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QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
FIXATION OF RADIOACTIVE RESIDUES
OCTOBER - DECEMBER, 1961

By

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QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
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INTRODUCTION

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

Research and development work continued in the studies of radiant-heat spray calcination, pot calcination, and problems related to these operations. Mock-up of the calciner cell-layout for the High-Level Radiochemistry Facility was started.

The preferred development emphasis for production treatment of Hanford Purex high-level wastes has changed from bulk calcination to extraction and separate storage of the relatively long-lived, heat-producing radionuclides (e. g., cesium, strontium, and rare earths) and in-tank solidification and storage of the bulk salts after adequate decay of the shorter-lived radionuclides. This approach has been accepted as offering over-all advantages at Hanford as an integrated approach to waste management and fission product recovery. Thus, research and development work on this program of the Division of Production is reported.

Sorption studies using natural minerals, synthetic inorganic zeolites, and resins were continued to explore and develop the place of sorption processes in the over-all waste fixation picture. In addition, studies are reported on extraction of specific radionuclides by ion exchange and solvent extraction in relation to the integrated concept stated above.

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-71374, July-September, 1961.

RESEARCH AND DEVELOPMENT PROGRESS

CALCINATION AND SOLIDIFICATION STUDIES (R. E. Burns,

R. L. Moore, A. M. Platt, W. H. Swift)

Procurement and construction of the equipment for the calciners for the High-Level Radiochemistry Facility are proceeding on schedule. Mock-up of the equipment with a "dummy" cell wall and manipulators is in progress preparatory to cold demonstration operations. Installation in the High-Level Cell is currently scheduled to begin by April.

Development work on liquid-level detection elements and use of draft tubes in batch calciners is reported. Also, as a result of the re-orientation of the Hanford production waste program, the subject of in-tank solidification of bulk salt wastes is introduced, and results of development work are summarized. Both submerged combustion and hot gas sparging have been used. Studies aimed at definition of solid waste characteristics are included.

Spray Calcination

(R. T. Allemann and U. L. Upson)

High-Level Radiochemistry Facility Equipment

A simplified line diagram of the piping of the in-cell system¹ and an isometric sketch of the probable layout of the radiant-heat spray calciner, melt pot, and their associated equipment² were reported previously. The system is designed to process full-level Purex 1WW at a feed rate of one gallon per hour until the 0.8-gallon melt pot is filled. Thus, if a 10-fold volume reduction is achieved, a run of eight hours' duration will be possible, equivalent to processing the waste from approximately 0.2 ton of irradiated uranium. The spray calciner is constructed of Inconel and has a heated length of five feet of nominally 10-inch diameter pipe (tapers

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1. Pearce, D. W. Quarterly Progress Report - Research and Development Activities - Fixation of Radioactive Residues - January-March, 1961, HW-69176. April 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.

from 11 to 9 inches). The melt pot is constructed of schedule 40, 5-inch diameter stainless steel pipe and is 13 inches high (operating level - 9 inches). The spray calciner will be heated to 700-900 C by electrical resistance heating, i. e., by passing a high-amperage current through the calciner. The melt pot will be heated to 900 C with a 15 kw induction heater.

Mock-up of the calciner cell-layout has been started in the north-east corner of the 325-A Building. The spray calciner is mounted on its supporting framework which can be moved up and down with four jacks driven by an air motor. The purpose of the vertical mobility is to allow the melt pot to be removed and to allow the spray nozzle to be changed. Two spare manipulators have been mounted on a mock-up cell wall in proper relation to the in-cell equipment and are being used to test in-cell operation. One of the manipulators near the calciner has been shortened by one foot to allow reaching the spray calciner nozzle. The nozzles being used on the spray are a modified commercial item. They are welded together to eliminate gasket leaks, and the clean-out needle is sealed with a welded stainless steel bellows.

The off-gas train which is included in the mock-up consists of a sintered stainless filter, an all-glass condenser, a Raschig ring-packed scrubber, a second scrubber, a silica gel bed, and two AEC filters. Presently, the second scrubber is simply a bubbler, but it is to be replaced with a larger version of the successfully-tested electrostatic bubble scrubber. The new bubble scrubber has a preionizing stage to allow the particles to achieve a greater charge before impinging on the scrubbing liquid. Design gas flow is 2 cfm.

Included in the off-gas train are five gas samplers. These samplers are cellulose membrane filters mounted in disposable plastic holders. The filters can be valved in or out of the off-gas system by turning three valves simultaneously with an air-operated piston. After sampling, the filter holder is to be removed from the sampler by operation of a toggle clamp, and the sample is then counted with the in-cell gamma spectrophotometer. The prototype gas sampler works well.

The liquid sampler, used for sampling the condensate and scrubbing liquids, is shown in Figure 1. This sampler is mounted vertically, and a sample vial is pressed against a silicone rubber sealing gasket by a toggle action lever. The liquid is pulled through the line with a vacuum until the lines are purged. Reverse suction then leaves the sample vial half full of liquid. The vial can then be removed to the in-cell gamma spectrophotometer for counting. Line flush is accomplished by use of a stainless steel liquid supply cup in place of the sample vial.

The electrical connections to the mock-up calciners are in progress. Two 440 volt outlets were brought into the 325-A Building. Presently being connected are the variable transformers and the reduction transformers which supply the low voltage-high amperage heating current to the column. A surplus motor-generator induction heating unit was obtained for heating the pot calciner after it was determined that a coaxial line would be able to bring the power efficiently through the cell wall. A test run was made with a 15 kw unit which heated a melt pot to 1000 C in less than ten minutes.

Pipe-fitting of the mock-up unit is being performed, and cold operation of the unit should begin in February. Work is still continuing on some equipment items such as tables, stands, and the melt pot carrying cart with its radioactivity scanning probe. Installation in the High-Level Cell should begin by April.

Batch Calcination

(J. J. Shefcik)

(Not charged to Division of Reactor Development)

The batch calcination of an aqueous waste generally involves two steps; i. e., solidification by boiling off the water and acids and calcination. During the first step the waste solution is continuously added to maintain the pot nearly full of the boiling solution. A device is required to detect the solution levels and to transmit a signal compatible with a flow control system. The sensing element must be able to withstand high levels of radiation, temperature and acidity. In addition, cost must be considered since the sensing device will not be removed from the calcination vessel.

FIGURE 1
Liquid Sampler

Negative #0611905-4
AEC-GE RICHLAND, WASH.

Three liquid-level detection elements were tested in the pilot plant batch calcination facility. The solution used was simulated Purex high-level, formaldehyde-treated waste. The devices tested were: (a) an air-purged dip tube with a steam bleed into the air supply, (b) an alumina-jacketed capacitance probe, and (c) a 1/16-inch diameter, stainless steel-sheathed, chromel-alumel thermocouple heated by an alternating current. The thermocouple, which was inserted from the top of the pot, was formed into a "U" such that the junction pointed upwards. In a previous run¹ with the junction pointed down, all sensitivity was lost when a heavy coating of solids formed on the thermocouple. The sensing elements were positioned so that the thermocouple junction was 6 to 8 inches above the normal liquid level, the dip tube was submerged 4 inches, and the 15-inch-long capacitance probe was half submerged. The solution level was occasionally varied during the run to observe instrument response.

During the boil-down to incipient calcination, only the air-purged dip tube with a steam bleed gave satisfactory liquid level indication. In previous runs when there was no steam bleed or when the steam flow was lost, the dip tube became plugged. A constant flow of steam into the air supply to the dip tube proved to be effective in eliminating plugging problems. Both the heated thermocouple and the capacitance probe became heavily coated with solids. The loss in sensitivity by the thermocouple was gradual but ultimately was complete. The capacitance probe still detected changes in solution level near the end of the run but with a sensitivity reduced by an order of magnitude.

A major portion of the time cycles for batch calcination is consumed in the boil-down step. The factors that establish the boil-off rate include the heat flux, foaming and entrainment. Investigations were undertaken to ascertain what improvements could be made in the permissible heat flux by the insertion of a draft tube within the calcination vessel.

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1. Irish, E. R. Quarterly Progress Report - Research and Development Activities - Fixation of Radioactive Residues - July-September, 1961. HW-71374. October 13, 1961.

Two draft tubes, each two feet in height, were tested in a 6-inch diameter by 3-foot high cylindrical vessel. The ratios of the cross sectional areas outside the draft tubes to those inside were 1 and 0.55 for the smaller and larger tubes, respectively. The energy was supplied from an induction coil outside the pot. The draft tubes were submerged in water. The boiling action induced circulation of the liquid vertically around the tube.

In the tests with water, an improvement of 4 to 8 per cent was measured with the larger diameter tube. No measureable improvement was noted with the smaller tube.

Two runs were made with simulated Purex high-level waste solution in an 8-inch diameter by 2-foot high annular pot with a draft tube incorporated. The draft tube was 17.5 inches in height, and the cross sectional area between the draft tube and the outer pot wall was 55 per cent of that between the tube and the inner pot wall.

The simulated waste solution used in the first run was the same as that used in prior runs that exhibited extensive foaming. An air sparge had been found necessary to control the foaming. With the draft tube present, foaming was not a serious problem and no air sparge was required. The boil-off rate was increased by approximately 15 per cent over the previous run.

The waste solution in the second run was simulated Purex, formaldehyde-treated waste, chemically adjusted to yield a calcine that would melt at a temperature of less than 900 C. Circulation of the boiling solution through the draft tube occurred throughout most of the run, and no solids deposition on the pot wall was apparent. The circulation ceased only when the boiling slurry became highly viscous. During the calcination and melt-formation step, no adverse effects due to the presence of the draft tube were noted.

In-Tank Solidification

(J. Dunn, V. P. Kelly, J. E. Mendel, W. V. DeMier)

(Not charged to Division of Reactor Development)

Submerged Combustion or Hot Gas Sparging

Submerged combustion or the direct contact of hot gases with a solution to be heated and concentrated is considered as a potential, simple means of concentration of wastes in large underground storage tanks. Preliminary work was aimed at entrainment control. Extensive investigation by Rey¹ has resulted in a system for entrainment control of the off-gas stream from submerged combustion concentrators which removes many of the drawbacks of this efficient method of reducing liquid volumes. Studies resulted in establishment of performance characteristics of semi-works scale submerged combustion units using water and various salt solutions.

Correlated test data established that various effects could be disregarded in the over-all de-entrainment or could be circumvented by equipment design. For example, the boil-up rate in a tank of fixed diameter establishes the superficial vapor velocity in the vapor space of the evaporator. Entrained droplets with terminal settling velocities equal to or less than the established vapor velocity are carried along with the vapor toward the condenser. In the test equipment investigation, this velocity was less than 1 foot per second, whereas commercially designed evaporators operate at vapor velocities of greater than 2 feet per second. Less than a 2-fold decrease in entrainment was measured when the boil-up rate was decreased by one-half, indicating that the effect of boil-up rate on entrainment is not of major importance. Foaming was visually observed to have practically no effect on entrainment, but rather the addition of anti-foam agents actually increased the de-entrainment problem since the addition of such agents tends to reduce the surface tension of the solution.

1. Rey, G., et al. AICHE Journal, Vol. 7, No. 2: 299-302. June, 1961.

The major variable affecting entrainment was found to be the gas temperature entering the solution. As shown in Figure 2, this effect is quite pronounced. Experimental work determined that several methods could be employed to arrive at the optimum entrance gas temperature of about 750 F. One method transfers a portion of the sensible heat of the gas through the walls of the combustion tube to the bulk of the solution prior to entry of the gases into the solution, in effect cooling the combustion products as well as preheating the solution.

Additional semi-works scale tests employing a propane burner rated nominally at one million Btu/ hr were aimed at resolving questions of solids deposition pattern, hydration phenomena, and process control techniques as well as the volume reduction necessary for immobilization of synthetic waste solutions. These tests were conducted in 5000-gallon tanks. The equipment which was used previously by Rey, et al., was modified to elevate the burner itself above the solution level, thus providing a greater length of combustion tube to reduce the entrance gas temperature to approximately 750 F before dispersing it into the solution. The bottom portion of the combustion tube was also provided with a crow's-foot distributor to eliminate complete blocking in the event that the normal gas distributor holes became plugged during operation. Hot gases are discharged into an air-lift circulator tube surrounding the combustion tube. Thus, the concentrating material is vigorously circulated.

The following results were obtained in a series of runs:

1. The entrance gas temperature could be maintained below 750 F without the addition of excess air because the longer combustion tube permitted dissipation of heat through the tube wall to the solution.
2. The air-lift circulator ceases to function when the liquid submergence becomes less than 20 per cent of the total lift.
3. Scaling of the air-lift circulator and combustion tubes does not occur where these components are wetted by the circulated solution.

FIGURE 2

Effect of Entrance Gas Temperature on Entrainment
by Hot Gas Sparging

4. Solids deposited evenly across the bottom of the 5000-gallon tank, but scale-up (to ca 75-foot diameter) was not studied.
5. The presence of chemically-degraded Purex solvent (30 per cent tri-n-butyl phosphate in hydrocarbon diluent) does not result in foaming problems as the organic readily distills away.
6. Evaporation of a synthetic Purex alkaline waste supernatant solution to 41.5 per cent of the original volume results in essentially complete solidification after subsequent cooling to 40 F.
7. There was no tendency for the distribution ports to plug during operation.

Waste Characteristics

Laboratory studies were conducted to determine the characteristics of the solids which would be produced by in-tank solidification of radioactive waste solutions by sparging with a hot gas. Solutions simulating Purex coating removal waste, supernatant liquid from stored alkaline Purex 1WW, and combinations of these two wastes were evaporated to dryness while being sparged with either air only or a 50-50 mixture of air and carbon dioxide. Solids produced during sparging with air only are deliquescent on exposure to air at laboratory temperatures and humidity. Those produced with carbon dioxide in the sparge gas appear stable to laboratory air. When the air-carbon dioxide mixture was used for sparging, solids tended to cake on and plug the sparge tube. Equipment to measure the vapor pressure of the terminal slurry as a function of temperature has been built and calibrated.

The thermal conductivity of solids in waste storage tanks is one of the factors about which more information is needed in order to estimate temperature profiles. A promising experimental method for in-tank determination of thermal conductivity has been investigated. The method,

based on the line heat source technique, was first suggested in 1888¹ but was not successfully used until 1948.² It is based on the principle that if heat is supplied to an infinite solid at a constant rate along a line, the temperature rise, with time, of a point near the line is a function of the rate of energy input and the thermal conductivity of the solid. If the sample is large enough to prevent surface temperature change during the course of the test, the sample may be considered infinite. Correction for deviation of practical equipment from the theoretical line source can be made by simple mathematical treatment of the experimental data. The method does not require a knowledge of the exact location or measurement of the thermocouple spacing because all temperature measurements are made at one point. Although certain minimum sample dimensions must be met, no special sample geometry is required.

In view of the apparent amenability of the line heat source method to in-tank measurement of the thermal conductivity of waste sludges, the design of a suitable sensing element and assembly of the necessary auxiliary equipment were undertaken. The element is illustrated in Figure 3. The element is heated by means of a constantan heating coil wrapped around the thermocouple wires. The unit is enclosed in a stainless steel sheath. Auxiliary equipment required for the method is comprised of a millivolt recorder and a regulated power source. For in-tank measurements the element will be attached in a horizontal position to the end of a pipe and lowered to the desired location in the tank before the solids deposit. Power and thermocouple leads will be extended to the auxiliary equipment at the ground surface.

Equipment for obtaining samples of sludge in high-level waste storage tanks was demonstrated. Following unsuccessful attempts to sample sludge with a push-type sample tube, a rotary core drill was

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1. Schleiermacher, A. L. E. F. Wiedemann Annalen Physik: 34. 1888.
 2. van der Held, E. M. F. and F. G. van Drummen. Unpublished paper given before Congress of Applied Mechanics. 1948.

FIGURE 3
In-Tank Thermal Conductivity Element

developed employing special shielding cask and handling techniques. The core drill has a standard double tube core barrel, with a 2-foot long, 7/8-inch inside diameter, stainless steel inner sample tube. This assembly is shown in Figure 4. The core bit is a hole-saw type steel bit designed to prevent damage to the 3/8-inch thick steel liner in Hanford waste tanks. Pilot drilling tests involved a variety of materials: plaster of Paris, firebrick, and both calcined and dried synthetic wastes. The first in-tank sampling operation with the core driller was carried out in a Hanford Purex waste tank. A visually-identified sludge sample was successfully retrieved; that is, foreign material with the appearance of sludge was observed to be blocking the end of the sample tube. Positive identification of the material is currently awaiting detailed hot-cell inspection and analysis.

Off-Gas Treatment

(G. B. Barton)

Ruthenium Absorption on Silica Gel

The absorption of ruthenium tetroxide by silica gel (Davision Grade 42, washed free of indicator, then air dried) was measured at 25, 55, and 84 C. Another sample of this silica gel was loaded with formaldehyde vapor, and then its ruthenium absorbing capacity was measured at the same temperatures. These capacity measurements were made by drawing a stream of air, saturated with ruthenium tetroxide vapor, through 5-gram beds of silica gel until they were saturated. The beds were then dissolved in a mixture of sodium hydroxide and sodium hypochlorite to give solutions of sodium perruthenate whose concentrations could be measured spectrophotometrically. The results are shown in Table I.

The untreated gel remained yellow or slightly gray for the duration of the experiments (4-8 hours), whereas the formaldehyde-treated gel turned black immediately. The black color was found to be due largely to a surface coating that partially dissolved in sodium hydroxide with the formation of sodium ruthenate. Some of the black compound was examined by X-ray diffraction and was found to be amorphous as formed. After

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FIGURE 4
Waste Sludge Core Drill Assembly

TABLE I
CAPACITY OF SILICA GEL FOR ABSORPTION
OF RUTHENIUM TETROXIDE

<u>Temperature, C</u>	<u>Without Formaldehyde, mg Ru/g SiO₂</u>	<u>Formaldehyde-Treated, mg Ru/g SiO₂</u>
25	7.2	64
55	1.8	73
84	1.2	24

heating to 250 C, some weak lines could be measured and after heating to 500 C, a well-defined pattern was obtained. This did not correspond to the published patterns for RuO₂ or other ruthenium oxides and so was not identified.

The concentration of sodium ruthenate resulting from dissolving the formaldehyde-treated samples in sodium hydroxide decreased as the absorption temperature increased, indicating more complete decomposition at the higher temperatures.

The above results, coupled with the decontamination factor measurements published previously,¹ indicate the best operating conditions to be the lowest operating temperature possible without condensing water (or acid) in the gel.

Vapor Pressure of Ruthenium Tetroxide

Measurements are nearly complete on the vapor pressure of ruthenium tetroxide from sulfuric and nitric acid solutions of various concentrations of ruthenium and acid and containing excess periodic acid. It was found that the vapor pressure increased linearly with ruthenium concentration to the measured limit of ca 0.06M. Increasing concentrations of nitric and sulfuric acid reduced the vapor pressure of ruthenium tetroxide, at a given ruthenium concentration. A topical report on this work will be prepared during the coming quarter.

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

Kinetics of Thermal Decomposition of Ruthenium Tetroxide

Studies of the kinetics of decomposition in heated glass tubes were initiated. These indicated nearly complete decomposition (> 99 per cent) when an air-RuO₄ stream was passed through a tube of 0.58 cm ID heated to 150 C. The flow rate used gave an average residence time of 0.34 minutes. These results were obtained by use of a chemical method of measuring concentration of ruthenium tetroxide in the gas stream. They were rather irregular, so an in-line system was set up for use of a Cary spectrophotometer to measure the concentration differences continuously.

Absorption Spectrum of Ruthenium Tetroxide in Air

In conjunction with the above-mentioned kinetic experiments, the absorption spectrum of ruthenium tetroxide vapor in air was measured. It was immediately evident, as Figure 5 shows, that there was a band structure to the two electronic states excited in the ultraviolet. Apparently these offer some opportunity for analysis and possible refinement of the thermodynamic data.

SORPTION AND EXTRACTION STUDIES - (G. J. Alkire, R. E. Burns, C. E. Linderoth, R. L. Moore)

Laboratory studies continued on the kinetics of cesium adsorption on zeolites. The use of Boyd's equation to evaluate loading rate constants for organic resins was extended and found applicable to the zeolites studied. Loading rate constants were evaluated as a function of temperature, flow rate, and bulk concentration of ion being adsorbed.

In the Micro Pilot Plant, extended experiments were continued to demonstrate the application of laboratory findings to the decontamination of fuel processing plant condensate streams. Use of an Amberlite IR-120 (a sulfonated polystyrene resin) column in series with a clinoptilolite column for decontaminating Purex Tank Farm condensate was evaluated. The efficiency of these materials for removing strontium and cesium varied with the pH, the optimum pH being about 4. Strontium was primarily removed by the resin, and cesium was primarily removed by the clinoptilolite.

FIGURE 5

Ultraviolet Absorption Spectrum of Ruthenium Tetroxide Vapor in Air
(10 cm Fused Silica Cells, Cary Model 12 Spectrophotometer)

Recent experiments have shown that the cesium capacity of Duolite C-3 (a sulfonated phenol) resin is affected more by the buffer capacity of the waste solution than by the pH. Ammonium salts were found to be superior to sulfuric acid in eluting cesium from Duolite C-3. A second High-Level Cell experiment with actual neutralized Purex high-level waste supernatant solution demonstrated that adjusting the waste to 2M sodium hydroxide nearly doubles the capacity of the resin compared to using untreated waste. Data from preliminary laboratory experiments with clinoptilolite indicate excellent removal of cesium from formaldehyde-treated Purex 1WW waste. Greater than 100 column volumes can be processed before 50 per cent cesium breakthrough is observed.

Studies were made to explore the feasibility of a solvent extraction process, using D2EHPA (di-2-ethylhexyl phosphoric acid), for removal of strontium and the rare earths from formaldehyde-treated Purex 1WW.

Fundamental Research

(L. L. Ames)

(In part charged to Division of Reactor Development)

Laboratory work continued on a study of cesium removal from solution by zeolites in the film diffusion region. Zeolites studied included clinoptilolite, erionite, phillipsite, Type A and a gel having a six-to-one alumina-to-silica ratio.

Table II shows the ability of Boyd's¹ loading equation, $\ln(1-F) = -Rt$, to describe a set of curves obtained in the film diffusion region where:

F = fraction of loading,

R = loading rate constant; constant at any value of F, and

t = elapsed time since loading began.

-
1. Boyd, G. E., A. W. Adamson, and L. S. Myers, Jr. "The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites: II. Kinetics," J. Am. Chem. Soc. 69: 2836-2848. 1947.

Experimental conditions common to Tables II through V, unless otherwise noted, include an influent solution containing $1.0 \times 10^{-3} \text{N CsCl} + 1.0 \times 10^{-8} \text{N Cs}^{134}$, an influent pH of 6.0, a temperature of 25 C and a flow rate of 12.8 l/hr/cm^2 . Shallow beds used in the study contained 500 mg, 0.25 to 0.50 mm, sodium-based exchangers.

TABLE II
TEST OF EQUATION FIT

<u>Exchanger</u>	<u>t@F = 0.2</u> <u>sec</u>	<u>R@F = 0.2</u> <u>sec⁻¹</u>	<u>t@F = 0.3</u> <u>sec</u>	<u>R@F = 0.3</u> <u>sec⁻¹</u>
Erionite	90	0.00248	144	0.00252
Phillipsite	138	0.00161	213	0.00167
Type A	168	0.00132	255	0.00139
Clinoptilolite	184	0.00120	276	0.00129
Gel	195	0.00114	294	0.00121

TABLE III
EFFECT OF TEMPERATURE ON LOADING RATES

<u>Exchanger</u>	<u>R at 25 C, sec⁻¹</u>	<u>R at 50 C, sec⁻¹</u>
Erionite	0.0024	0.0051
Clinoptilolite	0.0012	0.0031
Vermiculite	0.0013	0.0033
Type A	0.0013	0.0031

Temperature effects, as shown in Table III, are proportional to the effect of temperature on the film diffusion coefficient, and hence loading rate.

A linear relationship was found between loading rate and column flow velocity as shown in Table IV.

TABLE IV
EFFECT OF FLOW RATE ON THE LOADING RATE OF ERIONITE

<u>Exchanger</u>	<u>Flow Rate, 1/hr/cm²</u>	<u>R/Flow Rate</u>	<u>R, sec⁻¹</u>
Erionite	19.2	0.000165	0.00317
Erionite	12.8	0.000175	0.00224
Erionite	4.4	0.000175	0.00077
Erionite	0.6	0.000284	0.00017

Results with organic resins ¹ indicate that loading rates in the film diffusion region are directly proportional to concentration of incoming cation. Table V shows that within the margin of experimental error the loading rate does change by an amount proportional to the cesium concentration in the influent solution.

TABLE V
EFFECT OF CESIUM CONCENTRATION ON LOADING RATES

<u>Exchanger</u>	<u>Cesium Normality</u>	<u>R, sec⁻¹, for 1.0 x 10⁻⁴ N Cs⁺</u>	<u>Cesium Normality</u>	<u>R, sec⁻¹, for 1.0 x 10⁻³ N Cs⁺</u>
Erionite	1.0 x 10 ⁻⁴	0.00043	1.0 x 10 ⁻³	0.0051
Clinoptilolite	1.0 x 10 ⁻⁴	0.00034	1.0 x 10 ⁻³	0.0031
Vermiculite	1.0 x 10 ⁻⁴	0.00035	1.0 x 10 ⁻³	0.0033
Type A	1.0 x 10 ⁻⁴	0.00033	1.0 x 10 ⁻³	0.0031

The zeolites, as cation exchangers, apparently react in the same manner as the organic resins within the experimental conditions used here. Since the kinetics of organic resin exchange reactions are known, the techniques used to study them may be conveniently used to study inorganic cation exchange reactions. It should be emphasized, however, that the use of Boyd's equation in the present instance is purely empirical. The equation was not derived to cover the conditions of its present usage.

1. Ibid.

Low- and Intermediate-Level Wastes
(B. W. Mercer and J. M. Skarpelos)

Equilibrium experiments were conducted to study the effect of various cations on the removal of trace radiocesium and radiostrontium from dilute salt or acid solutions. Tables VI and VII show column equilibrium distribution coefficients, δ , * in 0.01 molar solutions for a sulfonated polystyrene resin (Amberlite IR-120), a sulfonated phenol-base resin (Duolite C-3), a natural zeolite (clinoptilolite), and an aluminosilicate gel (Decalso). The coefficient, δ , is used instead of K_d for comparing the heavier inorganic exchangers with the lighter organic exchangers. In addition, the δ values in the tables approximate the number of column volumes of solution that can be put through a column of the exchanger at normal flow rates to 50 per cent breakthrough of the cesium or strontium.

TABLE VI
CESIUM EQUILIBRIUM DISTRIBUTION COEFFICIENT, δ

0.01 Molar Cation	Amberlite IR-120	Duolite C-3	Clinoptilolite	Decalso
H ⁺	1.1×10^3	2.5×10^3	5.0×10^4	---
NH ₄ ⁺	3.5×10^2	4.9×10^2	2.5×10^3	1.6×10^3
Li ⁺	1.4×10^3	4.9×10^3	2.1×10^5	1.3×10^5
Na ⁺	4.3×10^2	2.2×10^3	2.8×10^4	3.2×10^4
K ⁺	2.1×10^2	6.1×10^2	2.3×10^3	2.3×10^3
Mg ⁺⁺	47	2.2×10^2	1.4×10^5	1.4×10^5
Ca ⁺⁺	36	1.6×10^2	8.8×10^4	7.2×10^4
Al ⁺⁺⁺	<100	<100	1.7×10^5	---

$$* \delta = \frac{c/m/ml \text{ bed}}{c/m/ml \text{ solution}} = (K_d)(\text{Packed-bed density})$$

TABLE VII
STRONTIUM EQUILIBRIUM DISTRIBUTION COEFFICIENT, δ

0.01 Molar Cation	Amberlite IR-120	Duolite C-3	Clinoptilolite	Decalso
H ⁺	4.0×10^5	1.3×10^5	1.6×10^3	--
NH ⁺ ₄	2.3×10^5	3.8×10^4	2.0×10^3	8.0×10^4
Li ⁺	6.2×10^5	3.7×10^5	$>1.0 \times 10^6$	$>1.0 \times 10^6$
Na ⁺	1.3×10^5	5.0×10^4	1.0×10^5	2.8×10^5
K ⁺	1.8×10^5	5.0×10^4	1.3×10^3	3.0×10^5
Mg ⁺⁺	3.8×10^2	2.0×10^2	2.6×10^5	5.3×10^4
Ca ⁺⁺	1.4×10^2	76	2.8×10^2	8.2×10^3
Al ⁺⁺⁺	<100	<100	4.8×10^5	--

The packed-bed densities used for calculating δ were 0.524, 0.400, 0.736, and 0.736 g/ml for Amberlite IR-120, Duolite C-3, clinoptilolite and Decalso, respectively. The experiments were conducted at 25 C in a range of pH 4-7, except for hydrogen ion and aluminum ion (pH-3). Mixing time was 72 hours.

Particular emphasis has been given to seeking out those exchangers or conditions which will permit large volumes of waste to be processed through the exchange column before breakthrough is reached. Economic waste fixation is directly dependent on the volume of waste processed through the column if the exchange column is not to be regenerated and reused.

Clinoptilolite is capable of removing trace cesium and strontium from large volumes of dilute solutions of lithium, sodium, magnesium and aluminum ion before reaching breakthrough. But relatively large amounts of hydrogen, ammonium or potassium ion will greatly reduce the capacity to adsorb strontium. However, in the presence of hydrogen, ammonium, and alkali metal cations, strontium can be effectively adsorbed from large volumes of solution with Amberlite IR-120.

Decalso exhibits a generally high selectivity for all the ions tested in neutral solutions. Furthermore, since it was the most selective of the

exchangers examined for strontium in the presence of calcium, it may prove useful for decontaminating natural water containing calcium. Duolite C-3 resin was more selective for cesium in the pH 4-7 range than Amberlite IR-120, but its useful high selectivity for cesium is only exhibited above pH 11.

Replacing hydrogen or ammonium ions with other ions such as lithium, sodium, or magnesium will extend the life of a clinoptilolite bed. For example, ammonium ion can be replaced with sodium by adding sodium hydroxide to the solution containing ammonium ion and boiling off the ammonia. In 0.01M sodium solution, free of ammonium ion, the trace cesium capacity of clinoptilolite would be increased 10-fold and the trace strontium capacity 50-fold.

Laboratory and Micro Pilot Plant experiments have indicated that more optimum decontamination of Purex Tank Farm condensate might be achieved if the waste were passed through a sulfonated polystyrene cation resin column in series with a clinoptilolite column. MPP Run 19 was performed to evaluate the use of this combination.

MPP steam stripper operation continued to remove the major amounts of ammonia and organic from the condensate waste. During the run, the stripper bottoms were passed through a one-liter bed of Pittsburgh Chemical Company acid-leached, type CAL activated carbon in a 4-inch diameter column at a flow rate of 1.2 ml/min/cm^2 (0.3 gpm/ft^2) in order to remove residual organic not removed by the stripper. The effluent from the carbon column was passed through 0.25 liter of Amberlite IR-120 (a sulfonated polystyrene resin) in the hydrogen form, followed by 0.25 liter of clinoptilolite (particle size 0.5 to 0.9 mm) in the hydrogen form, in separate 1-inch diameter columns at a flow rate of 18 ml/min/cm^2 (4 gpm/ft^2).

After 2200 liters of waste which had been adjusted from a pH of 6.5 to a pH of 2.4 by addition of nitric acid had been processed, the acid addition was stopped and the pH of the feed gradually increased and reached 6.5

towards the end of the run. The pH of the feed stream to the Amberlite IR-120 column and that to the clinoptilolite column are illustrated in the upper portion of Figure 6.

The resin removed Cs^{137} most efficiently when no acid was added. The concentration of the isotope in the effluent from the resin column was never less than its MPC_w during the run. While the presence of added acid adversely influenced the efficiency with which the mineral removed Cs^{137} , the concentration of the isotope in the effluent from the column was below its MPC_w for the entire run. Cesium-137 removal by the two adsorbents is illustrated in the lower portion of Figure 6.

The resin removed Sr^{90} most efficiently when the pH was about three. The concentration of the isotope in the effluent from the resin column did not reach its MPC_w until 5400 liters had been treated. The mineral column removed very little additional Sr^{90} during the run. Strontium-90 removal during the run is illustrated in Figure 7.

High-Level Wastes

(K. C. Knoll, J. L. Nelson, W. W. Schulz)

(In part charged to Division of Reactor Development)

The selectivity of Duolite C-3 phenolic cation exchange resin for cesium is known to increase at high pH. Recent experiments have shown that the buffer capacity of the waste affects resin capacity more than pH per se. Column experiments with Cs^{137} in 2 N sodium carbonate (pH 11.8) and 2 N sodium sulfate brought to the same pH with 2 N sodium hydroxide exhibited marked differences in breakthrough points. The 50 per cent breakthrough points for carbonate and sulfate solutions were 208 and 137 column volumes, respectively.

Sorption was demonstrated to be dependent on total cesium concentration even in high sodium systems where cesium is in the "trace" concentration range. The 50 per cent Cs^{137} breakthrough points for a synthetic waste are given in Table VIII for three levels of cesium concentrations.

FIGURE 6

Cesium-137 Removal by Amberlite IR-120 Followed by Clinoptilolite from Purex Tank Farm Condensate and pH of Feed Streams for MPP Run 19

FIGURE 7
Strontium-90 Removal by Activated Carbon,
Amberlite IR-120 and Clinoptilolite
from Purex Tank Farm Condensate for MPP Run 19

TABLE VIII
EFFECT OF CESIUM CONCENTRATION
ON DUOLITE C-3 RESIN SORPTION

<u>Cesium Concentration, M</u>	<u>Column Volumes to 50 Per Cent Breakthrough</u>
3.2×10^{-3}	15
4.0×10^{-4}	22
1.0×10^{-5}	50

The influent sodium concentration of these solutions was about 9 M, so that Na-Cs ratios were from 3×10^3 to 1×10^6 . Thus, it appears that some exchange sites on Duolite C-3 are highly selective for cesium, but that the number of these sites is very low. Care must be exercised in evaluating such exchangers with synthetic waste solutions to be sure that cold cesium levels are known accurately. These results explain why nearly ten times the volume of coating waste supernatant solution can be processed to 50 per cent Cs¹³⁷ breakthrough as neutralized Purex high-level waste supernatant solution.

Additional experiments have been made on elution of Cs¹³⁷ from Duolite C-3. Ammonium salts and ammonium salt-acid mixtures are better eluting agents than acid alone. Illustrative data are shown in Table IX.

TABLE IX
ELUTION OF Cs¹³⁷ FROM DUOLITE C-3 RESIN

<u>Eluting Agent</u>	<u>Elution Volume (Bed Volumes)</u>	
	<u>50 Per Cent Elution</u>	<u>98 Per Cent Elution</u>
5N H ₂ SO ₄	4.6	10.3
1N H ₂ SO ₄ + 4N (NH ₄) ₂ SO ₄	2.0	2.7
0.1N H ₂ SO ₄ + 4.9N (NH ₄) ₂ SO ₄	2.2	3.3
5N (NH ₄) ₂ SO ₄	2.2	3.4

A second High-Level Cell experiment was completed to remove Cs^{137} from actual neutralized Purex high-level waste supernatant solution with Duolite C-3 resin. A column 2 inches in diameter and 8 feet long was used. In this experiment, the waste was adjusted to 2M sodium hydroxide. The 50 per cent Cs^{137} breakthrough occurred at 24 column volumes as compared to 13 column volumes when no sodium hydroxide was added. The rather low Cs^{137} capacity was due to the 10^{-3}M cesium concentration in the waste. Elution of the Cs^{137} was accomplished with 1M sulfuric acid. The concentration of Cs^{137} in the eluate increased to five times the waste influent level by the second column volume, then slowly decreased. Elution was essentially complete at 18 column volumes. The sulfuric acid did not attack the resin as did the nitric acid in the previous run.

An experiment was undertaken to determine the feasibility of high-efficiency removal of cesium by clinoptilolite from Purex acid 1WW waste after formaldehyde treatment. All previous experiments had been on the neutralized waste. The synthetic waste used contained 0.45M HNO_3 , 0.6M Na^+ , 0.17M Fe^{+++} , and small amounts of aluminum, chromium, and nickel as well as $5.5 \times 10^{-4}\text{M}$ Cs^+ . The results of these column experiments are given in Table X.

TABLE X
REMOVAL OF Cs^{137} FROM FORMALDEHYDE-TREATED
PUREX 1WW WASTE BY CLINOPTILOLITE

<u>Residence Time</u> <u>in Column, minutes</u>	<u>Column Volumes to:</u>		
	<u>Bulk DF of 50</u>	<u>2 Per Cent Breakthrough</u>	<u>50 Per Cent Breakthrough</u>
1	30	20	94
5	61	42	117
25	102	96	113

The data presented for a bulk DF of 50 indicate the points at which Cs^{137} concentration of the accumulated effluent is 2 per cent of that in the influent; that is, 98 per cent removal. When the residence time is high and a steep breakthrough curve is representative, the 2 per cent breakthrough

point is essentially the same point. The data indicate that a 1-minute residence time is too low for efficient column usage and that a 10 to 20-minute residence time may be adequate.

Batch contact studies with synthetic waste solution have been made to explore the feasibility of a solvent extraction process, using D2EHPA as the extractant, for high-efficiency removal of strontium and the rare earths from Purex 1WW. The studies were made with solutions simulating Purex acid 1WW after formaldehyde treatment. The synthetic waste was made 0.35 M in acetic acid and 0.12M in HEDTA (hydroxyethelenediamine triacetic acid) and brought to desired pH with sodium hydroxide. Distribution ratios were measured for sodium, iron(III), chromium(III), europium, cerium, promethium, strontium, zirconium, ruthenium, aluminum and nickel at equilibrium pH values ranging from 2.9 to 4.6. Analytical data for nickel and aluminum are not yet available. Distribution ratios, E_a^O , were less than 0.02 for iron, chromium, ruthenium and zirconium for all pH values included. For europium, promethium, cerium and strontium, E_a^O values ranged from 1 to greater than 1000. For all except strontium, E_a^O increased with increasing pH. Data indicate that separation of strontium and the rare earths from other radioactive constituents, except calcium, present should be possible in this system. Separation of strontium from rare earths and calcium in a IB (partitioning) column has already been demonstrated in the Hanford Hot Semi-Works recovery of strontium.

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