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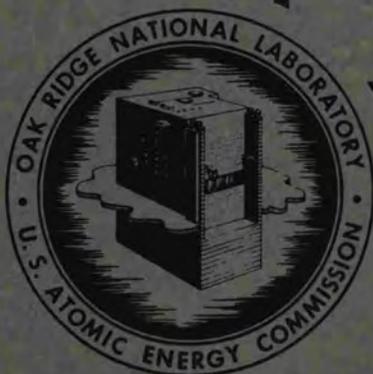
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THE REMOVAL OF FISSION PRODUCTS FROM
AN ACID ALUMINUM NITRATE SOLUTION
BY CO-PRECIPITATION METHODS

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THE REMOVAL OF FISSION PRODUCTS FROM AN ACID ALUMINUM NITRATE
SOLUTION BY CO-PRECIPIATION METHODS

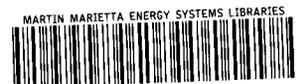
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ABSTRACT

The removal of the major long-lived fission products by co-precipitation from an acid aluminum nitrate solution has been studied. Of the methods investigated the most efficient and economical treatment was found to be the co-precipitation of ruthenium and cesium with copper ferrocyanide; of strontium with barium sulfate; of zirconium and niobium with zirconyl phosphate; and of the rare earths and yttrium with cerium oxalate. Approximately 95 per cent of the added tracers and carriers were removed from solution in a precipitate of about 50 grams per liter at a cost of 1.5 cents per liter.

INTRODUCTION

The use of nuclear energy for power production magnifies the problem of safe disposal of radioactive wastes. The composition of these radioactive wastes will depend on reactor design, fuel element type, and fuel reprocessing. A typical waste solution from a given type of reactor and fuel processing system has the composition listed in Table I. From these data a synthetic acid aluminum nitrate stock solution was prepared using stable isotopes in amounts equal to the given concentrations of the radioactive ions. Because niobium is precipitated and ruthenium is converted to a non-cationic form on prolonged standing in the acid aluminum nitrate solution, these carriers and tracers were not added to the stock solution until immediately before tests with these ions were undertaken.

The purpose of this study was to evaluate precipitation techniques for the removal of fission product ions from the synthetic acid aluminum nitrate solution. Because of the low concentration of the fission products, suitable cations were added as "carriers" to co-precipitate the respective fission products. Procedures were investigated which would precipitate the fission products leaving the aluminum in solution, thus minimizing the volume of radioactive sludge to be disposed. The aluminum is present in a concentration of 43 gms/liter as compared with a total concentration of fission products of 0.2 gm/liter. Precipitation methods were evaluated both for the acid aluminum nitrate solution as well as for this solution made strongly basic with NaOH.

The criteria for a given chemical procedure were 95 per cent removal of the radioactivity and minimum cost of chemicals. The removal of the major long-lived fission products (Sr^{90} - Y^{90} , Ru^{106} , Zr^{95} - Nb^{95} , Cs^{137} , Ce^{144} - Pr^{144}) was studied using tracers supplied by the Operations Division, ORNL. In each phase of the

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TABLE I

Fission Products in Aluminum Nitrate Waste Solution **

Element	Isotope	Weight % Present		Activity % Present	
		Isotope	Element	Isotope	Element
Rubidium	85,87	1.5	1.5*	0.0	0.0
Strontium	88	1.7	5.7	0.0	9.3
	89	1.2		9.1	
	90	2.8		0.16	
Yttrium	89	0.9	1.9	0.0	7.3
	90	0.0		0.16	
	91	1.0		7.1	
Zirconium	90,91,92,93,94,96	13.6	15.6	0.0	12.2
	95	2.0		12.2	
Niobium	95	1.0	1.0	10.8	10.8
Molybdenum	95,97,98,100	10.1	10.1	0.0	0.0
Technetium	99	3.1	3.1*	0.0	0.0
Ruthenium	101,102,104	2.9	4.0	0.0	8.2
	103	0.9		8.0	
	106	0.2		0.19	
Rhodium	103	1.0	1.0*	0.0	0.2*
	106	0.0		0.19	
Palladium	105,106,107,108,110	0.7	0.7*	0.0	0.0
Tellurium	125,126,128,130	1.5	1.5*	0.0	0.5*
	127m	0.0		0.05	
	129m	0.0		0.43	
Cesium	133, 135	9.0	13.3	0.0	0.1
	137	4.3		0.10	
Barium	137,138	4.3	4.7	0.0	8.7
	140	0.4		8.7	
Lanthanum	139	4.5	4.5	0.0	42.9 (all rare earths)
	140	0.0		9.8	
Cerium	140,142	7.8	13.2	0.0	
	141	1.6		12.8	
	144	3.8		3.5	
Praseodymium	141	2.5	3.0	0.0	
	143	0.5		9.5	
	144	0.0		3.5	
Neodymium	143,144,145,146,148,150	11.8	11.8	0.0	
	147	0.1		3.2	
Promethium	147	1.8	1.8	0.59	
Samarium	147,149,151,152,154	1.7	1.7	0.00	
			100.1 %		100.2 %

*These elements and their radioisotopes were not added to the stock solution because of their low concentration.

**U-235 was assumed to have been irradiated 30 days, after which the irradiated material was cooled 30 days. The fission yields on which the calculations are based are from Blomeke, J. O., CF-54-12-52 (1954); and the half-lives of the fission products from Hollander, J. M., Perlman, I., and Seaborg, G.T., Revs. Modern Phys. 25,469 (1953). Of the fission products, 99.0% by weight are accounted for; however, it has been assumed that the noble gases and iodine are lost. The total weight of the fission products is 0.20 gm/l of waste solution.

investigation, the effects of temperature, dilution, reagent concentration, and treatment time were evaluated.

EXPERIMENTAL PROCEDURES AND RESULTS

I. Treatment in Basic Solution

Of the fission products present in the acid aluminum nitrate solution, yttrium, ruthenium, zirconium, niobium, and the rare earths may be precipitated and filtered from the solution following addition of an excess of sodium hydroxide. In the presence of excess caustic, aluminum forms soluble $Al_2O_3 \cdot 3Na_2O$. However, approximately 2 grams of aluminum hydroxide per 100 ml of solution precipitated, carrying with it about 50 per cent of the cesium and strontium activity present.

To increase the removal of the Sr^{90} , calcium or strontium carriers were added and precipitated as the carbonate or phosphate. There was no significant difference in the removal obtained at a given temperature by the use of either the carbonate or phosphate precipitation techniques. Precipitation was more complete at $68^\circ F$ and $220^\circ F$, than at $30^\circ F$, yielding higher removals of the strontium-90. Separation of the precipitate by filtration, though time consuming, was more effective than separation by centrifugation. Calcium carbonate precipitation of strontium was preferred to the calcium phosphate precipitation because of its lower chemical cost.

As adopted, the procedure consisted of the slow addition of 100 ml of boiling aluminum nitrate stock solution, containing 100 mg Ca^{++} , to 80 ml of 18 M sodium hydroxide and 100 mg sodium carbonate. Following boiling and stirring for 15 minutes, the solution was clarified by settling for 30 minutes and filtered through Whatman No. 42 filter paper. A dried precipitate weighing 3 grams was obtained from an initial solution volume of 100 ml; the final volume of supernatant liquor was 140 ml. Table II lists the per cent removal values for the various tracer radionuclides added to the original stock solution.

TABLE II

Removal of Fission Products After Basic Treatment

100 ml Aluminum Nitrate Solution Made Basic with 80 ml 18 M NaOH at 220° F,
with 0.1 gm Ca⁺⁺ and 0.1 gm Na₂CO₃ Added

Radionuclides	Percent Removed Radiochemical Analysis*	Percent Removed Relative Counting Measurement **
Ce ¹⁴⁴	99.9	98.3
Sr ⁹⁰	97.7	97.0
Y ⁹⁰	--	99.0
Ru ¹⁰⁶ -freshly prepared	99.0	--
-aged 8 weeks	--	52.1
Zr ⁹⁵	96.3	91.5
Total Zr ⁹⁵ - Nb ⁹⁵	95.6	88.0
Cs ¹³⁷	52.2	44.9

* All tracers combined in one solution

** Separate solutions used for each tracer

The large differences in ruthenium removal reported for the two series of analyses in Table II can be explained by the differences in age of the ruthenium in the acid aluminum nitrate solution. The longer the ruthenium remained in the solution, the less Ru^{+++} was available for reaction with the sodium hydroxide, hence the lower removal of this particular ion in the aged sample.

Attempts to increase the removal of Cs^{137} over that reported in Table II by the addition of ferric or manganese ferrocyanide, potassium ferrocyanide plus lead acetate, sodium ferrocyanide plus calcium chloride, sodium metaphosphate, stannous chloride, or clay soil, with or without added potassium carrier, were unsuccessful.

The cost of chemicals for obtaining the removals cited in Table II is approximately 5 cents per liter of solution, as summarized in Table III.

II. Treatment in Acid Solution

In order to precipitate the fission products without precipitating the aluminum, studies were undertaken to develop procedures for removing the individual fission products from the acid aluminum nitrate solution. Although considerable information on formation of precipitates of the critical radionuclides in aqueous solution has been reported, (1)(2)(3) the presence of the aluminum nitrate and the high nitric acid concentration (0.16 M) inhibited the formation of such precipitates in many instances.

For clarity, the studies with each tracer are described separately.

Strontium Removal. The addition of barium, lead, or strontium salts and sulfuric acid to the acid aluminum nitrate stock solution resulted in the formation of sulfate precipitates of these salts which carried appreciable amounts of strontium-90 activity. A comparison of the removal efficiency of the various salts on the basis of chemical cost showed that the barium was most effective. Studies with barium at various temperatures showed that it was most efficient for the removal of the strontium activity at temperatures of 30°F and 220°F . If the acid is added to the acid aluminum

TABLE III

The Chemical Cost* of Treatment in Basic Solution

Reagent	Gms. Required Per Liter	Equivalent to Lbs. of Chemical	Cost Per Lb. (cents)	Treatment Cost (Cents per Liter)
NaOH	576	1.28 NaOH	3.85	4.93
Ca++	1.0	0.0062 CaCl ₂	15.00	0.09
Na ₂ CO ₃	1.0	0.0022 Na ₂ CO ₃	1.35	<u>0.003</u> 5.02

*Based on data given in Chemical and Engineering News Quarterly Report on Current Prices (First Quarter 1955)

nitrate solution indiscriminately, aluminum is also precipitated. To avoid this, the procedure described below was developed.

One hundred ml of boiling aluminum nitrate stock solution containing the strontium-90 tracer and 1 gm Ba⁺⁺ was added to 100 ml of boiling water containing 5 ml of concentrated sulfuric acid. This mixture was stirred for 15 minutes and filtered. A removal of 88 per cent of the strontium was obtained and there was no evidence of aluminum in the precipitate.

Subsequent studies showed that the presence of the sulfuric acid inhibited the removal of yttrium-90 and cesium-137, hence 8 grams of sodium sulfate were substituted for the 5 ml of concentrated sulfuric acid. This change in procedures resulted in an increase in the removal of the Sr⁹⁰ to 94 per cent.

Other procedures which were tried but which proved to be ineffective employed lead, strontium, or barium carriers with sodium silicate, silica gel, sodium metaphosphate, ferric ferrocyanide, calcium fluoride, lead sulfide, bismuth phosphate, barium silicofluoride, barium oxalate, zinc oxide, pulverized clay, iodic acid, tannic acid, or cupferron. A preformed BaSO₄ floc was also tried but was found to be ineffective.

Yttrium Removal. Since Sr⁹⁰ - Y⁹⁰ are in secular equilibrium and are counted together, Y⁹⁰ removal efficiencies were determined for all of the reagents cited in the preceding paragraph. The Y⁹⁰ radiations were separated from those of Sr⁹⁰ by counting the samples through 170 mg/cm² of aluminum absorber. For all of the procedures reported, yttrium removals were less than 35 per cent. Ineffective removals were also obtained with strontium selenate, chromic arsenide, manganic sulfate, calcium metaphosphate, copper ferrocyanide, lead chromate, and lead iodide.

Removals of 50 to 80 per cent were obtained by precipitating calcium fluoride with 500 mg Ca⁺⁺ and 10 ml 49 % hydrofluoric acid per 100 ml of aluminum nitrate

stock solution. However, large amounts of aluminum were precipitated along with the yttrium.

Stable oxalate precipitates, specific for yttrium and rare earth removals⁽⁴⁾ were produced when the stock aluminum nitrate solution was diluted with at least 2 parts of water and was maintained at temperatures below 30° F. Cerium oxalate, being more effective than barium oxalate and less expensive than yttrium oxalate, was used to carry the yttrium and rare earth radionuclides. For precipitating the cerium salt, ammonium oxalate was found to be more effective than either oxalic acid or sodium oxalate.

In summary, the adopted procedure consists of dilution of 100 ml of the aluminum nitrate stock solution with 200 ml of water, addition of 120 mg Ce⁺⁺⁺, and cooling of the resultant solution to 24-26° F. A cold saturated solution containing 8 gm ammonium oxalate was added to this solution to form the cerium oxalate precipitate, and the mixture was stirred for 1 minute and centrifuged in contact with ice. A stable precipitate could be maintained at temperatures below 30° F. By this procedure 90 per cent of the yttrium originally added to the stock solution could be removed.

Cerium Removal. The cerium oxalate precipitate was found to be equally effective in the removal of the Ce¹⁴⁴ added to the original stock solution. The barium sulfate procedure reported for strontium removal was also very effective for the removal of the added Ce¹⁴⁴ (96 per cent), whereas this same procedure accounted for a removal of only 35 per cent of the Y⁹⁰. Because of its lower cost as compared with the cerium oxalate procedure, the barium sulfate treatment was preferred for the removal of the Ce¹⁴⁴.

Cesium Removal. The removal of Cs¹³⁷ from the acid aluminum nitrate solution can be effected by precipitating copper ferrocyanide or by precipitating ammonium phosphomolybdate. The precipitation of the ammonium phosphomolybdate was accomplished by the addition of 500 mg ammonium molybdate and 1.0 ml concentrated phosphoric acid

per 100 ml of the stock aluminum nitrate solution. After heating to 110° F, stirring, settling overnight, and centrifuging, almost complete decontamination of the solution was obtained. For effective removal long settling times are necessary.

Cs¹³⁷ was also efficiently removed by either copper ferrocyanide or ferrous ferrocyanide⁽⁵⁾ precipitates, but the former was more effective and thus selected for further study. Lower temperatures increased the removal of Cs¹³⁷ with copper ferrocyanide. Costwise, this procedure was preferred to the ammonium phosphomolybdate precipitation.

The procedure that was finally adopted consisted of the addition of 150 mg Fe(CN)₆⁻⁴ to 100 ml of the aluminum nitrate stock solution, cooling to 30° F, addition of 50 mg Cu⁺⁺ to precipitate copper ferrocyanide, stirring, and filtering. Despite the time involved, filtration was preferred to centrifugation because of the viscous nature of the precipitate. This procedure resulted in the removal of 95 per cent of the added Cs¹³⁷.

Other reagents that were tried but which proved ineffective included silicomolybdic acid, hydrofluosilicic acid, antimonious chloride, silicotungstic acid, ammonium cobaltinitrite, potassium hexacyanoferrate, perchloric acid, and chlorostannic acid.

Ruthenium Removal. The ferrocyanide precipitation used for the removal of cesium was reported (5) to be effective for the removal of ruthenium. However, the use of this procedure indicated that removals were temperature dependent, with highest removals obtained at 220° F. A study of Cu⁺⁺, Fe⁺⁺⁺, Mn⁺⁺, Ni⁺⁺, and Co⁺⁺ ferrocyanides showed that the copper ferrocyanide was most efficient for the removal of the Ru¹⁰⁶ from boiling aluminum nitrate stock solution.

Best decontamination was obtained through the use of the following procedure: Two hundred mg Fe(CN)₆⁻⁴ was added to 100 ml boiling stock aluminum nitrate solution

and the copper ferrocyanide was precipitated with 60 mg Cu^{++} . The mixture was stirred for five minutes and filtered, with a removal of 90 per cent of the ruthenium. Apparently the removals obtained were independent of the time of contact between ruthenium and the stock aluminum nitrate solution.

In the earlier studies reported for the removal of ruthenium from the basic solution, the removal of ruthenium was a function of the age of the ruthenium in the solution. On standing, the brown color imparted to the aluminum nitrate solution by the ruthenium chloride disappeared over a period of weeks, or could be removed by boiling. This could be explained⁽⁶⁾ as being caused by the conversion of the cation to a ruthenate. Since the ruthenium in the reactor waste solution will probably be several weeks old at the time of treatment, its age must be considered in interpreting removal efficiencies. One advantage of the procedure described above for the removal of the ruthenium from the acid aluminum nitrate stock solution is that it appears to be almost independent of the age of the ruthenium.

Bubbling hydrogen sulfide into an aluminum nitrate stock solution containing Cu^{++} or Pb^{++} produced a heavy sulfide precipitate which accounted for a removal of about 60 per cent of the ruthenium activity, the removal depending on the age of the solution. The distillation of ruthenium in the presence of sulfuric acid and potassium permanganate was also evaluated, but removals of less than 50 per cent were obtained.

Zirconium and Niobium Removals. Those reagents showing any promise for the removal of the radionuclides reported thus far were evaluated for the removal of Zr^{95} - Nb^{95} from the acid aluminum nitrate stock solution. The precipitants studied included lead sulfide, copper sulfide, barium fluoride, calcium fluoride, copper ferrocyanide, ferrous ferrocyanide, barium sulfate, and lead sulfate. Removals by these procedures were less than 50 per cent. Removals of 60 to 75 per cent were

obtained with barium fluozirconate, ammonium phosphomolybdate, and zirconium orthosilicate. Slurrying with zinc oxide was ineffective. About 95 per cent of the combined Zr^{95} - Nb^{95} activities were removed with 50 mg Zr^{+4} plus 150 mg phenylarsonic acid per 100 ml of stock aluminum nitrate solution. However, the high cost of chemicals precludes the use of this procedure.

The precipitation of Zr^{+4} as zirconylphosphate in acid solution has been reported.⁽⁷⁾ This procedure was evaluated using 48 mg Zr^{+4} per 100 ml boiling solution and 0.12 ml concentrated phosphoric acid, followed by a two hour settling time, to permit complete precipitation of the phosphate. Removals of 90 per cent of the combined Zr^{95} - Nb^{95} radionuclides in equilibrium were obtained. The zirconium removal was estimated from the difference in count rate obtained by using appropriate aluminum absorbers and was found to be 95%. The addition of 100 mg Zr^{+4} and 1.0 ml concentrated phosphoric acid to 100 ml of boiling stock aluminum nitrate solution gave higher decontamination factors, but a very voluminous sludge was produced.

III. Combined Removal of Radionuclides from Acid Solution

The procedures developed in Section II for the single radionuclides were combined for their simultaneous removal from the acid aluminum nitrate solution. Since no single procedure of those described in Section II was equally effective for the removal of all of the radioactive materials present, it was necessary to modify the techniques and conditions of test to obtain the maximum overall removal of the radionuclides. For example, the rare earths, yttrium, and cesium are most effectively removed from cold solutions, whereas the other nuclides of interest were more effectively removed from hot solutions; yttrium is removed only at a 1 to 2 or greater dilution of the stock aluminum nitrate solution; the procedure for the removal of cesium interferes with the most effective removal of ruthenium, making it advisable to remove the ruthenium before the cesium; the zirconium precipitate is soluble in an acid oxalate solution, so this

precipitate must be separated before oxalate is added; the cerium precipitate dissolves in phosphoric acid, hence the latter had to be previously removed as zirconyl phosphate; and sodium sulfate had to be substituted for the sulfuric acid to permit subsequent removal of the cesium and yttrium.

The procedure finally adopted takes cognizance of these factors and is as follows:

1. To 100 ml of boiling stock acid aluminum nitrate solution containing tracer concentrations of Sr^{90} - Y^{90} , Zr^{95} - Nb^{95} , Cs^{137} , Ce^{144} - Pr^{144} , and Ru^{106} , add 200 mg $\text{Fe}(\text{CN})_6^{-4}$, 60 mg Cu^{++} , 48 mg Zr^{++} , and 0.12 ml concentrated phosphoric acid. Stir for 5 minutes, let settle two hours, and filter through Whatman No. 42 paper.

2. Heat filtrate to boiling, add 1 gm Ba^{++} and pour slowly into 100 ml water containing 8 gm Na_2SO_4 . Boil the mixture for 30 minutes.

3. Cool to 24-26° F, add 100 ml water, 15 mg Ce^{+3} , 150 mg $\text{Fe}(\text{CN})_6^{-4}$, 50 mg Cu^{++} , and 1.0 gm ammonium oxalate (added slowly), stir in ice bath for one minute, centrifuge in contact with ice for 5 minutes and decant.

All reagents are added as nearly saturated solutions.

The results, which are given in Table IV, show that Step 1 is effective for the removal of ruthenium and almost all of the zirconium and niobium. Step 2 accounts for the removal of cerium and strontium, and Step 3 for the removal of yttrium and cesium. If radioactive barium is present it will be removed with the strontium, while the trivalent rare earths will behave as cerium or yttrium. The overall removals show that all radionuclides with the exception of yttrium were removed in amounts exceeding 90 per cent of the original concentration in the acid aluminum nitrate stock solution. The primary reactions involved in this treatment



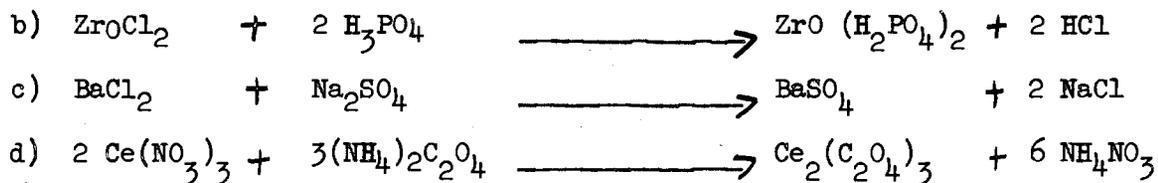
Table IV

Removal of Fission Products by Combined Acid Treatment

(Duplicate Results)

Radionuclide	Step (1)*		Per cent Removed Steps (2) and (3)		Final Average
Sr ⁹⁰	19	10	97.5	95.0	96.2
Y ⁹⁰	14	7	87.3	83.0	85.2
Ru ¹⁰⁶	87	80	90.1	91.1	90.5
Ce ¹⁴⁴	11	13	99.4	99.2	99.3
Cs ¹³⁷	53	51	98.4	99.4	98.9
Total Zr ⁹⁵ -Nb ⁹⁵	97	97	98.2	97.3	97.7
Zr ⁹⁵	97	97	98.0	96.1	97.0

* Removal calculation based on estimated liquid volumes.



The cost of treatment, based on amounts of chemicals used in the batch experiments described, is given in Table V.

The dried precipitate weighed 5.0 grams per 100 ml of initial stock solution treated; the final volume of supernatant totaled 300 ml.

SUMMARY AND CONCLUSIONS

Procedures were developed for the removal of the major fission products from a simulated reactor fuel element processing waste solution. Tracers were used for evaluating the selected methods of decontamination. These included Sr^{90} - Y^{90} , Zr^{95} - Nb^{95} , Cs^{137} , Ce^{144} - Pr^{144} , and Ru^{106} . The final procedures were evaluated in terms of their removal efficiency and of the cost of chemicals. A simple method is described for the removal of the radionuclides from the synthetic waste solution made basic with sodium hydroxide. However, a more economical and efficient method (from the standpoint of decontaminating efficiency) consists of the removal of the radionuclides from the acid aluminum nitrate solution. The cost of chemicals used in the two methods were 5.0 and 1.5 cents per liter, respectively.

The reagent concentrations selected were the lowest which would give satisfactory and reproducible results. Higher concentrations or repeated chemical additions increased removals slightly, but not in proportion to the increased amounts of chemicals used. The overall decontamination factors based on percentage of each of the radionuclides present in the initial solution (Table I) were 13 and 27 for the basic and acid treatments, respectively. Approximately 5.0 grams of dried

TABLE V

Cost* per Liter of Aluminum Nitrate Solution Processed by Combined Acid Treatment

Reagent	Weight Per Liter (grams)	Weight of Chemical (lb.)	Cost per lb. (cents)	Cost per Liter of Solution (cents)
Fe(CN) ₆ ⁻⁴	3.5	0.0178 Na ₄ Fe(Cn) ₆ · 10H ₂ O	15	0.267
Cu ⁺⁺	1.1	0.0093 CuSO ₄ · 5 H ₂ O	12	0.112
Zr ⁺⁴	0.48	0.0041 ZrOCl ₂ · 8H ₂ O	35	0.142
Na ₂ SO ₄	80.0	0.1762 Na ₂ SO ₄	2	0.035
Ba ⁺⁺	10.00	0.0396 BaCl ₂ · 2H ₂ O	6	0.238
(NH ₄) ₂ C ₂ O ₄	10.0	0.0220 (NH ₄) ₂ C ₂ O ₄ · H ₂ O	30	0.660
Ce ⁺⁺⁺	0.15	0.0010 Ce(NO ₃) ₃	33 (assumed)	0.033
H ₃ PO ₄	1.2 ml	0.0048 H ₃ PO ₄	7	<u>0.034</u>
				1.52

* Based on data given in Chemical & Engineering News Quarterly Report on Current Prices (First Quarter 1955).

sludge resulted from the treatment of 100 ml of the acid aluminum nitrate solution; the supernatant volume amounted to about 300 ml.

The procedures herein described have application in the treatment of intermediate level wastes. To effect higher decontamination factors, other procedures, such as ion exchange or solvent extraction, might be employed in conjunction with the coprecipitation methods described. For high level wastes, these decontamination factors are inadequate to permit release of these waste materials into the environment, but may be adequate to permit discharge of the liquid wastes to lined pits. The precipitates, which contain most of the activity, could then be retained in smaller tanks, thus reducing storage costs.

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