+2} \text{ (aq)} \rightleftharpoons Sr^{+2} \text{ (Resin)}_2 + 2H^+ \text{ (aq)}.$$

If the mass action constant at one or two dilute concentrations of a particular ion is determined, calculation of K_d values for trace radioisotopes at other dilute concentrations of the ion may be possible.

Micro Pilot Plant

The Micro Pilot Plant steam stripper previously described(1) has operated for nearly 3000 hours, satisfactorily removing greater than 97 per cent of the ammonia and organic impurities from Purex Tank Farm radioactive condensate waste. The condensed overheads amount from 4 to 7 volume per cent of the feed and consist of two phases. The concentrations of various isotopes present in the organic and aqueous phases are indicated in Table VI. Because Cs^{137} is not detected in the overheads, even though it is present in the feed in concentrations greater than any other radioisotope, entrainment of the feed is considered to be minor.

TABLE VI

RADIOISOTOPES PRESENT IN STEAM STRIPPER OVERHEADS

Radioisotope	Concentration in Aqueous Phase ($\mu c/ml$)	Concentration in Organic Phase ($\mu c/ml$)
Iodine-131	5.9×10^{-6}	2.7×10^{-3}
Ruthenium-106	5.6×10^{-6}	3.4×10^{-4}
Zirconium-Niobium-95	9.4×10^{-7}	not detected
Cesium-137	not detected	not detected

---

(1) Irish, E. R. op. cit.

In order to effect further reduction of the organic in the stripper bottoms, the stream was passed through a bed of 10 liters of Pittsburg Chemical Company acid-leached, type CAL activated carbon in a 4-inch diameter, 50-inch long column at a flow rate of 1.2 ml/min/cm^2 (0.3 gpm/ft^2). During MPP Runs 16 and 17 this stream was passed through the activated carbon without any adjustment of pH. During Run 18 the stream was adjusted to a pH of 3 by addition of nitric acid before passage through the activated carbon.

The activated-carbon bed effluent was then passed through 0.25 liters of adsorbent in a 1-inch diameter column at a flow rate of 18 ml/min/cm^2 (4 gpm/ft^2). During Run 16 the adsorbent tested was highly regenerated Amberlite IR-120 (a sulfonated polystyrene resin) in the hydrogen form. Following the passage of 3000 liters of waste, this resin was regenerated with 1500 ml (6 column volumes) of 4$\underline{N}$ nitric acid. This regenerated resin was then used in Run 17. During Run 18 the adsorbent tested was clinoptilolite, having a particle size of 0.5 to 0.9 mm, which had been placed in the hydrogen form by treatment with about 3000 ml of 4$\underline{N}$ nitric acid.

Gross beta decontamination factors (DF) across the adsorbent beds ranged from 50 to 100 during Run 16, 15 to 30 during Run 17, and 10 to 30 during Run 18. Most of the gross beta activity in the effluent is due to Ru^{106} which is not effectively removed by any of the materials tested to date. Cs^{137} removal during Runs 16 and 17 is illustrated in Figure 10 and during Run 18 is illustrated in Figure 11. Essentially no Cs^{137} is removed by activated carbon. Sr^{90} removal during Runs 16 and 17 is illustrated in Figure 12, and during Run 18 is illustrated in Figure 13. The initial operation of the activated-carbon column removed Sr^{90} with a DF of greater than 100, but after about 1000 liters (100 column volumes) were treated, the DF leveled out at about 5 to 10. Using the same carbon column during Run 18 and lowering the pH to 3 caused Sr^{90} to be leached out of

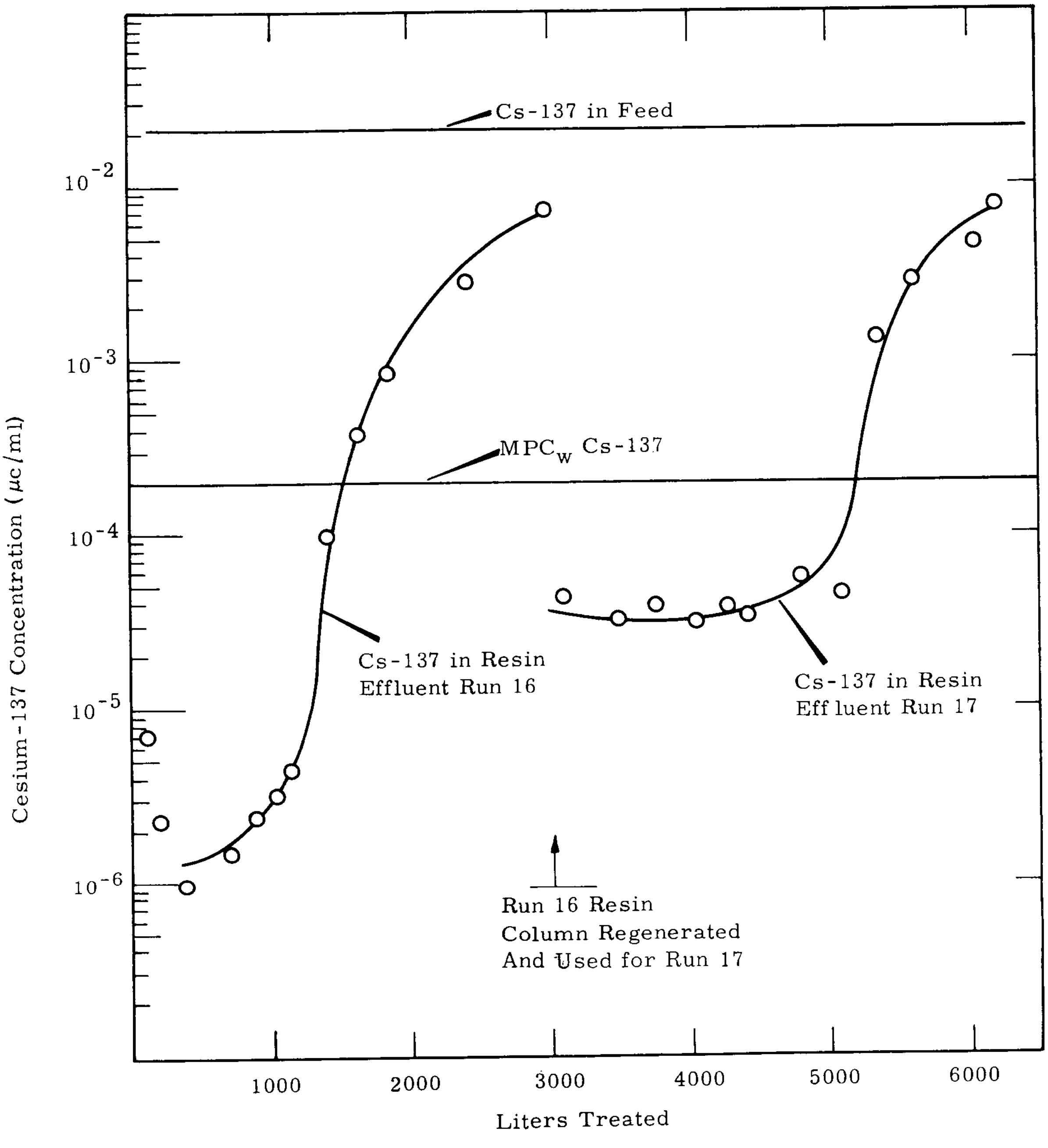

FIGURE 10

Cesium-137 Removal by Activated Carbon and Amberlite IR-120
from Purex Tank Farm Condensate,
MPP Runs 16 and 17

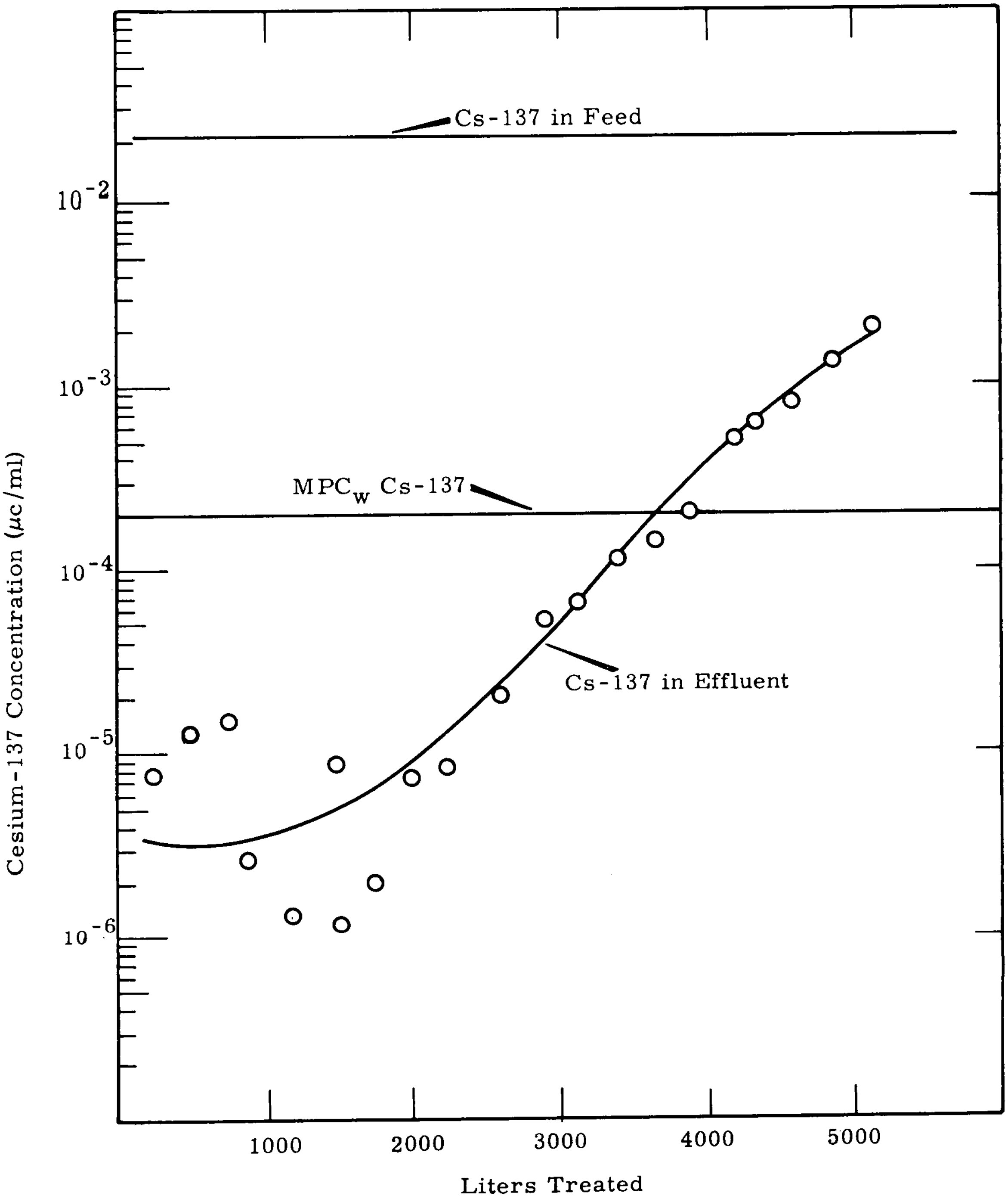

FIGURE 11

Cesium -137 Removal by Activated Carbon and Clinoptilolite
from Purex Tank Farm Condensate,
MPP Run 18

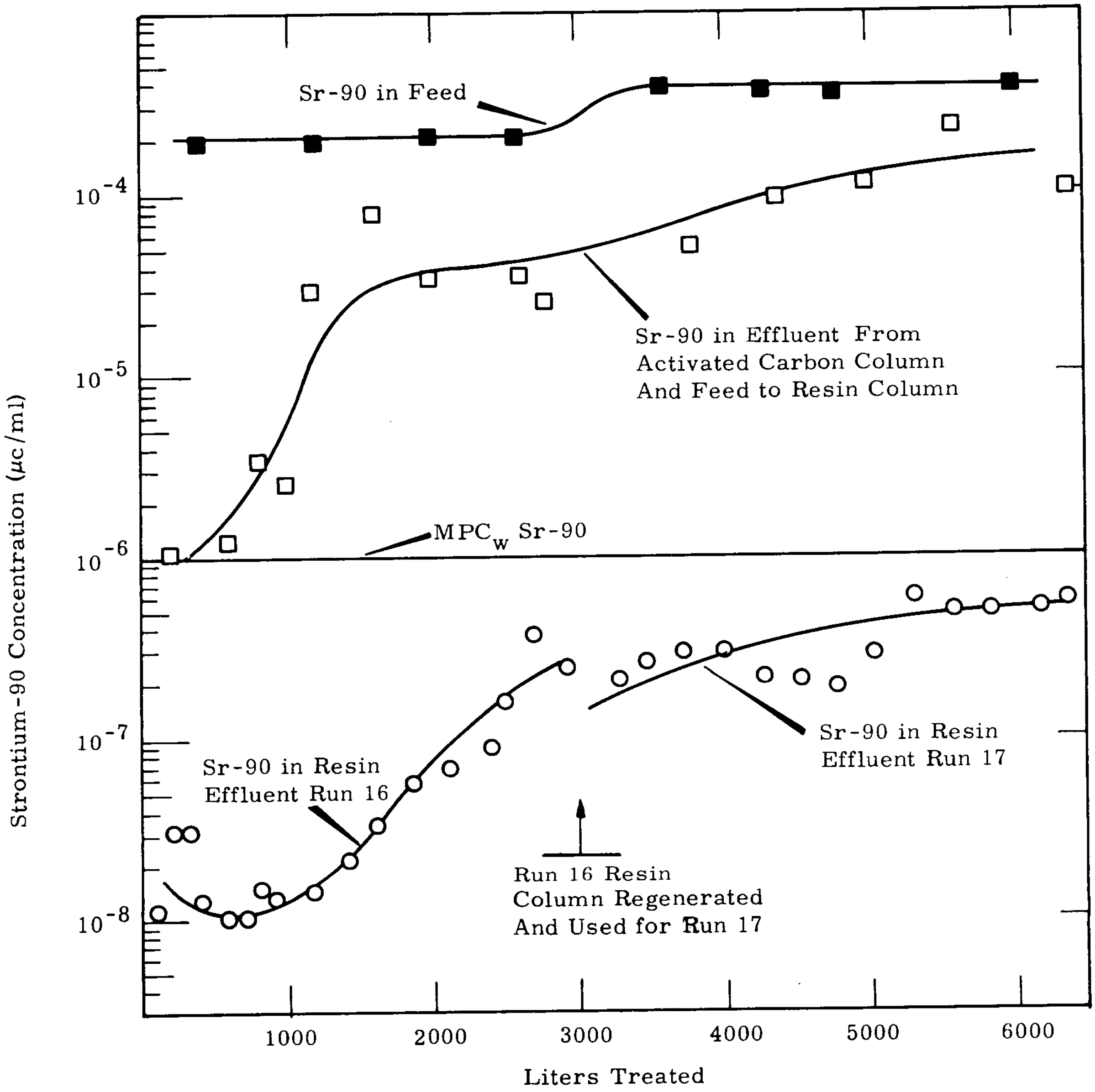

FIGURE 12

Strontium-90 Removal by Activated Carbon and Amberlite IR-120
from Purex Tank Farm Condensate,
MPP Runs 16 and 17

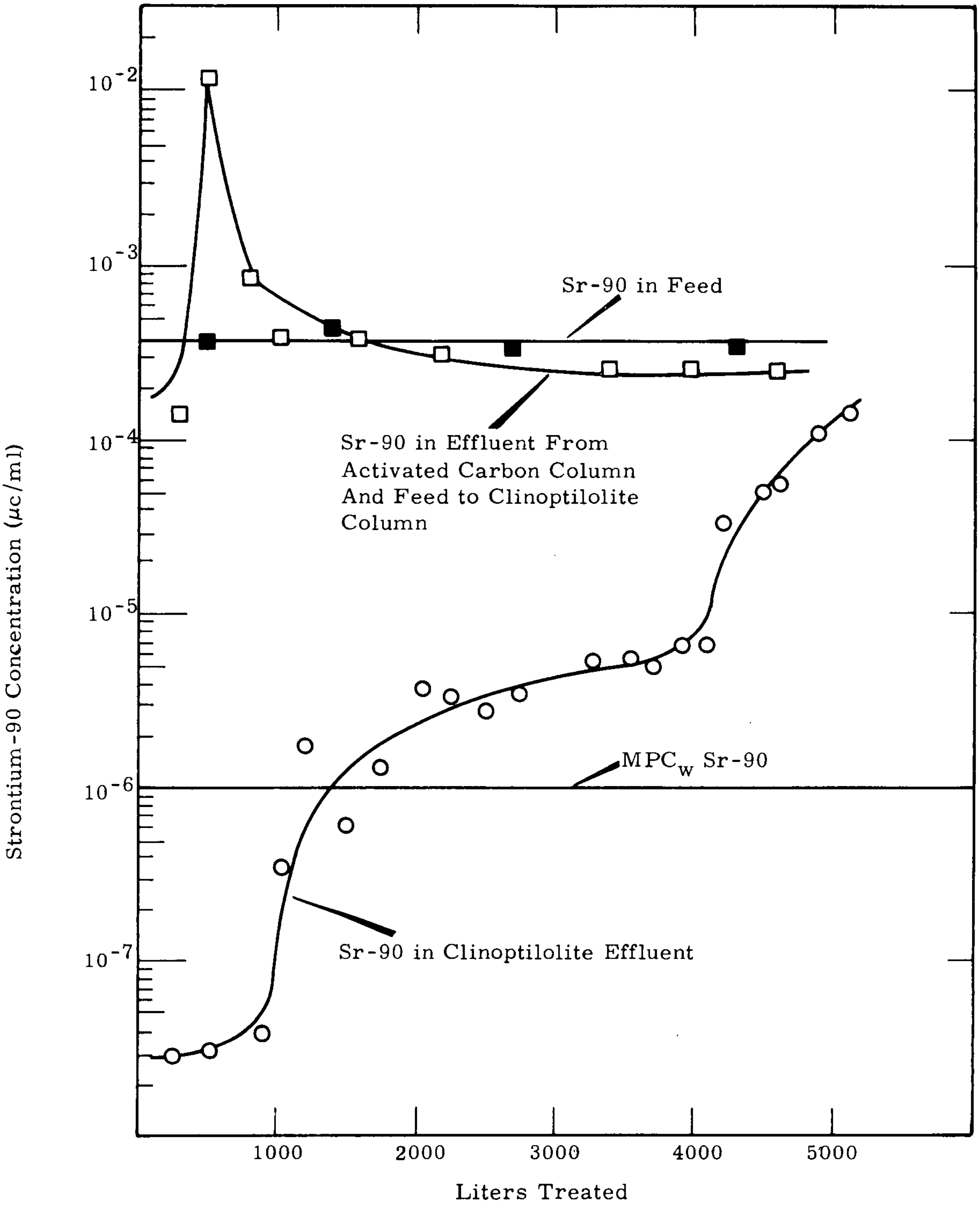

FIGURE 13

Strontium-90 Removal by Activated Carbon and Clinoptilolite
from Purex Tank Farm Condensate,
MPP Run 18

the carbon during the first 1000 liters of waste treated as indicated by one sample of the carbon effluent with a concentration nearly 30 times the feed concentration.

Comparison is made in Table VII of the capacity of Amberlite IR-120 and clinoptilolite for removing Cs^{137} and Sr^{90} at various ammonia concentrations with the point at which the effluent concentrations of the radioisotopes reach their MPC_w as the end point.

TABLE VII

CAPACITY OF AMBERLITE IR-120 AND CLINOPTILOLITE FOR Cs^{137} AND Sr^{90} IN PUREX TANK FARM CONDENSATE

Run No.	Adsorbent	Ammonia Concentration, mg/l	Capacity for Cs^{137} col vol	Capacity for Sr^{90} col vol
MPP 18	Clinoptilolite-H	5 to 6	15,000	5,400
MPP 12	Clinoptilolite-Na	ca 160	5,800	negligible
MPP 17	Amberlite IR-120-H	4 to 5	8,800	>14,800
MPP 16	Amberlite IR-120-H	6 to 7	6,000	>12,000

Elution and regeneration of the Amberlite IR-120 with 6 column volumes of 4N nitric acid was easily accomplished. Nitric acid elution of clinoptilolite was not effective; however, 6 column volumes of 5N ammonium nitrate removed most of the activity adsorbed on the column.