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CATEGORY - WASTE DISPOSAL

Contract Number AT-33-1-GEN-53

MOUND LABORATORY
Operated By
MONSANTO CHEMICAL COMPANY
MIAMISBURG, OHIO

QUARTERLY REPORT

FOR

LIQUID WASTE DISPOSAL RESEARCH

JANUARY - FEBRUARY - MARCH, 1950

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Date: April 1, 1950

Approved By:

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INTRODUCTION

At the present time three samples of second-cycle neutralized wastes and one sample of first-cycle neutralized wastes have been received from Hanford. Analysis of these solutions indicate a fairly uniform macro-chemical composition. The relative radioactive composition of the waste solutions depends mainly upon the age of the individual solutions. First-cycle wastes have nearly ten thousand times as much activity as second cycle wastes.

Because the fresher wastes contain more of the short-lived fission products, especially zirconium and columbium, any process developed to decontaminate current wastes will be able to decontaminate stored wastes. For this reason we will concentrate future effort more and more on the fresher wastes. Since, furthermore, the relative composition of the first-cycle wastes is essentially that of the second-cycle wastes, we can use second-cycle neutralized wastes as a dummy solution and spike these wastes with first-cycle wastes.

Experimental work by the Research Group consisted mainly in adapting better analytical methods, in refining previously reported processes, and in investigating the possibility of using silica gel and tannic acid to remove zirconium and columbium from waste solutions.

The Design Group devoted their efforts during this period to the design, installation, and operation of a small scale pilot unit which was used to test on a continuous basis the various decontamination processes developed by research. The apparatus was built in such a way that each method could be tested separately or in combination with others. For this

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work three-year-old second-cycle crib waste was used as the starting material, although in several instances this waste was spiked with small amounts of one-year-old first-cycle waste to increase the variety and level of activities present in the feed material.

The preliminary runs made to date with this apparatus were designed primarily to show the feasibility and practicality of the decontamination processes rather than to ascertain the most favorable conditions for, or to obtain design data concerning each. The decontamination methods investigated so far, some more fully than others, include: the iron scrub, ferrous ferrocyanide precipitation, sodium hydrosulfite reduction, tannic acid precipitation, attapulugus clay absorption, silica gel absorption, sulfide precipitation, and neutralization.

SUMMARY

A complete radiochemical analysis has been made on the sample of first-cycle neutralized waste. A gravimetric analysis has also been made on the sludge in the sample of first-cycle waste.

Antimony has been shown to be in the pentavalent state in the waste solutions.

Both tannic acid and silica gel can be used to remove zirconium and columbium from the neutralized wastes. In addition to zirconium and columbium, silica gel also adsorbs some cesium, ruthenium, and rare earth elements. By the addition of sodium hydrosulfite and sodium sulfite to waste solutions, a greater removal of activity is obtained by the precipitation of ferrous ferrocyanide. An improvement in the method of precipitating ferrous sulfide has been made.

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In all of our experiments the greatest difficulty is experienced in the removal of antimony and ruthenium.

With the three-year-old second-cycle waste a combination process involving an iron scrub, a ferrous ferrocyanide precipitation, and neutralization appears most feasible. Process time is a minimum and hold up of large volumes of solutions unnecessary. With this combination a reduction in activity of from 2000 to 250 counts per minute per milliliter was consistently attained, a reduction in volume of 500 to 1 (original volume of waste per burial volume) was accomplished, and no processing difficulties were apparent with the scale of equipment used. Each of the three operations was indispensable although the order in which they were performed had no effect on activity removal, except that neutralization must, of course, follow the iron scrub.

When a sodium hydrosulfite reduction was followed by a ferrous ferrocyanide precipitation, equally good decontamination was found. However, the sulfite must be added one half to one hour prior to the cyanide precipitation, and decontamination was not complete until approximately three days had elapsed. Such a process could not be considered as a continuous one but might be applicable to the current Hanford waste procedure to reduce tankage time.

When an iron scrub was carried out in the presence of hydrogen sulfide, followed by a neutralization step again, equally good reduction in counts was experienced at low feed pH's. However, the amount of precipitate was large, and the sulfides formed presented difficult solid - liquid separation problems.

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The iron scrub-ferrocyanide-neutralization process when applied to the spiked second-cycle crib waste (three years old) reduced the activity from 125,000 to 23,000 counts per minute per milliliter and a second treatment from 23,000 to 5,000. Analysis indicated that those activities present in the second-cycle crib waste were reduced to the same order of magnitude (200 to 300 counts per minute per milliliter) and zirconium, columbium, and the rare earths represented the remaining activity.

Attempts to employ a tannic acid precipitation in conjunction with the aforementioned process improved the removal of zirconium, columbium, and the rare earths to only a slight extent. A small amount of tannic acid did, however, improve flocculation of the ferrous ferrocyanide precipitate.

The one attempt to remove zirconium, columbium, and the rare earths by absorption on attapulgus clay and another on silica gel look promising. When the effluents from these two operations were subjected to the iron scrub, ferrous ferrocyanide precipitation, and neutralization process, a reduction in activity of 59,000 to 350 counts per minute per milliliter with the clay and a reduction of 37,000 to 300 counts per minute per milliliter with the gel was obtained.

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MANPOWER ANALYSIS

Twenty-nine man months were devoted to this problem this quarter.

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DETAILED REPORT

Analysis

Beta Counting

Unless otherwise mentioned, all counting was done in a Nuclear Measurements Corporation PC-1 windowless chamber large enough to admit a two-inch circular slide upon which a 0.50 milliliter sample was mounted. No corrections have been made for self-absorption.

Radiochemical Analysis

In the body of this report reference will be made to each of the samples of first-cycle and second-cycle waste solutions which have been

received. For this reason the analysis of each of these solutions is listed in Table I. As it would be expected, the fresher solutions for a given cycle contain the most activity.

The results of a gravimetric analysis of the sludge contained in the sample of first-cycle neutralized wastes is recorded in Table II. In view of the fact that the total insoluble solids formed in the present Hanford process represent about one per cent by volume of the total liquid wastes and that silica accounts for twelve per cent of the water insoluble material in the liquid wastes, it does not appear to be worthwhile to further concentrate the beta-active elements in the sludge at this time.

At the present time we find that the sulfuric acid-permanganate¹ distillation process for the analysis of ruthenium is more satisfactory than the perchloric acid distillation method.

By using the method of Willard and Furman² we have been able to show that the antimony in the waste solutions is in the pentavalent state. The reduction of pentavalent antimony is difficult in solutions of intermediate pH. Furthermore, unless trivalent antimony is immediately removed, it will be quickly oxidized to the pentavalent state. This is the explanation of the difficulty we have encountered in the removal of antimony from the neutralized wastes.

Process Development

Adsorption on Silica Gel

In our previous quarterly report³ we reported the same results as observed by Weisblatt and Bench⁸ for the removal of cesium by fuller's earth. Weisblatt and Bench were using metal waste solutions while we used second-cycle waste solutions.

In the report ORNL 49-9-178 on the use of silica gel for the removal of zirconium and columbium from dissolver solutions, Baldwin and others⁴ report an optimum pH range of -0.3 to 2.5. Poor results were obtained at pH values greater than 2.5. We have found, however, that zirconium and columbium can be removed by silica gel from neutralized waste solutions. Moreover, at the lower pH's recommended by Baldwin, we find that no activity is removed. The difference is due to the fact that Baldwin is concerned with fresh redox wastes while we are working with aged bismuth phosphate wastes.

We have studied the properties of silica gel by placing 10 milliliters of 20 to 65 mesh gel, which has been treated as recommended by Baldwin, in a 50-milliliter burette and passing the neutralized wastes over the gel at a flow rate of 0.2 milliliter per minute. The results for eleven 50-milliliter batches of second-cycle waste (original observed activity 2,000 counts per minute per milliliter) spiked with first-cycle waste (final observed activity 750,000 counts per minute per milliliter) is shown in Figure 1. It is apparent from this curve that the fresh silica gel has a slightly greater capacity than the used gel and the capacity of the gel has not yet been reached. Upon examination of the column it was found that nearly all of the activity was in the first centimeter of the gel.

In Table III we have recorded the results obtained by passing 50 milliliters of Crib No. 3 (Table I) through a column of silica gel at three different pH's.

Coprecipitation With Tannic Acid

Tannic acid has been used as an analytical reagent for zirconium and columbium.⁵ The following set of experiments were carried out to determine

whether or not it would be applicable with the first-cycle and second-cycle neutralized wastes.

In these experiments the solutions used were second-cycle neutralized wastes (initial activity 2,000 counts per minute per milliliter) spiled with first-cycle neutralized wastes (final observed activity 36,000 counts per minute per milliliter). Preliminary experiments indicated that better results were obtained when the tannic acid is added to the waste solutions at a pH of 2 and when the final precipitation is carried out at a pH of 8. Slightly better decontamination is obtained when the waste solutions are contacted for five hours with iron filings and tannic acid, than by contacting with tannic acid and ionic iron. This difference is easily seen by reference to the data in Table IV where the reagents used and the percentage activity removed after adjusting to a pH of 8 are recorded.

From the curve in Figure 2A it can be seen that best results are obtained if the tannic acid is allowed to stand in the waste solutions at a pH of 2 for a short time before ferrous tannate is precipitated. The curve in Figure 2B shows that under the conditions of our experiments, that is, high phosphate content and a final pH of 8, a large excess of ferrous iron is required in order to obtain best results. In this case the final precipitate consists mainly of ferrous phosphate.

Analysis of the supernatant solutions shows that 50 per cent of the remaining activity consists of cesium (which has been consistently removed by carrying out a ferrous ferrocyanide precipitation on these supernatants, while remaining activity is due to antimony and ruthenium. Thus, zirconium and columbium can be removed by this method.

Decontamination Using Ferrous Sulfide

Various methods have been used to precipitate ferrous sulfide in second-cycle neutralized wastes. The results of these methods are tabulated in Table V. In every experiments listed one milligram per milliliter of ferrous iron was used. Method 1 consists in adding the iron to the waste solution, adjusting the pH to 11 and then passing in hydrogen sulfide. Method 2 consists in passing hydrogen sulfide into the wastes solution at a pH of 3.6 and, after adding the iron, raising the pH to 6.5. Both of these methods are discussed in the previous quarterly report.⁶ Method 3 is carried out as follows:

1. Adjust the pH of the waste solution to 9.3 with 50 per cent sodium sulfide.
2. Allow the solution to stand 12 to 18 hours.
3. Adjust the pH to 3.5 with concentrated hydrochloric acid.
4. Add the calculated amount of ferrous ammonium sulfate.
5. Allow the solutions to stand for several hours.
6. Adjust pH to 4.5 to 5.3 with sodium sulfide.

In order to further reduce the activity of a solution of second-cycle neutralized wastes, whose initial activity of 2,000 counts per minute per milliliter had been boosted to 750,000 counts per minute per milliliter by the addition of first-cycle wastes and then reduced to 20,200 counts per minute per milliliter by passage through a column of silica gel, it was necessary to increase the acidity of the waste solution to half-molar acid and to agitate this acid solution with 10 milligrams per milliliter of iron

filings. At the end of five hours the pH of the solution was adjusted to 5 to 5.5 with sodium sulfide. When this procedure was repeated using fresh iron filings, the final activity was 150 counts per minute per milliliter.

Decontamination By Ferrous Ferrocyanide

In the previous quarterly report⁷ the formation of ferrous ferrocyanide as a means for removing cesium and ruthenium was discussed in detail. It was found that, whereas 15 parts per million of ferrous ferrocyanide would remove 99 per cent of the cesium from Crib No. 1, 600 parts per million were required to remove 99 per cent of the cesium from Crib No. 2, (for radiochemical analysis of these solutions, see Table I). The differences were found to be due to the higher ammonium ion content in Crib No. 2. Similarly because of the differences in composition of the two solutions, 72 per cent of the gross activity could be removed from Crib No. 1 by 3,000 parts per million of ferrous ferrocyanide whereas only 50 per cent of the gross activity could be removed from Crib No. 2 by the same amount of ferrous ferrocyanide.

In all of the previous work sodium sulfite had been used as a reducing agent to prevent the formation of ferric ferrocyanide. It has been found that the use of both sodium sulfite and sodium hydrosulfite, together, increased the amount of activity removed from Crib No. 2. At the same time smaller amounts of ferrous ferrocyanide are required. In Table VI are recorded the results obtained by adding sodium sulfite alone and sodium sulfite and sodium hydrosulfite together to waste solutions at a pH of 2. In each case 320 parts per million of ferrous ferrocyanide was precipitated after adjusting the pH to 6. One important conclusion from these experiments

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since the reactions involving both hydrosulfite and ferrocyanide ions are slow is that the longer the reagents are allowed to stand the more activity is removed.

The increased activity removal obtained by using sodium hydrosulfite is probably due to its stronger reducing power and the simultaneous formation of sulfides.

In the tannic acid, ferrous ferrocyanide, and ferrous sulfide methods the remaining activity has been shown to be due mainly to ruthenium and antimony.

BENCH SCALE WORK

The small scale experimental pilot unit used to test the worth of the various decontamination methods in continuous operation is shown in Figure 3. The two 4-liter feed bottles, used alternately to allow continuous flow, were located approximately eight feet above the rest of the apparatus. This hydraulic head allowed flow rates up to six gallons per hour through the system. It was found that the iron scrub columns functioned better at a flow rate of 100 milliliters per minute or 1 1/2 gallons per hour. The iron scrub operation received more attention than the other decontamination methods because it was considered the most favorable method for the removal of certain active metallic ions and was a good reducing agent for these ions. Also, the ferrous ion was required as a precipitating agent with ferrocyanide and tannic acid, and the iron scrub seemed the best way of introducing this reagent.

The work using this pilot unit can be classified into two parts that involving three-year-old second-cycle crib waste and that involving the three-year-old crib waste spiked with small amounts of one-year-old first-cycle waste.

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A. Three-Year-Old Second-Cycle Crib Waste

This waste when assayed on the Nuclear Measurement Corporation PC-1 counter contains 1,000 counts per minute per 500 lambda mount or 2,000 counts per minute per milliliter. When the geometry factor of this instrument (50 per cent) and self absorption is considered the absolute activity of this waste amounts to very nearly 10,000 disintegrations per minute per milliliter. However, in this report all counts listed or referred to are those obtained by doubling the direct count of a 500 lambda mount of the solutions on a 2-inch circular glass slide in the PC-1 counter

The methods studied in attempts to decontaminate this waste were the iron scrub, ferrous ferrocyanide precipitation, reduction with sodium hydrosulfite, sulfide precipitation, and neutralization

1. Iron Scrub

Each of the six columns used for this operation have a cross-sectional area of 2 square centimeters and a bed height of 10 centimeters. The solution to be scrubbed was passed through the bed, floating the powder, so that entrained solids would not load the bed, and the generated hydrogen bubbles would not cause excessive channeling. Early experiments indicated that six columns were sufficient for the complete removal of those active elements removable by this reagent. Magnetic traps were incorporated in the line after each column to remove iron fines, thereby insuring the individuality of each unit. Samples were taken after every column from which activity, dissolved iron, and pH determinations were made.

After the optimum flow rate was ascertained by visual inspection of column operation, a series of tests was performed to determine the effect on

activity removal and iron dissolution of variations in the pH of the feed solution. The results of these tests are shown in Figures 4, 5, and 6. The iron powder used was that which passed 50 and was retained on 60 Mesh U.S.B.S. screens. Powder of finer mesh investigated earlier yielded a greater percentage carry over due to entrainment and a much greater rate of dissolution. Coarser powder will be studied at a later date.

It was found by a gamma survey of the columns after a considerable volume of waste had been passed through the series that each column in the series was approximately 70 per cent efficient in that 70 per cent of the removable activity available to each column was removed by that column. Also, often a volume of waste (20 liters) equivalent to 1,000 times the volume of the iron powder in one column had been passed through the series, the first column in the series was still removing over 50 per cent of the available activity. At this point some passivity was noted in the column. After 1,500 volumes, almost complete passivity was indicated by the lack of hydrogen evolution and the lack of color change due to the reduction of chromates present. The tests with this batch of iron was halted at this point although over 40 per cent of the available activity was being removed by the first column. No attempts were made to depassivate the iron. Mounts on acid (dilute hydrochloric acid and nitric acid) and water washes showed little activity removal from the iron by this operation.

At the lower feed acidities (above pH 4.5) iron phosphate formed in the columns, while in those at a pH of 4.5 or lower, the phosphates formed after passage through the columns. The phosphate, when formed in the columns, coated the iron powder and decreased activity removal efficiency. The coating was easily removed by acid washes.

The iron scrub operation was studied later in conjunction with other decontamination processes.

2. Ferrous Ferrocyanide Precipitation

This process was first studied in conjunction with the iron scrub operation. The first runs were made by introducing potassium ferrocyanide at 600 parts per million (amount found necessary by research) to the influent acidified to a pH of 4.5. At this pH approximately 300 parts per million ferrous ion (stoichiometric amount) would be dissolved by passage of the solution through the six iron columns at a flow rate of 100 milliliters per minute. When neutralized to a pH of between seven and eight, the effluent had an activity count of 200 to 300 counts per minute per milliliter as compared to an original feed count of 2,000 counts per minute per milliliter. Under these conditions, however, the cyanide precipitate coated the iron powder, and activity removal was thus reduced after eight to ten liters of solution had been passed through the columns. Acid rinses would not remove this coat easily. Therefore, later runs were made by adding potassium ferrocyanide to the effluent from the iron scrub operation as shown in Figure 7 (Treatment A and D).

Several runs were made, not with a stoichiometric amount of ferrous ion and ferrocyanide ion, but with an excess of each. The greater amount of ferrous ion was obtained by performing the iron scrub at a pH lower than 4.5. No improvement in activity removal was experienced in either case.

Because of the difficulty of filtering iron phosphate, either a stoichiometric or excessive amount of ferrocyanide ion was used in later runs.

These runs were designed specifically to ascertain the weights and volumes of the precipitates formed. The results are given in Table VII.

Filtration of the ferrous ferrocyanide precipitate was accomplished much more easily than the other iron precipitates studied to date.

3. Sodium Hydrosulfite Reduction

An investigation was made on the use of a strong reducing agent in conjunction with the iron scrub-ferrocyanide-neutralization process. Varying amounts of sodium hydrosulfite was added to the influent to this process but no improvement was noted in activity removal. Another run in which the iron columns were by-passed was made with 600 parts per million of this reagent added to learn the necessity of the iron scrub under these conditions. Here the count was reduced from 2,000 to 730 counts per minute per milliliter, only a slight improvement over a cyanide precipitation without this reducing agent and much poorer than when the iron scrub was used. Work in the laboratory did show, however, that the counts could be reduced from 2,000 to 300 counts per minute per milliliter with this reagent in conjunction with the cyanide precipitation if the sulfite was added one-half to one hour before the cyanide precipitation was performed and if this precipitate was allowed to contact the solution for at least 64 hours after the precipitation operation. This scheme could not be used practically under continuous processing conditions but might find application where settling and storage tanks are in current use for waste handling.

4. Hydrogen Sulfide Precipitation

Three runs were made using a feed saturated with hydrogen sulfide in which waste thus treated was subjected to an iron scrub and neutralization.

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Poor results were obtained in the first run where the gas was introduced just prior to the scrub. When the gas was allowed to remain in contact with the solution 24 hours prior to the scrub operation, decontamination equivalent to the cyanide precipitation process was obtained. However, a much lower pH (2 to 3) was required, which resulted in a large quantity of iron dissolving and subsequently left a very high percentage of solids (as sulfides) to be removed from the liquid. The sulfides coated the powder and also presented serious solid-liquid separation problems.

5. Neutralization

Very early in this work one test was made to determine the optimum pH for neutralization. The effluent from an iron scrub-ferrous ferrocyanide process was divided into three portions and each was neutralized to a different pH with sodium hydroxide. The results are shown in Table VIII.

Consequently, all later effluents in these investigations were neutralized to a pH as near 7.5 as possible.

6. Decontamination

Analysis of the crib waste used in these investigations is shown in Table I. The decontamination accomplished by the various methods and combination of methods described above is shown graphically in Figure 7. The lower limit of activity remaining after each of these processes appears to be between 200 and 300 counts per minute per milliliter. Analysis of the effluents that are within this range indicates that 80 per cent of the remaining activity is antimony-95 and the rest ruthenium-107 in every case.

B. Spiked Three-Year-Old Second-Cycle Crib Waste

In order to increase the variety and amounts of activity in feed solutions one to three milliliter of one-year-old first-cycle waste was added per liter of the three-year-old second-cycle crib waste. Influent counts of 37,000 counts per minute per milliliter to 125,000 counts per minute per milliliter were thus obtained. Analysis of the first-cycle waste is given in Table I.

When these spiked solutions were subjected to the iron scrub-ferrous ferrocyanide-neutralization process under the optimum conditions determined for the less active second-cycle crib waste, the count was reduced from 125,000 counts per minute per milliliter to 23,000 counts per minute per milliliter. This process repeated on the same solution lowered the count from 23,000 counts per minute per milliliter to 5,000 counts per minute per milliliter. Analysis showed that zirconium, columbium, and the rare earths represented the largest majority of the remaining activity, and when these activity counts were subtracted, the resulting activity was 80 per cent antimony-95 and 20 per cent ruthenium-107 and was in the order of 300 counts per minute per milliliter.

Several runs were attempted using tannic acid in conjunction with this process. Decontamination was improved to the extent that one pass through the system reduced the activity content of the waste to the same order of magnitude that was obtained with two treatments without this reagent. To improve activity removal by this method, varying amounts of tannic acid were used (50 to 500 parts per million) and lower feed pH's were attempted

Little or no gain was experienced. It was found that when 50 parts per million of tannic acid was added, better flocculation was obtained with the ferrous ferrocyanide precipitation. This step was not of any value, however, as the tannates formed presented serious filtration problems.

Work done by the Research Group indicated attapulgus clay or silica gel was efficient for the removal of zirconium, columbium, and the rare earths. Consequently, the iron in the scrub columns was replaced with these materials and two runs made, one with each. The solution had to be routed through the series of six columns twice before a constant activity value was obtained in the effluent when the attapulgus clay was used and three times when the silica gel was used. The first set of two runs with the clay reduced the count per minute per milliliter from 59,000 to 5,000 and the set of three with gel from 37,000 to 2,000 counts per minute per milliliter. The effluent from these runs were subjected to the iron scrub-ferrous ferrocyanide-neutralization process and the activity in both cases were reduced to the order of 300 counts per minute per milliliter. Analysis of feeds and effluents of these two runs is given in Table IX.

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2. Willard and Furman, Elementary Quantitative Analysis, p. 383, Van Nostrand, New York (1940).
3. Quarterly Report for Liquid Waste Disposal Research, MLM-406, p. 15.

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4. Baldwin et al., Feasibility Report on Recovery of Fission Zirconium and Columbium from Redox Process Waste Solutions Using Silica Gel, ORNL 49-9-178.
5. Schoeller and Wall, Analyst 61, 585-90 (1936).
6. Quarterly Report for Liquid Waste Disposal Research, MLM-406, pp. 10-13.
7. Quarterly Report for Liquid Waste Disposal Research, MLM-380, pp. 7-12 and MLM-406, pp. 13-14.
8. Bench and Weisblatt, Separation of Cesium from Sodium by Means of Fuller's Earth, K-443.

Table I

RADIOCHEMICAL ANALYSIS OF CRIB WASTE SOLUTIONS

<u>Element</u>	<u>Crib No. 1^a</u> <u>c./min./ml.</u>	<u>Crib No. 2^b</u> <u>c./min./ml.</u>	<u>Crib No. 3^c</u> <u>c./min./ml.</u>	<u>First Cycle^d</u> <u>c./min./ml.</u>	<u>Milligrams</u> <u>Carrier</u> <u>Used</u>	<u>Form of Element</u> <u>During Counting</u>
Ru ¹⁰⁶	295	1150 ^e	6,000	245,000	5	Oxide
Cs ¹⁰⁷	205	300		130,000	5	Silicotungstate
Sb ¹²⁵ , Te ^{125m}	80	772 ^e		1,000,000	2,5	Sulfide, Oxide
R. E.		157		5,700,000	5	Chloride
Zr ⁹⁵ , Cb ⁹⁵	5	53	13,000	85,300,000	10	Fluoride
Sr ⁸⁹		6		35,000	5	Sulfate
Pu				30-40		
Total Observed						
By Direct						
Counting	800	2,000	30,000	90,000,000		

a. Second cycle neutralized waste, estimated age 3 1/2 years.

b. Second cycle neutralized waste, estimated age 2 1/2 years.

c. Second cycle neutralized waste, estimated age 3 months, analysis incomplete.

d. First cycle neutralized waste, estimated age 1 year.

e. Revised values March 10, 1950.

Table IIGRAVIMETRIC ANALYSIS OF WATER WASHED SLUDGE
FOUND IN FIRST CYCLE NEUTRALIZED WASTES

<u>Element</u>	<u>Per Cent of Sludge</u>
Fe_2O_3	16.8
P_2O_5	10.2
SiO_2	12.2*
Bi_2O_3	20.9
Al_2O_3	3.7

* This value is low due to presence of fluoride.

Table IIIPERCENTAGE REMOVAL OF ACTIVITY* BY SILICA GEL

<u>pH</u>	<u>Beta</u>	<u>Alpha</u>
1.0	0.0	0
8.8	84	100
11.8	80	100

* Initial activity 30,000 c./min./ml.

Table IV

REMOVAL OF ACTIVITY WITH TANNIC ACID

<u>Experiment</u>	<u>Initial pH</u>	<u>Reagents Present</u>	<u>mg. ml.</u>	<u>Time of Contacting Hours</u>	<u>Reagents Added</u>	<u>mg. ml.</u>	<u>Final pH</u>	<u>Per Cent* Removal</u>
1	2.0	Fe ⁰ Tannic Acid	5. 0.1	5	—	—	8.1	96.6
2	2.0	Fe ⁰	5.	5	Tannic Acid	0.05	8.0	96.6
3	2.0	Tannic Acid	0.05	5	Fe ⁺⁺	5.	8.0	96.0
4	2.0	Fe ⁺⁺	0.05	5	Tannic Acid	0.1	8.0	96.0
5	2.0	Fe ⁺⁺	0.05	5	Tannic Acid	0.05	8.0	95.7
6	2.0	Fe ⁺⁺	5.	5	—	—	8.0	90.5
7	7.8	Tannic Acid	0.05	8	—	—	7.5	91.0

* Initial Activity 36,000 c./min./ml., 90 per cent zirconium and columbium

Crib No. 2 spiked with first-cycle neutralized wastes.

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Table V

ACTIVITY REMOVAL BY PRECIPITATION OF FERROUS SULFIDE

<u>Method</u>	<u>Waste Solution*</u>	<u>Per Cent Removal</u>	<u>Final Count Per Minute Per Milliliter</u>
1	Crib No. 1	50	400
	2	10	1800
2	Crib No. 1	77	184
	2	30	1400
3	Crib No. 2	94	120

* Initial Activity	Crib No. 1	800 c./min./ml.
	2	2000 c./min./ml.

Table VI

REMOVAL OF ACTIVITY* BY FERROUS FERROCYANIDE

Experiment	Reducing Agent (mg./ml.)		Time of Standing (Hours)		Gross Activity Removed	No. Experiments
	Na ₂ SO ₃	Na ₂ S ₂ O ₄	Before Adjustment	pH After pH Adjustment		
1	0.5	—	1	—	37±3	6
2	0.5	0.1-0.3	1	—	61±5	12
3	0.5	0.3	18	—	72±2	4
4	0.5	0.3	48	—	80±1	3
5	0.5	0.3	48	24	85±1	3

* Crib No. 2, Initial Activity 2000 c./min./ml.

Table VIIWEIGHT AND VOLUME OF PRECIPITATE FORMED

(Original Solution pH 4.5)
(Iron Dissolved 300 ppm.)
($\text{Fe}(\text{CN})_6^{-4}$ Added 600 ppm.)
(Neutralized to pH 6.5-7.5)

Percentages of Original Solution

<u>Settled Volume</u>	<u>Centrifuged Volume</u>	<u>Filtered Volume</u>	<u>Filtered Weight</u>
6-8	3-4	0.1	0.4

Table VIIIEFFECT OF NEUTRALIZATION ON EFFLUENT FROM
IRON SCRUB-FERROUS FERROCYANIDE PROCESS

<u>Original Solution pH</u>	<u>Iron Dissolved</u>	<u>$\text{Fe}(\text{CN})_6$ Added</u>	<u>Portion</u>	<u>pH Neutralized</u>	<u>Effluent c./min./ml.</u>
			A	7.5	220
4.5	300 ppm.	600 ppm.	B	10.5	300
			C	12.0	470

Table IX

RUN NUMBER 67
(Treatment B,A,D,F)

<u>Influent (59,000 c./min./ml.)</u>		<u>Effluent (369 c./min./ml.)</u>	
<u>Element</u>	<u>c./min./ml.</u>	<u>Element</u>	<u>c./min./ml.</u>
Zr-Cb	51,000	Zr-Cb	45
Ru-Sb	2,190	Ru-Sb	282
Te	600	Te	10
Cs	365	Cs	28
R. E.	5,660	R. E.	4

RUN NUMBER 68
(Treatment C,A,D,F)

<u>Influent (37,000 c./min./ml.)</u>		<u>Effluent (300 c./min./ml.)</u>	
<u>Element</u>	<u>c./min./ml.</u>	<u>Element</u>	<u>c./min./ml.</u>
Zr-Cb	31,500	Zr-Cb	38
Ru-Sb	1,880	Ru-Sb	217
Te	440	Te	0
Cs	300	Cs	22
R. E.	3,560	R. E.	23

The decontamination affected by the various methods attempted with the spiked three-year-old second-cycle crib waste is shown graphically in Figure 8.

REMOVAL OF ACTIVITY BY SILICA GEL

NOTE: ORIGINAL ACTIVITY - 720,000 C/MIN./ML.

pH - 7.5

PER CENT Cd^{95} AND Zr^{95} - 90 PER CENT

BATCH VOLUME - 50 ML.

VOLUME OF SILICA GEL - 10 ML.

FLOW RATE @ 0.2 ML/MIN.

FIGURE 1

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A
DECONTAMINATION OF WASTES WITH TANNIC
ACID AS A FUNCTION OF TIME

B
DECONTAMINATION OF WASTES WITH TANNIC
ACID WITH VARYING AMOUNTS OF IRON

FIGURE 3

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FIGURE 8

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DECLASSIFIED