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ROUND LABORATORY
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RESEARCH ON REACTOR WASTE DISPOSAL
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INTRODUCTION

Mound Laboratory was authorized in January, 1949 to embark upon a long range and extensive study of the radioactive liquid waste disposal problem. This study was initiated because of the seriousness of the waste disposal problems at the various sites working on the atomic energy program.

Certain specifications should be set up before beginning the development of a process for handling a specific waste. These specifications depend, among other things, upon the species of radioactive elements with which we are dealing and the recovery value of these elements.

Such a process should require a minimum of shielding; the radioactive material, after processing, should occupy the minimum volume obtainable by practical methods, and the resulting solution sent to the environment should be below established environmental tolerances for both radioactive and nonradioactive materials.

In the absence of established environmental tolerances, the investigations reported herein have been directed for the most part in developing general methods of removing radioactivity from certain waste solutions to as low a value as practical.

The crib wastes appeared to be one of the most pressing problems. Of the crib wastes, the second decontamination-cycle supernatants after neutralization appeared to be the best on which to start because of their relatively uniform composition. This waste contained some fission products and small amounts of plutonium. Fortunately these wastes presented few problems in handling because their level of activity was low.

SUMMARY

Laboratory work on second decontamination-cycle wastes has centered mostly around ferrous sulfide precipitation, ferrous ferrocyanide precipitation, and preformed adsorbent methods. The best results have been obtained with ferrous sulfide as a precipitant in conjunction with an adsorbent. It has been possible to take the freshest second decontamination-cycle waste solution available and to remove all the activity countable by treating first with activated carbon in the presence of hydrogen sulfide and then precipitating ferrous sulfide three times under the same conditions. Equally good results were obtained by passing the same original solution through an activated carbon column and subsequently through an activated alumina column impregnated with ferrous iron.

The ferrous ferrocyanide precipitation method has removed as much as 97.9 per cent of the activity. This treatment may have application where process time and storage capacity are of little concern, such as in a cascade system.

On a continuous basis of processing second-cycle crib wastes, a possible method exists in a treatment consisting of silica gel adsorption, activated alumina adsorption, metallic iron scrub, ferrous ferrocyanide precipitation, neutralization, and filtration. The burial volume of concentrate from such a method is very low compared to the original waste volume, and expensive process-solution storage is not required in the processing operations. The activity level in the final supernatants could be maintained below 300 counts per minute per milliliter.

Decontamination of "fresh" first-cycle wastes is best accomplished by repeated scavenging with ferrous sulfide. Where column operation proves desirable, passage through silica gel will remove better than 99 per cent of the gross activity, thus permitting further processing to be accomplished with relatively little shielding. Repeated use of the silica gel appears possible by stripping with oxalic acid.

Ferrous sulfide scavenging of wastes has given decontamination factors of the order of 60, leaving residual activity of 5×10^6 counts per minute per milliliter. A significant amount of this residual activity is carried by a precipitation of ferrous hydroxide. Additional activity is removed with manganese dioxide yielding an overall decontamination factor of 1×10^4 .

SECOND CYCLE WASTE

One of the liquid waste streams sent to cribs at Hanford is the present separations process second decontamination cycle waste. This stream contains varying amounts of radioactive antimony, cesium, niobium, rare earths, ruthenium, strontium, tellurium, and zirconium. The exact amount of each element depends on the age of the stream at the time it is discharged to the ground. An analysis of the salt content is shown in Table 1. Radiochemical analyses of the three second decontamination cycle waste solutions received at Mound Laboratory are given in Table 2. Henceforth these solutions will be referred to as designated in the table. All counts in this report were made on a Nuclear Measurements Corp., FC-1, windowless chamber instrument at 50 per cent geometry. All mounts were made on glass slides. All counts given in this report are beta counts except where otherwise designated.

LABORATORY RESEARCH

Ferrous Sulfide Precipitation Process

The use of ferrous sulfide as a precipitant has been found quite effective as a decontaminant for radioactive waste solutions. It may be used singly or, as will be discussed later, in conjunction with other adsorbents.

For the study of the ferrous sulfide precipitation method alone, ferrous sulfate and hydrogen sulfide were added to Crib No. 3 solution at a pH of 2.8. After standing for 24 hours, the pH of these solutions was increased by the addition of sodium sulfide. The removal of activity by this precipitate over the pH range of from three to seven is shown in Figure 1. Also shown is the removal of the iron by the precipitation of the sulfide at the various pH's. The fact that all of the iron is not yet removed at the pH where the best activity removal occurs indicates that the phenomenon is one of adsorption and not coprecipitation.

Analyses of the supernatant solutions has shown that the activity remaining is due mainly to ruthenium, antimony, tellurium, and niobium. These elements form stable nitroso, oxo, or fluo complexes which may not be readily adsorbed by the ferrous sulfide precipitate. However, a reaction with a slow rate might occur in the presence of sulfide ion which would convert these complex ions to a form which might be adsorbed. The pH of the solution was adjusted to 3.2 and the iron and hydrogen sulfide added, and after varying intervals of time the pH was readjusted to 4.5. Curve A of Figure 2 shows the effect of the time delay. Apparently 24 hours standing time is sufficient to reduce the count to the lowest possible value at the pH of 3.2. Therefore, a series of experiments were carried out in which the solutions were saturated with hydrogen sulfide at a pH of 3.2, allowed to stand for 24 hours, raised to a pH of 4.5 with sodium sulfide, and then allowed to stand again for varying times before centrifugation. Curve B shows the improved results. The remaining count was still decreasing at 410 hours when the experiment was stopped. It was possible to increase the rate of post precipitation by heating

TABLE I

SALT CONTENT OF SECOND DECONTAMINATION-CYCLE WASTE

COMPONENT	PER CENT BY WEIGHT
WATER INSOLUBLE MATERIAL	0
NaN_3	6.3
NaH_2PO_4	6.0
NH_4NO_3	0.5
Na_2SO_4	0.5
$(\text{NH}_4)_2\text{SiF}_6$	0.01
$\text{Na}_2\text{Cr}_2\text{O}_7$	0.05
TOTAL	13.96

TABLE II

RADIOCHEMICAL ANALYSES OF SECOND DECONTAMINATION-CYCLE WASTE SOLUTIONS**

ELEMENT	CRIB No. 1 (CTS./MIN./ML.)	CRIB No. 2 (CTS./MIN./ML.)	CRIB No. 3 (CTS./MIN./ML.)
Ru^{106}	295	817	6.075
Cs^{137}	205	175	1.080
Sr^{90} , Te^{130}	80	346	3.240
RARE EARTHS	-	157	10.860
Zr^{90} , Nb^{90}	5	53	2.140
Sn^{90}	-	6	-
Pu	-	-	150 ⁺
GROSS BETA	800	2.000	29.000

** NO CORRECTIONS MADE FOR SELF ABSORPTION OF PRECIPITATES INVOLVED IN THE ANALYSES.

* ALPHA COUNT

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the solution to 85° C. Several hours of heat is equivalent to days of standing. The results of the heat treatment are shown in Figure 3.

It is known that the surface characteristics of iron sulfides change on aging, thus a study of the effect of age on the precipitates at various pH's was carried out. Iron and hydrogen sulfide were added to Crib No. 3 solution which had been adjusted to a pH of 3.5. After standing for one day the pH was adjusted to the desired value and allowed to stand for an additional thirty days. As can be seen in Figure 4, the optimum pH for the removal of activity is 4.4.

Under the optimum conditions plus a few modifications an effort was made to obtain the best possible results by this method. Each of the three second decontamination-cycle wastes received at the Mound Laboratory has been treated as described below to give exceptionally good results.

(Crib No. 1)

By reducing this waste solution with 10 milligrams of metallic iron per milliliter at a pH of 2.7, and then saturating with hydrogen sulfide at a pH of 4.5, the activity was reduced from 800 to 270 counts per minute per milliliter. A second treatment removed the remainder of the activity.

A second experiment was carried out with varying amounts of ferrous ion to supply a reducing medium. After addition of the iron, the solution was saturated with hydrogen sulfide, adjusted to a pH of 4.5, and allowed to stand for 18 hours. The process was repeated after centrifuging the precipitate and counting the solution. The effect of the iron concentration on both the first and second treatments is shown in Figure 5.

(Crib No. 2)

About 100 milliliters of this waste was passed through 50 grams of 100-mesh metallic iron at a flow rate of 0.1 milliliter per minute and a pH of 3.1. This solution was saturated with hydrogen sulfide. Only one treatment reduced the count from 2,000 to 40 counts per minute per milliliter.

(Crib No. 3)

A more drastic treatment was required to reduce the count of this waste to the lowest possible value. After shaking with activated carbon (Nuchar 000) for 18 hours at a pH of 5.9, the solution was saturated with hydrogen sulfide. This treatment reduced the beta count from 29,000 to 3,000 counts per minute per milliliter and the alpha count from 150 to 0 counts per minute per milliliter. The second step involved the addition of one milligram of ferrous iron per milliliter of supernatant after adjusting the pH to 2.5 with hydrochloric acid. The pH was then readjusted to 4.8 with sodium sulfide. This procedure reduced the counts further to 2,200 counts per minute per milliliter. Two repetitions of the second step brought the count down to zero.

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Ferrous Ferrocyanide Precipitation Process

The precipitation of ferrous ferrocyanide in a reducing medium has been found to be very effective in the removal of radioactivity from solution. The reducing medium is felt to be necessary to reduce the ruthenium present to the bivalent state which permits the precipitation of rutheno ferrocyanide. Cesium and rare earth metals are also removed almost completely by this method, probably by adsorption on the surface of the precipitate.

The method consists of the reduction of the second-cycle waste solution (Crib No. 3) with sodium sulfite and sodium dithionite. Potassium ferrocyanide is next added, followed by the addition of ferrous sulfate.

The reduction step is rather slow, as is shown in Figure 6. The reducing agents were allowed to stand in the waste solutions at room temperature for varying lengths of time before precipitating. The rate of the process can be increased greatly by heating as shown by Figure 7, with the best removal of activity being obtained with two hours of heating at 85° C.

The effect of the pH on the reduction of the solution, and consequent removal of activity is shown in Figure 8. Sodium dithionite is a stronger reducing agent in slightly acid and slightly basic solutions than in neutral solutions. Improved results are obtained at both the acidic and basic pH's, and the best results were obtained at a pH of 4.0. Here again the aging effect on the removal of activity is shown.

The results of the ferrous ferrocyanide precipitation method on the three second decontamination-cycle waste solutions received by Mound Laboratory are given in Table III.

TABLE III

DECONTAMINATION OF SECOND-CYCLE WASTES BY THE FERROUS FERROCYANIDE METHOD

CRIB SOLUTION No.	INITIAL ACTIVITY (CTS./MIN./ML.)	FINAL ACTIVITY (CTS./MIN./ML.)	PER CENT REMOVAL
1	800	70	91.3
2	2,000	300	85.0
3	29,000	600	97.9

Preformed Adsorbents

The decontamination of second decontamination-cycle waste (Crib No. 3) was investigated by shaking a given volume of waste with enough activated carbon (Nuchar 000) to give a concentration of four grams of carbon per liter of waste. The activity removal is

shown in Figure 9 as a function of the pH both in the presence and absence of hydrogen sulfide. The alpha count, which was 150 counts per minute per milliliter, was reduced to background. The increased acidity of the solutions at pH's of 2 and 3 may account for the poor activity removal at these values.

Comparative tests were run with silica gel and activated alumina on the same solution, and the results are also shown in Figure 9. The tremendously greater capacity of Nuchar 000 is evident since 40 times as much alumina and silica gel were used to obtain results which were not as good. Other carbons were tried as adsorbents for the removal of activity at various pH values as shown in Figure 10. The improvement with the use of hydrogen sulfide to saturate the solution prior to treatment with carbon is shown in Figure 11.

A very effective method has been developed for the removal of activity by successive treatments with adsorbents and hydrogen sulfide. A total of 100 milliliters of waste solution which had been adjusted to a pH of 4.3 was passed successively through each of three columns packed as follows: Column A, one-half gram Columbia Activated Carbon 60; Column B, two grams activated alumina impregnated with ferrous iron applied from a water solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; Column C, 3.7 grams of the same material as used in Column B.

The 100 milliliters of solution was divided into 10-milliliter portions, and each portion was passed through each column 10 times. The starting solution (Crib No. 3) had a count of 24,470 counts per minute per milliliter at this time due to decay. Table IV shows the results after each column. This starting count is lower than that given in Table II due to decay.

The counts on the first effluent solutions from Column C were down to about the background for the method used to mount the slides. Even after the last 10-milliliter portion of the 100 milliliters of the solution had passed through the column, only 350 counts per minute per milliliter remained.

TABLE IV
REMOVAL OF ACTIVITY FROM SECOND DECONTAMINATION CYCLE WASTE WITH ADSORBENTS

NO. OF 10-ML. PORTIONS	COLUMN A	COLUMN B	COLUMN C
1	1810	420	80
2	1600	680	40
3	1860	860	260
4	1600	950	240
5	2920	550	410
6	2950	660	390
7	3060	1320	370
8	3050	2050	350
9	3990	1450	330
10	2690	1510	350

Other Adsorbents Formed "in situ"

A limited amount of work has been done with other adsorbents, in particular, silicotungstic acid and luteo phosphomolybdic acid. The indications are that these materials used as precipitants would be good for decontamination of wastes. However, it is felt that the methods would not be competitive with other less expensive methods that would do an equally good job. With this in mind, investigation of these materials was discontinued.

BENCH SCALE RESEARCH

Five decontamination process methods on Crib No. 3 have been investigated individually and in various combinations on a scale larger than had been used in the laboratory. The apparatus was set-up for continuous operation and such items as midget centrifugal pumps, rotameters, continuous pH recorders, electric mixers, commercial filter cloths, etc. were employed where necessary to simulate plant operating conditions as nearly as possible. Flow rates were maintained at 100 milliliters per minute, and total outputs amounted in some cases to 20 liters.

These process methods are: silica gel adsorption, activated alumina adsorption, activated carbon adsorption, metallic iron scrub, and ferrous ferrocyanide precipitation. A brief description of each is as follows:

Silica Gel Adsorption

Pyrex glass columns 8 square centimeters in cross sectional area and 50 centimeters long filled with 175 grams of 6 to 12-mesh silica gel were used. The gel was held in place by a glass-wool plug at the bottom. A solution pH of about 5.0 was determined to be optimum by research for the gross removal of activity by the gel. It was found that the solution pH was raised slightly upon passage through the columns. For these reasons the pH of the feed was adjusted to 4.5 before the adsorption operation was begun.

Activated Alumina Adsorption

The same columns were used here as with the silica gel, but to obtain equivalent volumes of adsorbent, 250 grams of activated alumina was required per column. The alumina also raised the solution pH slightly within the optimum pH range for activity removal of between 5.0 and 6.0.

Activated Carbon Adsorption

Pyrex glass columns 2 square centimeters in cross-sectional area and 10 centimeters long were used. All types of carbon investigated in the laboratory seemed to show the same relative adsorptive ability with crib wastes, but only two were obtainable in mesh size compatible to column operations. These were dried alkaline leacher (8 to 40 mesh) and Columbia Carbon, grade 6G (8 to 14 mesh). The addition of sulfide ion to the

solution was found to improve gross adsorption within the optimum pH range of 4.0 to 5.0. With the sulfide ion added (1 gram Na_2S per liter) the Columbia carbon appeared to be the better of the two types.

Metallic Iron Scrub

The columns used for this operation had a cross-sectional area of 2 square centimeters and a bed height of 10 centimeters. The solution to be scrubbed was passed up through the bed, floating the powder, so that entrained solids would not load the bed and the generated hydrogen would not cause excessive channeling. The tops of the columns were expanded to reduce the flow rate through this section, minimizing carry over. Also, magnetic traps were incorporated in the line after each column to remove iron fines, thereby insuring the individuality of each column. A pH of 4.5 or lower is required not only for optimum activity removal but also to keep iron phosphate from forming in the columns. The phosphate, when formed in the columns, coats the iron powder and decreases the activity-removal efficiency. However, this coating is easily removed by acid washes. A solution pH of 4.0 for the feed and iron powder passing No. 50 and retained on No. 60 mesh U.S.B.F. screens was used. At a feed pH of 4.0, 300 ppm of iron was dissolved throughout the series of columns. This amount of iron was necessary in later precipitation methods when various combination processes were investigated.

Ferrous Ferrocyanide Precipitation

This operation was studied mostly in conjunction with the iron scrub process. To the effluent from the iron scrub columns was added 600 ppm (stoichiometric amount) or more ferrocyanide as $\text{K}_4\text{Fe}(\text{CN})_6$. Either a stoichiometric or excessive amount of ferrocyanide ion was used because of the greater difficulty of filtering iron phosphate which forms when less than this amount is added. The reagent was added in a mixing chamber, and the resulting thin slurry was neutralized to a pH of between 6.5 and 7.5 and filtered through commercial filter cloth.

Individually, each of the above processes reduced the activity level in the crib wastes from 37,000 counts per minute per milliliter (based on 100-lambda mount) to the following values:

TABLE V

DECONTAMINATION ACHIEVED BY VARIOUS PROCESSES

METHOD NO.	PROCESS DESCRIPTION	EFFLUENT ACTIVITY (CTS./MIN./ML.)
1	SILICA GEL ADSORPTION	4,600
2	ACTIVATED ALUMINA ADSORPTION	6,500
3	ACTIVATED CARBON ADSORPTION	2,190
4 & 5	IRON SCRUB AND $\text{Fe}(\text{CN})_6^{4-}$ PRECIPITATION	1,650

Chronologically, the activated carbon adsorption study was preceded by the other process methods. With the other four it was found that for the best activity removal on a continuous operational basis all were needed and that only one sequence of methods was preferred. A description of this sequence of operations for a typical 8-liter run is as follows:

TABLE VI
ACTIVITY REMOVAL ON A CONTINUOUS OPERATIONAL BASIS

STEP NO.	DESCRIPTION	FLOW RATE OR VOLUME	SOLUTION PH ORIG.	PH FINAL	FINAL ACTIVITY (CTS./MIN./ML.)
1	PH ADJUSTED TO 4.5	8 LITERS (TOTAL FEED)	7.6	4.5	37,000
2	THRU - 4 COLUMNS - SILICA GEL	100 ML./MIN.	4.5	5.5	4,890
3	THRU - 4 COLUMNS - ACT. ALUMINA	100 ML./MIN.	5.5	6.0	4,200
4	PH ADJUSTED TO 4.5	8 LITERS (TOTAL SOLN.)	6.0	4.5	4,200
5	THRU - 6 COLUMNS - FE POWDER	100 ML./MIN.	4.5	5.9	810
6	600 PPM $\text{Fe}(\text{CN})_6^{4-}$ ADDED	100 ML./MIN.	5.9	5.9	300
7	PH ADJUSTED TO 6.8	100 ML./MIN.	5.9	6.8	260

In the above scheme of processing, sampling was continuous, and the activity levels shown represent composites of the samples taken after each operation shown. Intermittent sampling after the individual columns in the scheme indicated that no loss in efficiency of activity removal was experienced with the volume of waste processed. The ferrous ferrocyanide precipitate formed represented the following volumes and weights when compared with the original waste:

TABLE VII
PER CENT OF ORIGINAL WASTE IN FERROUS FERROCYANIDE PRECIPITATE

SETTLED VOLUME (PER CENT)	CENTRIFUGED VOLUME (PER CENT)	FILTERED VOLUME (PER CENT)	FILTERED WEIGHT (PER CENT)
6.8	3.4	0.1	0.4

At a later date studies were made on activated carbon adsorption with crib waste. Because of time considerations this was not studied in conjunction with the other four methods. In this investigation 4 liter batches were passed through six columns of Columbia Carbon 60, and under the best conditions good activity removal was obtained (2190 counts per minute per milliliter). Small samples of the effluents from these runs were subjected to a ferrous ferrocyanide and ferrous sulfide treatment in the laboratory. By either of these methods the activity levels were further reduced to below 300 counts per minute per milliliter.

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FIRST-CYCLE NEUTRALIZED WASTE

The feasibility of applying co-precipitation and adsorption processes for decontaminating relatively "fresh," highly-active wastes has been briefly investigated.

Radiochemical assay techniques indicated the following activity composition:

TABLE VIII

RADIOCHEMICAL ASSAY OF FIRST-CYCLE NEUTRALIZED WASTE

ELEMENT	(CTS./MIN./ML.)
Ru ¹⁰⁶	245,000
Cs ¹³⁷	130,000
Sr ⁹⁰ , Te ¹²⁶	1,000,000
RARE EARTHS	5,700,000
Zr ⁹⁵ , Nb ⁹⁵	85,300,000
Sr ⁹⁰	35,000
Pu	30.40

The high percentage of the short-lived fission products, zirconium and niobium, confirms the freshness of the solution.

Treatments found to offer the most promise for this waste are:

A. Formation of ferrous sulfide by

1. contacting with metallic iron in presence of sulfide, adjusting to optimum pH (4.0 - 5.0) for maximum activity removal
2. addition of ionic iron followed by adjustment to optimum pH with sodium sulfide.

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B. Passage through silica gel columns.

C. Passage through silica gel columns followed by precipitation "in situ" of ferrous sulfide.

TREATMENT A - FORMATION OF FERROUS SULFIDE

1. The original waste solution (pH 6.1) was acidified to a pH of 2.5 to 3.0 with hydrochloric acid. Eight milligrams of approximately 100-mesh metallic iron per milliliter was added. After saturation with hydrogen sulfide, the waste solution was placed on a wrist-action shaking machine for five hours. The pH was adjusted to 4.5 with caustic, the solution centrifuged, and the supernatant counted. This treatment was repeated four times, yielding an overall decontamination factor of 5.6×10^5 (Table IX).

TABLE IX

SUCCESSIVE FERROUS SULFIDE PRECIPITATIONS FROM FIRST-CYCLE WASTES

TREATMENT	(CTS./MIN./ML.)	PRECIPITATE FORMED BY CONTACTING METALLIC IRON IN PRESENCE OF H_2S	OVERALL DECONTAMINATION FACTOR	PRECIPITATE FORMED FROM IONIC IRON AND Na_2S	OVERALL DECONTAMINATION FACTOR
				(CTS./MIN./ML.)	
1ST FES PPT.	415.890		216	96.980	928
2ND FES PPT.	7.940		1.1×10^4	20.870	4.3×10^3
3RD FES PPT.	3.060		2.9×10^4	8.900	1.0×10^4
4TH FES PPT.	160		5.6×10^5	(No 4TH STEP)	

Under these contacting conditions a substantial portion of the iron is not dissolved. It is significant that no shielding is required after the first ferrous sulfide separation, no beta-gamma radiation being detectable with the "Cutie Pie" survey meter.

2. Similar results are obtained when the iron is introduced in the ionic form ($FeSO_4 \cdot 7 H_2O$) and ferrous sulfide precipitated by adjusting the pH to 4.5 with sodium sulfide. Time required for dissolving metallic iron is not necessary following this procedure. The data recorded in Table IX were obtained with eight milligrams ionic iron per milliliter, when the solution is allowed to stand in contact with the ferrous sulfide precipitates for approximately one half hour.

The optimum amount of iron required has not been established for this particular waste. In general, greater decontamination will be achieved with repeated treatments with smaller amounts of iron per treatment than if a large amount is used for one treatment.

No analysis has been made of the residual activity. The amount remaining is so small that it is not believed to be any one constituent, but a mixture conforming roughly to the original in composition. If such is the case, thorough scavenging with ferrous sulfide under the proper ionic environment might be expected to eliminate this activity. Evidence supporting such a view is obtained from the following data:

Waste Solution

First-cycle waste was diluted 1/200 with Crib No. 2 solution gassed with hydrogen sulfide at pH 3.2, and allowed to stand 24 hours. Dilution with a crib-waste solution was made to maintain a constant inactive salt content, since analysis of second-cycle and first-cycle neutralized Hanford wastes has indicated a fairly uniform macro-chemical composition. After separating the supernatant from the precipitate which formed, the solution counted 175,600 counts per minute per milliliter.

Treatment

The pH is adjusted to 0.35 with concentrated hydrochloric acid. Varying amounts of approximately 100-mesh metallic iron are then added, and the sample is placed on the shaking machine for five hours. The pH is then adjusted to 4.5 with caustic, and the supernatant is counted. The results are:

TABLE X

REDUCTION OF ACTIVITY WITH IRON POWDER

MG. FE/ML.	CTS./MIN./ML.
1	26,600
3	13,480
5	2,040
10	0

TREATMENT B - PASSAGE THROUGH SILICA GEL COLUMNS

Successive 10-milliliter portions of neutralized first-cycle waste (pH 6.1 as received) were passed over one milliliter of 20 to 65-mesh Davison's silica gel. This gel had been washed twice with 0.5 molar nitric acid, the cloudy supernatants having been decanted. A 25-milliliter buret with a glass wool plug to support the silica gel was used as a column. The column, glass wool support, and all glass containers were coated with "Dry Film" vapor (dichlorodimethyl silane) to prevent any adsorption of activity on glass surfaces. Each 10-milliliter portion was passed over the silica gel five times at a flow rate of about one milliliter per minute. Activity remaining in each of the 10-milliliter portions put through the column was as follows:

TABLE XI
ACTIVITY REMOVAL BY SILICA GEL

SAMPLE	CTS./MIN./ML. (REMAINING)	OVERALL DECONTAMINATION FACTOR
1ST 10 ML. PORTION THROUGH	113×10^3	795
2ND 10 ML. PORTION THROUGH	334×10^3	269
3RD 10 ML. PORTION THROUGH	603×10^3	149
4TH 10 ML. PORTION THROUGH	772×10^3	117
5TH 10 ML. PORTION THROUGH	103×10^3	87

Capacity of the gel falls off as throughput increases. The sorbed activity, however, can be stripped with a small volume of hot oxalic acid, making possible its reuse. No shielding would be required for subsequent treatments of the first 20 milliliters passed through such a column; relatively little shielding would be necessary for the remaining 30 milliliters.

TREATMENT C - SILICA GEL COLUMN FOLLOWED BY FERROUS SULFIDE SCAVENGING

First-cycle neutralized waste diluted 1/200 with Crib No. 2 solution was passed through a silica gel column as previously outlined. Gross activity remaining was 6,030 counts per minute per milliliter.

This solution was brought to a pH of 2.5 with hydrochloric acid, one milligram of approximately 100-mesh metallic iron per milliliter was introduced, and shaken for two hours. On neutralization to a pH of 4.5 with sodium sulfide, activity in the supernatant was reduced to 720 counts per minute per milliliter.

Two additional ferrous sulfide precipitations brought the count to 420 and 90 counts per minute per milliliter, respectively.

Ferrous ferrocyanide precipitations have proved ineffectual in removing gross activity from first-cycle neutralized wastes. Adsorbing agents such as activated carbon and clays have not shown as much promise as silica gel or ferrous sulfide scavenging for treatment of this waste.

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TABLE XII
RADIOCHEMICAL ASSAY OF WASTES

ELEMENT	CTS./MIN./ML.
Ru ¹⁰⁶	3,308,000
Cs ¹³⁷	26,866,000
Sr ⁹⁰	145,000
RARE EARTHS	3,298,000
Zr ⁹⁵	430,000
Te ¹²⁶	53,000
Sr ⁸⁹	432,000
Nb ⁹⁵	72,000
Pu	680

The total observed direct beta count at 1/100 dilution was 3.4×10^7 counts per minute per milliliter.

Ions making up the inactive salt content (total solids 10 per cent) are as follows:

TABLE XIII
SALT CONTENT OF WASTES

ION	CONCENTRATION (MG./ML.)
SODIUM	31.1
NITRATE	175.7
PHOSPHATE	9.7
SULFATE	21.3

Treatment of the waste by simple neutralization forms a white ferric phosphate precipitate up to about the neutral point after which ferric hydroxide begins to form. Either precipitate removes about 65 per cent of the gross activity and all the plutonium.

Our best decontamination results were obtained with a combination of scavenging agents, such as ferrous sulfide, ferrous hydroxide, and manganese dioxide, according to the procedure in Table XIV.

Absorbing agents such as activated carbon, silica gel, activated clays, and activated alumina removed no activity from the two molar acid waste. At pH's from 1.0 to 11.5, after the solids were centrifuged off, some additional activity was removed. The best results, however, left solutions having about 1.0×10^7 counts per minute per milliliter.

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Precipitation of ferrous ferrocyanide twice in succession under reducing conditions, decreased the count to 2.1×10^5 counts per minute per milliliter (Decontamination Factor 162), a reduction equivalent to that obtained with two ferrous sulfide precipitations. Since ferrous ferrocyanide precipitation gave poor results with "fresh" first-cycle wastes containing better than 90 per cent zirconium and niobium, it is concluded that ferrous sulfide scavenging is more effective as a general scavenging agent, and is particularly effective on fresh wastes.

TABLE XIV

DECONTAMINATION PROCEDURE FOR WASTES

STEPS IN TREATMENT	CTS./MIN./ML. REMAINING*	OVERALL DECONTAMINATION FACTOR
A. 1ST FeS PPT. ADD 3 MG. IONIC IRON AS $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$. BRING PH TO 1.0 WITH NaOH . ADJUST PH TO 4.0 WITH Na_2S . STAND 3 HR.	650,000	52
B. 2ND FeS PPT. ADJUST PH TO 1.0 WITH HNO_3 AND REPEAT STEP A.	500,000	68
C. $\text{Fe}(\text{OH})_2$ PPT. ADJUST PH TO 10.0 WITH NaOH REMOVING REMAINING IRON.	20,000	1.7×10^5
D. MnO_2 PPT. ADD 100 PPM. Mn AS KMnO_4 . REDUCE TO MnO_2 WITH NaHSO_3	3,000	1.1×10^4

* MOUNT MADE FROM 1/100 DILUTED SOLUTION TO AVOID SELF-ABSORPTION BY INACTIVE SALT.

PLUTONIUM IS REMOVED TO BACKGROUND COUNT BY THE FIRST FERROUS SULFIDE PRECIPITATION.

THE TOTAL CENTRIFUGED SOLIDS RESULTING FROM THIS SERIES OF TREATMENTS IS ESTIMATED TO BE OF THE ORDER OF FIVE PER CENT, CORRESPONDING TO A 1 TO 20 VOLUME REDUCTION.

FORMATION OF AN IRON SULFIDE PRECIPITATE WITH THE FERRIC IRON ALREADY PRESENT IN THE SOLUTION PROVED INEFFECTIVE.

A DIRECT MOUNT OF THE UNDILUTED SOLUTION AFTER STEP D GAVE 920 COUNTS PER MINUTE PER MILLILITER, INDICATING A SELF-ABSORPTION FACTOR OF THREE. THIS UNUSUALLY HIGH SELF-ABSORPTION FACTOR POINTS TO THE PRESENCE OF VERY SOFT RESIDUAL BETA ACTIVITY.

NO SHIELDING IS REQUIRED FOR SUBSEQUENT PROCESSING AFTER THE FIRST FERROUS SULFIDE SEPARATION.

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FIGURE 1

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FIGURE 2

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FIGURE 9

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FIGURE 10

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