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LABORATORY STUDIES ON THE GROUND DISPOSAL OF ORNL INTERMEDIATE-LEVEL LIQUID RADIOACTIVE WASTES

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HEALTH PHYSICS DIVISION

K. Z. Morgan, Director

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Abstract

Radioactive waste and ground water solutions were passed through columns of indigenous Conasauga shale to determine the sorptive behavior of the radionuclides. Cesium-137, the major radioactive constituent of the basic waste solution, was adsorbed very effectively with a shale/solution distribution ratio of 500. A small fraction of ruthenium-106, the only other radionuclide present in relatively large concentration, was adsorbed per unit weight of shale, but this adsorption occurred even when the radionuclide had previously passed through 200 feet of shale.

The ruthenium and the small amounts of cobalt-60 and antimony-125 present were removed by coprecipitation with lead dioxide after the addition of sodium hypochlorite.

By combining coprecipitation with adsorption on shale columns, it was possible to obtain decontamination factors of 2×10^3 for gross beta, 3×10^3 for gross gamma, 4×10^4 for cesium, and 2×10^2 for ruthenium. Because of these decontamination factors, the lead dioxide precipitation combined with the hydroxide precipitation now in use, followed by passage of the supernatant solution through a shale column, is recommended.

In addition, this alternative to seepage pit disposal would provide a more positive control of the usual environmental problems of external radiation and biological uptake.

Introduction

These laboratory studies were carried out to evaluate the usefulness and safety of seepage pits for the disposal of chemical wastes containing about one millicurie of radioactivity per liter. Other studies were concerned with the operation of these pits and provided information on the dispersion and distribution of the radionuclides in the pit environs.[1,2]

Due to the great increase in the volume of radioactive wastes, the Health Physics Division in 1951 initiated the disposal of the wastes into the ground via seepage pits. Although cesium was retained by the soil, ground water samples, collected from nearby test wells and open seeps, showed detectable amounts of radioactive ruthenium, cobalt, antimony, and stable nitrate. Laboratory studies were initiated to study the exchange capacity of the soil and to develop methods for the removal of these radioactive substances prior to pit disposal.

Waste and Soil Source and Characteristics

The intermediate-level radioactive liquid waste solutions discharged to the seepage pits originate primarily from nitric acid and sodium nitrate fuel element dissolution for recovery of fissionable material. The waste is collected in underground tanks to which sufficient sodium hydroxide is added to raise the pH of the solution above 9 and to precipitate insoluble hydroxides and carbonates such as those of iron and calcium, respecively. The precipitate carries with it the insoluble

radionuclides, including the rare earths, yttrium, zirconium, niobium, strontium, and a fraction of the ruthenium. How completely these radionuclides are removed depends on such factors as the pH of the solution, settling time, and the care of decantation. Approximately 10 million liters of this supernatant solution were pumped in 1956 from the tanks to three open seepage pits operated serially. The pits are excavated in Conasauga shale, some properties of which are given in Table I. At this stage, the solution having a composition similar to that shown in Table II contains the soluble hydroxides of cesium and antimony, the soluble nitro complexes of ruthenium and cobalt, and some residual insoluble radionuclides which ultimately settle to the bottom.

Study Methods

To obtain information on the suitability of the soil for waste disposal, the following laboratory experiments were conducted.

1. Tracer studies with cesium to evaluate soil column sorption test parameters.
2. Soil column and slurry studies with synthetic and actual waste solutions to trace the retention of radionuclides as a function of solution volume, exposure time, and ionic concentration.
3. Chemical studies to assess the removal of ruthenium by coprecipitation.

Table I

PROPERTIES OF OAK RIDGE SHALE*

Conasauga Shale of the Middle Cambrian Age; Excavated from Seepage Pit No. 2; Base Exchange Capacity 28.6 meq/100 grams

Mechanical Composition

Grain Size (mm)	Description	Percent
0.25 - 0.125	Fine sand	0.23
0.125 - 0.06	Very fine sand	0.92
0.06 - 0.002	Silt	86.7
Less than 0.002	Clay	12.2
Loss on Acid Treatment	$CaCO_3$	19.4

Electron Microscope Examination

Mica Type Mineral
Quartz
Halloysite (Small Amount)
Kaolin Group Mineral (None Detectable)

* Analysis by Geochemistry and Petrology Branch, Geological Survey, U. S. Department of the Interior, Washington, D. C.

Table II

Composition of Random Sample of Pit No. 3 Overflow

Collected October 19, 1956

Ionic Composition		Radioactive Composition (1-30-57)	
Ion	Concentration	Radionuclide	Concentration
Na^{+}	14 mg/ml	Cesium	660 x 10^{-3} µc/ml*
Al^{+3}	0.29	Ruthenium	94 " "
K^{+}	0.15	Cobalt	7 " "
Si^{+4}	0.020	Antimony	4 " "
NH_3	0.002	Strontium	7 " "
Fe^{+3}	0.001	Rare earths and Yttrium	7 " "
NO_3^{-}	21	Zirconium	1 " "
OH^{-}	2.9	Niobium	13 " "
SO_4^{-2}	2.1	Gross α	240 c/m/ml
CO_3^{-2}	1.8	Gross β	132,000 c/m/ml
PO_4^{-3}	0.20	Gross γ	308,000 c/m/ml
Cl^{-}	0.18		
Ca^{+2}	0.075		
Total Solids 47.			

* Cesium-137, ruthenium-106, cerium-144, and strontium-90 have daughters in radioactive equilibrium; antimony-125, has a daughter which may be in radioactive equilibrium with its parent.

Selection of Proper Soil Column Parameters

Column studies, employing cesium tracers, were conducted initially to determine the optimum dimensions of the column, weight of soil needed, particle size of soil, and waste solution flow rates to obtain maximum adsorption and minimum leakage of ions.

Soil for these studies was obtained from pit excavations in Conasauga shale. It was air-dried, broken into small pieces, fractionated into particle size ranges, and then dried at 110°C. Test columns were prepared by placing weighed amounts of the shale in glass columns followed by washing with distilled water.

Cesium tracer solutions were prepared by combining cesium chloride with cesium-137 in distilled water. The ratio of cesium salt to tracer was determined analytically; the tracer was counted with a Geiger-Muller beta counter or a well-type NaI (Tl) gamma scintillation detector.

Column tests were performed by passing a 0.1 M cesium chloride-cesium-137 tracer solution upflow through the shale at a constant mass velocity and counting the effluent solution constantly, periodically, or in fractions. The activity retained by the shale was calculated from the difference between influent and effluent activity, and was also obtained directly by counting the shale or a leachate which had been passed through the shale column. A check on sorption values was thus obtained by means of an activity balance, and experiments in which there was no agreement between the two sorptive values could be rejected.

Since there was no isotopic difference in the adsorptive behavior of cesium, the capacity of the shale for adsorbing ionic cesium could be calculated from the activity on the column and the ratio of the activity to the ionic concentration.

Sorptive Capacity of Shale

A 15.75-liter effluent sample from pit number 3 was passed through a shale column. No other sample was added in order to avoid changing the influent composition. Radiochemical analyses of the influent and effluent solutions and of the shale determined the effect of solution volume on removal efficiencies and the sorptive capacity of the shale. In addition, ground water collected from a well 200 feet from the seepage pits was analyzed and passed through similar columns to determine effect of passage through the soil on the sorption of radionuclides.

Shaking tests were performed by combining solution and shale in lusteroid tubes and attaching the tubes to a mechanical shaker. At intervals, the tube was centrifuged and the supernate sampled and counted. After the tests, supernate and shale were again separated by centrifuging, and both were counted.

Decontamination by Coprecipitation

Decontamination studies consisted of adding a salt of an insoluble hydroxide or oxide to the shale column effulent, stirring, and centrifuging, and then comparing the activity of the initial and final solutions. Because ruthenium, the major remaining radionuclide, is present

in the nitrate dissolver solution and hence in the pit waste in a number of noncationic forms not readily susceptible to removal by direct coprecipitation,[3,4] the oxidation of the ruthenium to the RuO_4^{-2} form was attempted with potassium permanganate[5] or sodium hypochlorite[6]. Assuming that the radioactive ruthenium was converted to this form, three different methods were then studied to determine which one was the most effective in removing ruthenium. 1) Anion exchange resins on the hydroxide cycle were added to adsorb the RuO_4^{-2}; 2) barium chromate was added to carry down the insoluble barium ruthenate[7]; and 3) the oxidizing agent was destroyed by heating the potassium permanganate with ethyl alcohol or adding Pb^{+2} to the sodium hypochlorite and coprecipitating ruthenium dioxide with manganese dioxide or lead dioxide, respectively.

The final experiments consisted of combining the hypochlorite-lead dioxide scavenging with the passage of the solution through shale columns. To 2.5-liter volumes were added 100 ml of 5 percent sodium hypochlorite, the solution was permitted to stand for 2 days, 200 ml of 150 gm/l lead acetate trihydrate were added, and the solution was decanted after standing for another 4 days. One solution was then passed through the shale columns, while another was subjected a second time to the same hypochlorite-lead oxide treatment before passage through shale columns. To prevent passage of some residual cesium through the shale because of insufficient equilibrium time, two 20-gm shale columns were connected in series, and the solution was passed through both. Radiochemical analyses of influent, supernatant solution, and column effluent were compared to obtain decontamination factors for the individual radionuclides.

Results and Discussion

Test Parameters

The cesium tracer studies indicated that a 20-gm, 10-20 mesh soil in a 2.5-cm diameter column with a liquid flow rate of 0.5 ml/min. gave optimum sorptive results. Cesium retention on the soil was to be expected because of the appreciable cation exchange capacity of the shale.[8,9] A maximum capacity of 22 milliequivalents/100 gm was found, and was confirmed by cation exchange capacity determinations using strontium nitrate plus strontium-89 tracer, and with the conventional ammonium acetate method.[10] As shown in Table III, the capacity was less than the maximum when the grain size exceeded 2.00 mm, suggesting that the average adsorption of ions in the ground would be less than the maximum obtained in laboratory studies because of inadequate surface contact between shale and solution. The decrease in capacity above 40 mesh may be the result of a soil type separation by sizing; in material as heterogeneous as weathered shale, the existance of several ion exchange materials of different capacity and average particle size is possible. The amount of shale in the column did not affect the retention of cesium if more than 5 gm was in the column. Any solution flow rate below 1 ml/min. was satisfactory.

Sorptive Capacity of Shale

The retention of cesium decreased, as shown in Table IV,[11] when the cesium concentration of the influent solution was decreased. Because

Table III

Influence of Particle Size, Column Diameter and Flow Rate on Cation Exchange Capacity of Local Conasauga Shale

Shale Aggregate Size (U.S. Standard Sieves) Passing-Retained on	mm	Shale Weight (gm)	Column Diameter (cm)	Flow Rate (ml/min)	Cation Exchange Capacity by 3 Methods (meq/100 gm) A	B	C
6 - 8	3.33 -2.38	10	--	--	--	--	16.8
		5	1.1	0.5	13.9	--	--
10 - 20	2.00 -0.833	10	--	--	--	--	18.9
		5	1.1	0.5	22.3	--	--
20 - 40	0.833- .420	10	--	--	--	--	20.1
		5	1.1	0.5	21.9	--	--
40 - 80	0.420-0.177	10	--	--	--	--	20.6
40 - 120	0.420-0.125	5	1.1	0.5	18.8	--	--
120 - --	0.125- --	10	--	--	--	--	16.2
		5	1.1	0.5	17.0	--	--
8 - 10	2.38 -2.00	10	2.5	1.0	--	22.7	--
10 - 20	2.00 -0.833	20	2.5	0.5	--	22.5	--
20 - 40	0.833-0.420	30	2.5	0.1	--	22.1	--
50 - 70	0.295-0.21	1	0.6	0.03	--	15.6	--
70 - 80	0.208-0.177	0.25	0.4	0.02	--	12.0	--

Method A: Shale saturated with 0.05 M $Sr(NO_3)_2$ solution containing Sr-89 tracer (determined by M. I. Goldman and A. Rudnick.[9])

B: Shale saturated with 0.10 M CsCl solution containing Cs-137 tracer.

C: Ammonium acetate method (determined by M. I. Goldman and A. Rudnick).[8]

Note: Unbroken cores, 7.6 cm in diameter, showed a cation exchange capacity approximately of 10 meq/100 gm when the flow rate was 0.01 ml/min. (tested by Bendixen and Goldman).

Table IV

Variation of Cesium Sorption on Conasauga Shale
With Cesium Concentration*

Concentration of Cesium in Solution (meq/liter)	Solution Volume (ml)	Concentration of Cesium on Shale (meq/100 gms)
378.	5	9.0
189.	5	9.0
37.8	30	8.8
18.9	30	7.4
3.78	150	6.9
1.89	300	6.5
0.378	360	5.1
0.189	562	3.9
0.0756	500	1.41
0.0378	448	0.73
0.0189	506	0.49
0.0038	443	0.141
0.0019	506	0.099
0.00081	738	0.066
0.00043	1128	0.034
0.00024	1274	0.020
0.00010	3820	0.020
0.00006	7900	0.019

* Data by T. W. Brockett.[11]

the concentration of the other ions in the distilled water solution was not known, no quantitative conclusion can be drawn from these values. However, the variation of adsorption with capacity suggests a Langmuir adsorption isotherm[9]

$$[Cs]_s = \frac{k' [Cs]_l}{1 + k'' [Cs]_l} \qquad (1)$$

where the subscripts s and l refer to the shale and the liquid, respectively, the values in the brackets are concentrations, and k' and k" are constants. At the small concentrations encountered in intermediate-level radioactive wastes, the value of $k'' \; Cs_l$ is small compared to unity, so that the distribution ratio of cesium on shale to cesium in solution is constant, and equal to k'. This conclusion may also be reached by considering the ion exchange reaction

$$Cs^+ + Na(shale) \longrightarrow Na^+ + Cs(shale) \qquad (2)$$

and writing the equilibrium constant based on the law of mass action[9]

$$K = \frac{[Na^+] \; [Cs(shale)]}{[Cs^+] \; [Na(shale)]} \qquad (3)$$

where the values in brackets refer to the activities--at great dilutions, the concentrations--of the substances. Again, when the cesium concentration is very small and does not alter appreciably the distribution of

the other ion (the sodium of equations 2 and 3), the ratio of cesium on shale to cesium in solution is constant. The cesium concentration in the waste solution, assuming a specific activity of 20 curies/gm for a radioactive concentration of 0.66 millicurie/liter and a molecular wight of 133, is 2.5×10^{-7} M (0.00025 meq/liter)[12], hence the concentration of cesium on the shale, from Table IV, would be 0.020 meq/100 gm if no other ions were present, giving a distribution ratio of 830 ml/gm. At these very low concentrations, more than half of the cesium is adsorbed irreversibly on soils, and cannot be displaced by concentrated solutions of salts or by concentrated mineral acids. This irreversiblity became less noticeable, and finally undetectable, at higher concentrations. This effect also may be caused by the presence of different adsorption sites in the heterogeneous exchange medium.

The time needed for radioactive cesium in solution and shale to reach equilibrium was determined by shaking the pit waste solution with local shale until the count rate of the supernatant solution had become constant. Ruthenium, cobalt, and antimony had been removed from the solution by the method to be described, so that only cesium was counted. As shown in Table V, the cesium is at first rapidly adsorbed, but the remainder is taken up very slowly. The distribution ratio at equilibrium is 14,500,000/17,200, or 840. That it is approximately equal to the distribution ratio for cesium adsorbed from distilled water is probably fortuitous; the depressing effect of the high concentration of

Table V

Variation of Cesium Sorption With Time

20 ml of Seepage Pit Number 3 overflow
shaken with 2.0 gm, 10-20 mesh local shale

Shaking Time (hours)	Solution Activity (d/m/ml)	Shale Activity (Calculated) (d/m/gm)	Shale Saturation (Per Cent)
0	1,470,000	0	0
0.08	370,000	11,100,000	76
0.17	200,000	12,700,000	88
0.25	136,000	13,300,000	92
0.33	103,000	13,700,000	94
1.0	70,000	14,000,000	96
2.0	65,000	14,100,000	97
3.0	52,000	14,300,000	98
18.	25,000	14,500,000	99.4
24	22,000	14,500,000	99.6
40.	18,600	14,500,000	99.9
112.	17,300	14,500,000	100.
184.	17,200	14,500,000	100.

sodium ions competing for ion exchange sites is counterbalanced in part by a higher cation exchange capacity of soil in a basic solution, and partially by the apparent increase in distribution ratio (See Table IV) at the very low equilibrium concentration (2.9×10^{-9} M).

In order to observe the effect of competing ions on the retention on shale of the major long-lived radionuclides, the combined ions in the concentrations listed in Table VI[8] were passed through shale columns at various pH values. The results, which would be applicable to the ORNL waste solution only if the neutrilization of the waste were not completed, indicate an increase in adsorption of all of the radionuclides in the presence of decreasing concentrations of hydrogen ions. Both the decrease in competition for exchange sites and increasing hydrolysis of some of the radionuclides is responsible for this. The adsorption of the ions at any pH increases with the valence of the ion, except for monovalent cesium, which is adsorbed as strongly as trivalent yttrium. This unusually high affinity of cesium for certain soils has been observed previously,[9] and is fortunate, since cesium decontamination of the waste solution must be carried out in the presence of large concentrations of other ions.

When waste solution from pit number 3 was passed through shale columns, the ions were removed in accordance with the results shown in Tables VII and VIII. Figure 1 illustrates the variation in column effluent activity as a function of throughput. If the shale were saturated with respect to the radionuclides at the end of the experiment, the

Table VI

Comparison of the Sorption of the Major Long-lived Fission Products on Conasauga Shale*

100 ml of aqueous solution passed over 10 gm of shale; pH adjusted with HNO_3 and NH_4OH

Radioelement	Concentration (meq/liter)	Per Cent Adsorbed			
		pH=1.5	pH=1.8	pH=3.5	pH=5.0
Cesium	0.2	79.	93.	98.	99.96
Strontium	2.4	8.	22.	85.	89.
Yttrium	0.4	80.	93.	98.	99.4
Ruthenium	0.1	--	37.	83.	--
Zirconium	0.6	84.	--	99.	--
Niobium	0.4	86.	--	99.99	99.99

* Taken from data obtained by M. I. Goldman and A. Rudnick.[8]

Table VII

Radiochemical Analysis of Pit Waste Before and After Passage Through Soil Column*
Count rate corrected for decay to 1-30-57

Radio-element	Radiation Counted	Counting Efficiency $\frac{c/m}{d/m}$	Influent Count Rate ($10^3 \frac{c}{m}$ per ml)	Effluent Count Rate (10^3 c/m per ml)					
				0-2 liter	2-4 liter	5-6 liter	7.0-7.5 liter	9.11 liter	14.0-14.5 liter
Cesium	γ	0.185	271.	5.30	23.8	58.4	103.	194.	263.
Ruthenium	γ	0.079	16.4	17.4		17.1	16.7	18.4	17.2
Cobalt	γ	0.39	5.74	4.25					4.94
Antimony	γ	0.166	1.43	1.58					1.58
Rare Earths and Yttrium	β	~0.10	1.47	0.42		0.53	0.59	1.18	1.02
Strontium	β	0.060	0.93	0.017		0.080	0.113	0.71	0.65
Niobium	γ	0.217	6.09	0.357					0.369
Zirconium	γ	0.214	<0.4						
Gross	α	~0.5	0.24						
Gross	β	~0.07	132.	24.3		43.8	64.0	105.	128.
Gross	γ	~0.2	308.	27.8	39.1	83.0	131.0	229.	296.

* Reported by H. A. Parker, Analytical Chemistry Division

Table VIII

Removal of Radionuclides by Shale Column

Influent: ORNL Seepage Pit No. 3 overflow; total of 15.75 liters.
Column: 10-20 mesh Conasauga Shale; initial weight 20.00 gm, final weight 20.66 gm.

Radio-element	Radio-nuclide	Specific Activity (μ curie per gm)		Total Activity on Shale (μ curie)	Total Influent Activity (μ curie)	Distribution Ratio μc/gm (bottom shale) / μc/ml (influent solution)
		Top Portion 9.43 gm	Bottom Portion 11.23 gm			
Cesium	Cs-Ba-137	320.	350.	6900.	10,000	530
Ruthenium	Ru-Rh-106	0.50	0.68	13.	1,500	7
Strontium	80% Sr-90 20% Sr-89	1.5	2.3	39.	110	320
Trivalent Rare Earths plus Yttrium	96% Y-90	1.2	1.8	32.	100	360
Cerium	Ce-Pr-144	0.28	0.54	9.		
Cobalt	Co-60	0.32	0.45	8.	110	68
Antimony	Sb-Te-125	0.005	0.005	0.1	60	1
Niobium	Nb-95	1.5	2.2	39.	200	--

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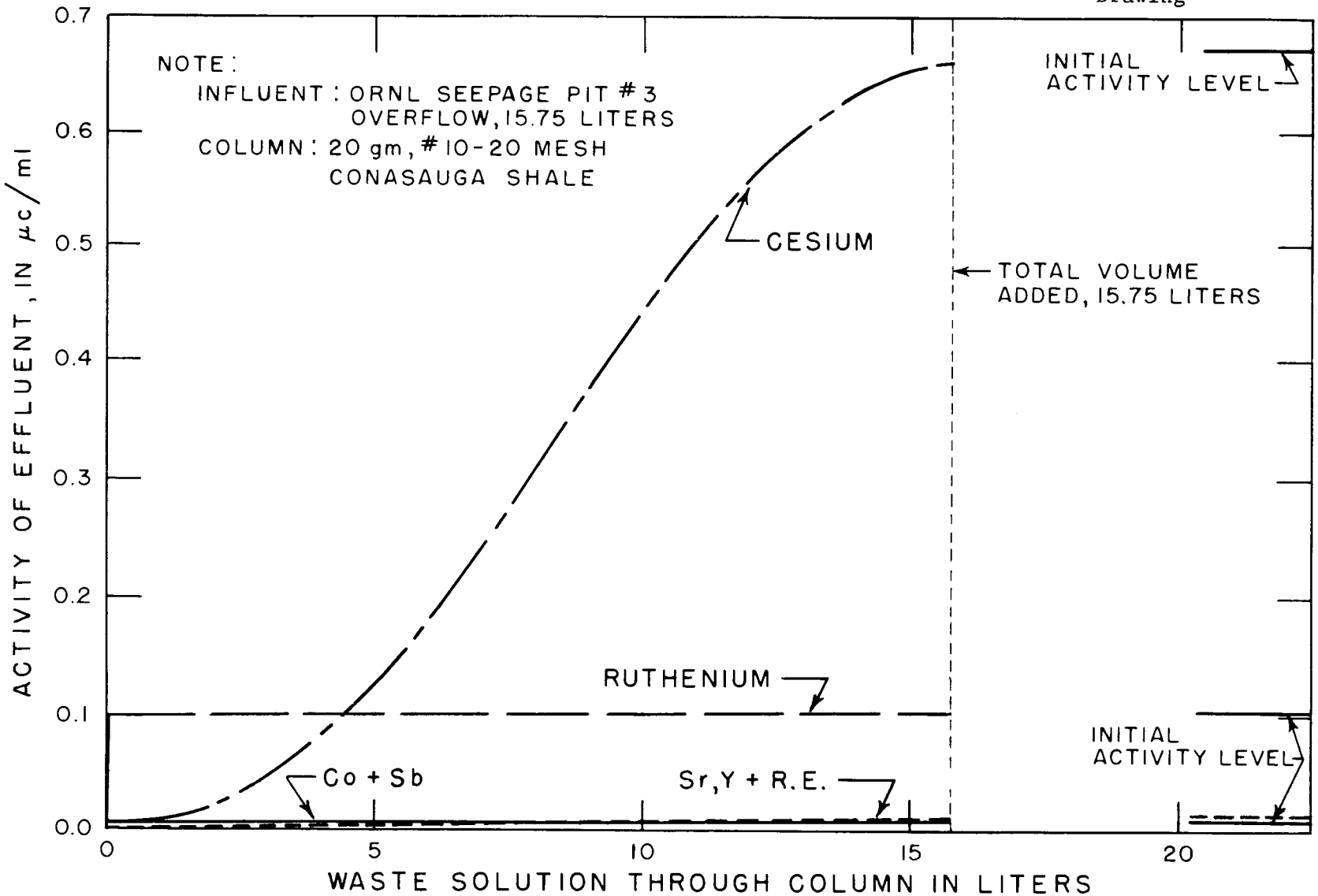

ACTIVITY OF SHALE COLUMN EFFLUENT

FIGURE 1

distribution ratios could be calculated from the quotient of the specific activity on the shale and the influent activity. It could also be determined graphically[13] from the quotient of the volume at the inflection point of the breakthrough curve and the shale weight (assuming that the breakthrough curve is as symmetrical as it has been drawn for cesium, and that the amount of liquid held in the column is small). Even in the absence of saturation, however, some conclusions can be drawn concerning the adsorption of the radionuclides.

The variation of cesium activity in the effluent is described by a typical ion exchange breakthrough curve. Activity in the initial 4 liters was small and probably caused by insufficient contact time in the 15 minutes during which the solution was in the column. After 15.75 liters, 99 per cent of the cesium passed through the column. The distribution ratio was 350/0.66, or 530, based on the specific activity in the initial, bottom portion of the column, and 8500/20, or 420, based on Figure 1. The saturation capacity of 0.35 millicurie/gm (assuming the bottom portion of the shale to be saturated) may be compared with a value of 0.34 obtained with the same solution but with different column dimensions.[14] It is lower by less than a factor of 2 than the capacity for cesium in distilled water.

The behavior of the radiocolloids--the insoluble hydroxides and carbonates--differed from that of cesium, but was not uniform. Radioactive strontium was almost completely adsorbed from the first 8 liters, while only 25 per cent of it was adsorbed from the remaining solution.

Of the rare earths and yttrium, approximately 30 per cent was found in the effluent for the first 8 liters, and 75 per cent in the subsequent 7.75 liters. Approximately 6 per cent of the niobium was found in the effluent throughout the experiment.* Because of the continuing adsorption of these radiocolloids at the end of the experiment, the values in the last column of Table VIII are less than the equilibrium distribution ratios, but probably not very much so. The relatively high initial rare earth plus yttrium activity in the effluent suggests that adsorption on shale cannot be depended on for high additional decontamination of these radionuclides, but that complete decontamination must be achieved by the hydroxide precipitation.

Only a small fraction of the ruthenium, cobalt, and antimony radionuclides were adsorbed on the shale. Even though the effluent cobalt activity did not reach influent activity after passing 15.75 liters of waste volume through the shale column, the effluent activity levels increased slightly with throughput. The ruthenium and antimony effluent activities, on the other hand, varied only within the experimental error of the analyses. The distribution ratios reported in Table VIII for these radionuclides indicate only that such distribution ratios can be attained. If it is assumed that the adsorbed ruthenium is a continuously produced cationic form in equilibrium with the greater part of the ruthenium (which is an anionic or nonionic complex), actual

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* Due probably to insufficient contact time in the column. Actually, most of the niobium was not adsorbed on the shale, presumably because of prior adsorption on tubing and glassware.

distribution ratios may be similar to that of cesium. If adsorption were by anion exchange, the distribution ratio would be as shown.

A ground-water sample containing 138,000 d/m/ml ruthenium-106, 4,000 d/m/ml cobalt-60, 60 d/m/ml antimony-125, and no detectable cesium-137 was taken from a well 200 feet distant from the pits. It was passed through the column to determine whether the adsorbable fraction of these radionuclides had been removed, or whether adsorption continued as the radionuclides passed through additional shale. After passing 200 ml of waste through the soil and washing the soil with water, it was found that 610,000 d/m of ruthenium, 30,000 d/m of cobalt, and no detectable antimony had been retained on the 20 gm of shale contained in the column. This suggests that the adsorption of at least the first two radionuclides continues as long as they are in contact with shale.

The column effluent samples were also analyzed for the nonradioactive ions listed in Table I to detect variation in ionic concentration which might warn of the imminent breakthrough of the radionuclides. No such variation occurred, influent and effluent concentrations being approximately equal. Because of the high concentration of sodium in the waste, the shale is probably saturated by it after passage of the first several milliliters of waste, and remains in the sodium form thereafter.

The adsorptive behavior of the radionuclides in this ORNL waste with Conasauga shale was similar to that reported previously for other soils.[15,16,17,18]

Decontamination by Coprecipitation

Decontamination of ruthenium, cobalt, and antimony was attempted by coprecipitation, a procedure that could be combined readily with the currently employed hydroxide precipitation. A number of salts of insoluble hydroxides were added to determine the effectiveness of a second hydroxide scavenging. Decontamination was poor, as indicated in Part A of Table IX, and did not increase to satisfactory proportions even after an appreciable increase in the carrier concentration.

After oxidizing the solution to change the radioactive ruthenium to the ruthenate, ruthenium decontamination by coprecipitating an insoluble ruthenate, adsorbing the ruthenate on anion exchange resins, or reducing the ruthenium to a tetravalent state and coprecipitating with another tetravelent ion were considered. Decontamination by the first method--coprecipitation with solutions containing 0.1 gm barium nitrate and 0.1 gm sodium chromate per 50 ml of waste--was ineffective for the removal of ruthenium. Slurrying with two successive 1 gm portions of anion exchange resins and filtration was more effective as indicated in Part C of Table IX. However, the highest decontamination was obtained using warm potassium permanganate as the oxidizing agent and manganese dioxide as the carrier (see Part B of Table IX), or with sodium hypochlorite and lead dioxide (see Table X. In addition to a ruthenium decontamination factor of approximately 15, some cobalt was carried by both precipitates. The addition of lead carrier also resulted in effective antimony decontamination, presumably because of the formation of insoluble lead antimonate.

Table IX

Removal of Ruthenium, Cobalt, and Antimony from Waste Solution

Solution: 50 ml of Seepage Pit No. 3 overflow after passage through shale column; count rate 53,000 c/m/ml

	Treatment	Percent Removal from Solution
A-1	Add 0.11 g $Pb(C_2H_3O_2)_2 \cdot 3H_2O$; separate ppt.	26
2	Add 0.86 g $Pb(C_2H_3O_2)_2 \cdot 3H_2O$; separate ppt.	55
3	Add 0.88 g $Fe(NO_3)_3 \cdot 6H_2O$; separate ppt.	55
4	Add 0.38 g $CoCl_2$; separate ppt.	22
5	Add 0.50 g $MgCl_2$; separate ppt.	26
B-1	Add 0.75 g $KMnO_4$; heat; separate ppt.	26
2	Add 0.75 g $KMnO_4$; boil with 1.5 ml ethyl alcohol; separate ppt.	85
3	Add 1.5 g $KMnO_4$; heat; separate ppt.	33
4	Add 1.5 g $KMnO_4$; boil with 3.0 ml ethyl alcohol; separate ppt.	92
5	Add 1.5 g $KMnO_4$ and 3.0 ml ethyl alcohol; separate ppt.	58
C-1	Add 2.0 g (moist wt) anion exchange resin; stir; separate resin (Dowex-1, Dowex-2, and IRA-400 resin used)	12-17
2	Add 0.05 g $KMnO_4$; heat; add 2.0 g Dowex-1; stir; separate ppt. + resin.	76
3	Add 1.5 g $KMnO_4$; heat; add 2.0 g Dowex-1; stir; separate ppt. + resin.	79

Table X

Removal of Ruthenium, Cobalt, and Antimony from
Pit Waste Solution by Lead Carrier After Oxidation with NaOCl

Treatment				Per Cent Removal			
Amount of 5 Per Cent NaOCl (ml/liter)	Standing Time (hours)	Amount Pb^{+2} (gm/liter)	Other Reagents (ml/liter)	Stirring Time: (hours)	0.1	24	90
40	0.5	7.5	--		57	69	76
40	0.5	7.5	6ml 19M NaOH		51	62	74
40	0.5	7.5	10ml conc. HNO_3		47	49	51
40	0.5	11.5	--		78	79	81
40	6.	11.5	--		83	88	--
20	6.	5.7	--		56	69	76
20	6.	11.5	--		74	80	--
40	1.	7.5	--		66	87	91
40	24.	7.5	--		81	91	93
40	66.	7.5	--		88	94	96
40	100	7.5 }	Repeated		--	--	99.5
40	44	7.5 }					

The hypochlorite-lead scavenging was preferred to the permanganate-manganese method because no heating was required by the former, and antimony was removed more effectively. By repeating the oxidation-reduction cycle, significant additional decontamination could be obtained. The oxidation and reduction of the ruthenium apparently proceeded slowly, because decontamination increased when the solution was permitted to stand both before and after the oxides were precipitated (see Table X).

To determine the feasibility of further decontamination of the original waste solution, liter volumes of the waste were subjected to oxidation by sodium hypochlorite followed by lead dioxide precipitation and passage of the filtrate through shale columns. Scavenging was accomplished with both one and two decontamination cycles; the two are compared in Table XI. The cesium activity leaving the first of the two successive shale columns had reached 7% of the influent activity after the passage of 3 liters. The effluent from the second column remained at less than 0.1% (as seen in Table XI), indicating the need for either the second column or very much slower flow rate. Although the lead dioxide precipitate formed slowly (initially white gradually turning brown), it settled rapidly. However, it was not immediately separated from the solution because of the slow ruthenium coprecipitation. The volume of the precipitate was approximately 60 cc/liter; the dried weight of the oxide, 9 gm/liter for a single precipitation.

Cesium may be removed by the method given, or by scavenging with phosphotungstic acid, ammonium alum, or a metal ferrocyanide at a lower

Table XI

Decontamination of the Waste Solution

Sample: 2.5 liters of Seepage Pit Number 3 overflow
Method: coprecipitation with PbO_2 followed by adsorption on two, 20-gm shale columns

Radio-element	Activity				
	Influent	Supernate: 1 cycle	Effluent	Supernate: 2 cycles	Effluent
		Count Rate in c/m/ml			
Gross α	40	*	*	*	*
Gross β	132,000	104,000	1,280	98,000	81
Gross γ	306,000	264,000	1,060	261,000	109
		Activity in 10^{-3} microcurie/ml			
Cesium	690.	630.	0.051	630.	0.017
Ruthenium	86.	5.9	5.6	0.39	0.36
Cobalt	1.1	0.14	0.12	0.068	0.046
Antimony	3.1	0.16	0.065	0.006	*
Strontium	0.49	0.023	*	0.023	0.011
Rare Earths + Yttrium	0.47	0.014	*	0.009	0.007
Niobium	0.14	*	*	*	*
Zirconium	*				

* Indicates no detectable activity

pH, or by adsorption on ion-exchange resin.[19-27] Ruthenium may be removed by the method described or by scavenging with sulfides or hydroxides at a lower pH, by electrolysis, or by volatilization from the acid solution.[19,21,27-33] Decontamination factors obtainable with these methods are approximately equal, being of the order of 10^2 for ruthenium and 10^4 for cesium. Factors affecting choice of methods include the cost of reagents, treatment, and storage of radioactive residue, simplicity, the requirement that certain nonradioactive ions be removed from the solution, and the possibility of reclaiming the radionuclides. For example, if the nitrate removal is also required, this may be accomplished by volatilization of the original dissolver solution, by electrolysis, or by an additional nitrate destruction procedure. If cesium recovery is desirable, the phosphotungstate or ammonium alum recovery may be applied at a controlled pH, or the shale may be leached with strong hydrochloric acid from which the cesium can then be recovered with silicotungstic acid.

Summary and Conclusions

Of the two radionuclides which constitute 95 per cent of the ORNL intermediate-level liquid waste discharge to seepage pits, cesium-137 is strongly adsorbed on local Conasauga shale and ruthenium-106 slightly. Given sufficient contact time, the cesium concentration in a solution in contact with an equal amount of shale can be reduced five-hundred-fold. The bulk of the other radionuclides in the waste solution can be removed effectively by the hydroxide precipitation now in use. However, cobalt-60 and antimony-125 resemble ruthenium in that these nuclides remain dissolved in a basic solution and are only slightly adsorbed on the shale.

Ruthenium can be removed from the waste solution by what is believed to be oxidation with sodium hypochlorite to the ruthenate form, followed by reduction to the tetravalent state, and coprecipitation with lead dioxide. Some cobalt was also carried by the precipitate, while antimony was removed as lead antimonate. Decontamination factors for ruthenium, cobalt, and antimony were 15, 8, and 19, respectively, for a single oxidation-reduction cycle, and 220, 16, and 520 for two consecutive cycles.

These laboratory findings should be checked on a pilot plant or field scale. However, preliminary findings show that scavenging precipitation combined with soil column adsorption offers the following potential advantages over direct seepage pit disposal: 1) more positive control of waste streams, 2) greater decontamination (132,000

c/m/ml of gross beta activity to 80 c/m/ml), 3) more direct control of external radiation, and 4) smaller land area necessary for disposal.

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