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HYDROGEN PEROXIDE AS A REAGENT IN PLUTONIUM RECOVERY

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HYDROGEN PEROXIDE AS A REAGENT IN PLUTONIUM RECOVERY

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ABSTRACT

Based on the Hanford report of the peroxide precipitation, a study has been made of the conditions which give the best results when hydrogen peroxide is used as a reagent for recovery. It has been shown that in nearly all respects the conditions given in the Hanford report are optimum. It has been shown that peroxide precipitations can be made from pure plutonium solutions and from solutions containing large amounts of other elements. The amount of plutonium left in the supernatant, regardless of impurities present, is usually less than 10 o/o of the amount originally present. Experiments have been shown that, under the conditions used for plutonium peroxide precipitation, uranium is the only other element which will precipitate. It has been further shown that separation can be achieved, even from this element, if the amount is of the order of 5 to 10 o/o or less. Purification factors have been determined for a series of elements based on single precipitations as well as on multiple peroxide precipitations. These factors range from approximately 50 to approximately 25,000. It has been shown that precipitates can be brought down from tri-and hexa-valent plutonium solutions which are identical to those brought down from tetra-valent plutonium solutions.

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Experience has indicated that decomposition of H_2O_2 by certain elements is a minor factor if the temperature is kept as low as possible. A method has been given for dissolving plutonium peroxide in large amounts. This method overcomes the usual foaming difficulties encountered in dissolving the peroxide. The possibility of using the peroxide precipitation as a purification method is discussed. Questions are posed which must be answered before this possibility can be accepted or rejected.

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HYDROGEN PEROXIDE AS A REAGENT IN PLUTONIUM RECOVERY

Introduction

Since the inception of the "Plutonium Recovery Group" in the early part of 1944, it has been necessary to develop many chemical methods for the separation of impurity elements from plutonium .These impurity elements have been such as to almost completely cover the range of the periodic system, and hence the method of separation used in any individual case was determined by the particular element or elements present as impurities, and also by the amounts of these elements present. The general methods which have been developed and used by the recovery group were based on the following chemical characteristics of plutonium: inability to form ammonio-complexes, non-amphoteric nature of the tetravalent hydroxide, high solubility of the hexavalent nitrate in ether, and low solubility of certain compounds in slightly acid solutions. In essentially all cases the impurity element(s) had one or more properties differing from these.

It is not the purpose of this report to discuss all the methods which have been used by the recovery group, (this has been done in other reports.[1]) but rather to give a detailed description of the experimental work carried out on the use of hydrogen peroxide as a reagent for recovery of plutonium from various solutions containing impurity elements, and to give the result obtained thereby.

When the amount of material passing through the recovery group began to become quite large, and when such impurity elements as cerium, lanthanum, thorium and zirconium began to be present as impurities in ever increasing amounts, it became apparent that the standard methods which had been developed, and successfully used up to that time, would not be adequate for further work on a large scale. Reports on the Hanford process[2] indicated that the precipitation of the peroxide of [illegible] satisfactory separation from such elements as lanthanum.

This process was used as a basis for further experimentation.

Experimental

I. Test of Hanford Conditions

According to the report of the Hanford Process, the best precipitation of plutonium peroxide is achieved when the solution is made up as follows:

0.035 M in plutonium
1.0 M in nitric acid
0.1 M sulfuric acid

To this solution is added enough 30 o/o H_2O_2 to completely precipitate the plutonium and to give an excess equivalent to 10 o/o of the total volume of the solution. The H_2O_2 is added very slowly while the solution is being vigorously stirred. The temperature of the solution during the addition of the H_2O_2 is held between 15° and 20° C. When the H_2O_2 has been added, the temperature is reduced to 4° C and the mixture is hel at this temperature without agitation for 9 to 10 hours. The supernatant may then be removed by decantation.

In order to test the criticality of the Hanford conditions, a series of experiments was carried out in which the above mentioned conditions were systematically varied.

1. Nitric acid concentration

It was found that the nitric acid concentration is rather critical. If the molarity is much higher than one the solubility of the plutonium peroxide is too high. If it is much lower than one, hydrolysis of the plutonium ion takes place and a precipitate of inferior characteristics is formed. It was also subsequently found that the acid concentration should be as high as possible to prevent other impurity elements from precipitating along with the plutonium.

2. Sulfuric acid concentration

Since it was known that the peroxide precipitate brought down from a solution containing sulfate ion always carried as much as twenty percent sulfate, to carry out the precipitation without the addition of sulfuric acid. The precipitate formed in the absence of sulfate ion was non-crystalline and therefore unsuitable for the purpose of recovery. In view of this, the sulfate concentration for all further work was set at the value recommended by Hanford.

3. Plutonium concentration

For general operations in the recovery of plutonium it is often impossible to fix the concentration of the plutonium at a value near that used by Hanford. For this reason a series of experiments was carried out using the Hanford acid concentrations, but varying the plutonium concentration over a wide range. The results of these experiments indicated that the plutonium concentration is not too critical. However, two factors must be balanced: precipitation from concentrated plutonium solutions will give a smaller total loss in the supernatant, but precipitation from a more dilute solution will give a better separation of impurities. The actual concentrations used in the recovery operations have been dependent on the amount of impurity present in any given solution.

4. Rate of addition of H_2O_2 and settling time after precipitation

The nature of the precipitate formed by rapid addition of the H_2O_2 was such as to make rapid and complete settling impossible. For this reason the stochiometric amount of H_2O_2 was added very slowly. The rate of addition of the excess was found to be unimportant.

The nine-hour settling period suggested by the Hanford report is unnecessary if the supernatant is to be separated from the precipitate by either filtration or centrifuguation. However, if the supernatant is to be removed by decantation, the long settling period is necessary.

5. Effect of temperature during and after precipitation

It is possible to carry out the precipitation at a higher temperature than that used at Hanford, but the solution must be cooled to approximately 5° C

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during the settling period. With one exception, which will be discussed later, it is best to carry out the precipitation at a temperature of 15° to 20° C.

II. Percent Recovery Using the Peroxide Precipitation

Using the conditions found to be best by the previously mentioned experiments, a series of precipitations was made using pure plutonium nitrate solution, and the amount of plutonium in the supernatant was determined by radioassay. The result of these experiments are given in Table I.

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TABLE I

Percent Recovery - No Impurities Present

Run	Pu Used milligrams	Plutonium in Supernatant milligrams	Percent Pu in Precipitate
1	6015	40	99.4 o/o
2	7881	61	99.2 o/o
3	4250	89	97.9 o/o
4	5405	197	96.4 o/o
5	1850	47	97.5 o/o

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The same procedure was used on a series of plutonium solutions containing various amounts of impurity elements. The results are given in Table II.

TABLE II

Percentage Recovery - Impurities Present

Pu Used mg	Plutonium in Supernatent mg	Percent Pu in Precipitate	Impurity Present
27	1.7	93.7 o/o	Ce Approx. 20 grams
1013	7.0	99.3 o/o	W Alloy 3 o/o
965	27.0	97.2 o/o	La 3 o/o Ce 3 o/o W 3 o/o
438	4.0	99.1 o/o	Au 3 o/o Ag 3 o/o Ca 3 o/o Fe Approx. 1.5 g
168	22.3	87.0 o/o	Fe 50 o/o
1018	29.1	97.2 o/o	Unknown
1300	6.0	99.5 o/o	Mg 3 o/o Fe 3 o/o
3024	88.6	97.1 o/o	3 gms. Th
3017	92.6	97.0 o/o	6 gms. Zr.
200	18.0	91.0 o/o	40 gms.
5000	56.4	98.9 o/o	Unknown
3012	207.0	93.1 o/o	Unknown

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III. Precipitation of Other Elements by H_2O_2 Under the Conditions Used for Plutonium

In order to determine the possibility of precipitation of other elements, which could conceivably be present as impurities in solution for recovery, the following series of experiments was carried out. A separate solution was made up for each element to be tested. The concentration of the element was fixed at 0.035 M, the HNO_3 concentration at 1.0 M and the H_2SO_4 concentration at 0.1 M. Hydrogen peroxide was then added to each of these solutions under the same conditions of temperature, agitation, etc., as was used in the case of the plutonium solutions. There was no precipitate formed with the following elements: Ag, Tl, Ca, Pb, Zn, Cd, Cu, Ni, Co, Ce, Fe, As, Sb, Bi, Zr, Th, and Se. Uranium precipitated as a yellow peroxide under the above conditions. Vanadium caused moderate decomposition of the peroxide, but no precipitate was formed.

IV. Effectiveness of Peroxide Precipitation in Separating Impurities from Plutonium

The experiments just described show that the majority of the possible impurity elements will not be precipitated under conditions which allow plutonium to precipitate. However, they did not prove that absorption or co-precipitation would not cause large amounts of impurity elements to follow the plutonium when it was precipitated. Nor did they prove that impurity elements would not prevent precipitation of plutonium. The following experiments were carried out in order to answer these questions.

1. To a solution of plutonium nitrate containing detectable amounts of only Mg and Ca (by "copper spark" spectrographic method) was added 5 o/o (by weight) of each of the following elements: Se, Zr, Cd, Ce, As, Bi, Ni, Tl, Sb, Fe, Th, Mg, Ca, and U. The solution thus prepared contained fourteen impurity elements amounting to 70 o/o of the weight of the plutonium present. The concentration was adjusted and the plutonium peroxide precipitated in the usual manner. The

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dissolved in nitric acid, and an aliquot analysed by the "copper spark" spectrographic method. Of the fourteen impurity elements originally present only Ca and Mg were detected. All other elements were present in amounts below the detection level of the analytical method used. In all cases this limit was below 0.6 o/o by weight. Table III shows the purification factor[3] for Mg and Ca.

TABLE III

Element	Amount with Pu before precipitation ppm	Amount with Pu After precipitation ppm
Ca	300,000	< 320
Mg	56,000	< 160

Thus, the best purification factor for the fourteen elements present was that of approximately 1000 for calcium and the poorest possible was that of approximately 8 for zirconium.

The result of the previously described experiment proved that the "copper spark" spectrographic technique was too insensitive to be used in determining the various purification factors with any degree of accuracy. For this reason a second solution was prepared containing pure plutonium nitrate to which has been added 5 o/o by weight of each of thirteen elements. The peroxide was precipitated in the usual manner, centrifuged, washed once with cold 1M HNO_3 and dissolved in concentrated HNO_3. The solution thus obtained was divided into aliquots and analysed by the best available method for the thirteen impurity elements. The results are shown in Table IV.

TABLE IV

All Elements Present to Extent of 50,000 ppm before Precipitation

Element	Remaining after Precipitation ppm	Element	Remaining after Precipitation ppm
Be	4.5	Cd	135.0
Mg	45.0	Sn	68.0

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[3] Purification factor = conc. before pptn./conc. after pptn.

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Ca	140.0	Ce	[redacted]
Cr	45.0	Th	~ 1000.0
Mn	1400.0	U	100.0
Co	N. D. < 23.0	Zr	~ 2000.0
Ni	41.0		

It can be seen that purification factors range from 10,000 (for Be) to approximately 25 (for Zr) - this in spite of the fact that the precipitate was washed only once.

3. The result of the two previous experiments, in which only one peroxide precipitation was carried out, raised the question as to the effectiveness of further peroxide precipitations. In order to answer this question a solution was prepared containing 5 grams of plutonium as the tetravalent nitrate and 0.5 grams of each of the following elements: Al, Cr, Mn, Ni, and Ca. The acid and plutonium concentrations were adjusted and the peroxide was precipitated. The precipitate was washed once with cold 1M HNO_3, and dissolved in HNO_3. A sample of the solution thus obtained was taken for analysis. The acid and plutonium concentrations of the remainder of the solution were adjusted, and again the peroxide was precipitated. The above discribed washing dissolving, sampling and precipitating was then repeated until the peroxide had been precipitated a total of three times. The analytical samples taken after each precipitation were used for the best available methods for the five elements in question. The results of this series of experiments are given in Table V.

Table V

All Elements Present to Extent of 100,000 ppm before Precipitation

Elements	After Precipitation No.1 ppm	After Precipitation No.2 ppm	After No.3 ppm
Al	30	12	3
Ca	445	155	48
Cr	148	16	<2
Mn	148	8	<2
Ni	148	[redacted]	<8

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Ca to approximately 50,000 for Cr and Mn after three precipitations.

V. Precipitation of Plutonium Peroxide from Solutions in Which Plutonium is Present in Tri-and Hexa-Valent States

1. In many cases it is advisable to dissolve the plutonium containing substance in HCl rather than in HNO_3. This is especially true in case of the metal and alloys which do not dissolve readily in HNO_3, and in the case of certain sulfide crucibles containing plutonium. In the latter case the sulfur liberated when these crucibles are dissolved in HNO_3 makes further treatment difficult. Many experiments have been carried out in which metal, or alloy, was dissolved in HCl to give the purplish-blue trivalent chloride solution. The concentration of acid and plutonium in this solution was then adjusted to the proper value and H_2O_2 added in the normal way. The first precipitate which forms is bluish in color, but after an excess H_2O_2 has been added, the color gradually changes to the normal green. The amount of plutonium remaining in the supernatant is essentially the same as in that from a normal peroxide precipitation.

In several cases cerium sulfide crucibles weighing 50 to 100 grams and containing as little as 25 mg of plutonium were dissolved in HCl and peroxided (after boiling off H_2S.) In these cases the amount of plutonium in the precipitate was generally better than 90 o/o while there was essentially no cerium (approximately 200 ppm) in the precipitate. This is the only satisfactory method that has been found for separation of small amounts of plutonium from large amounts of cerium. The supernatants from this precipitation still contain some plutonium, and no feasable method has been devised for its separation from the large amounts of cerium present.

2. It has been found that peroxide precipitation can be made to take place from solutions of the hexavalent nitrate provided certain modifications of procedure are used. All conditions are kept the same except that the H_2O_2 is added to a solution which is held at a temperature of 35° to 40°C rather than at 15° to 20°C. After the H_2O_2 has been added, the temperature is slowly lowered to 0° to 5°C and the mixture is held

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at this temperature for several hours. By following this procedure the hexavalent plutonium is reduced and a precipitation is realized which is similar in every respect to that from tetravalent solution.

VI. Decomposition of H_2O_2 by Impurities

Much has been written about the tendency of certain elements, such as iron, to cause decomposition of H_2O_2. This could greatly decrease the value of the peroxide precipitate. However, experience has shown that if the solutions are kept cool (around 0°C) this decomposition effect is so small as to cause no trouble.

VII. Dissolving Plutonium Peroxide

The dissolution of plutonium peroxide is a process which must be carried out very carefully if any appreciable amounts are to be put into solution at one time.

The peroxide is completely soluble in HNO_3 of a concentration between 5 and 16 normal. However, cold 16N HNO_3 will not immediately begin to dissolve a peroxide cake, but once the mixture has become heated, the reaction of solution becomes very rapid and vigorous. Large amounts of gas are evolved during the dissolving process, and the solution foams badly. The following procedure is recommended for dissolving peroxide cakes:

1. Have cake in a very large vessel, preferably one which is connected to a reflux condenser.
2. Cool vessel and cake well below 20°C in an ice bath, and add the amount of 16N HNO_3 necessary to dissolve the peroxide. This addition should be carried out very slowly. The mixture should be stirred.
3. Allow the vessel and its contents to be brought to a temperature of no more than 40°C. This temperature increase should take place very slowly and provision should be made for immediate cooling of the vessel if vigorous foaming begins.
4. Hold at this temperature until solution is complete. The green peroxide will at first seem almost unchanged, but gradually a purple solution will be seen above the precipitate. There is a slight evolution of gas during this stage of the operation.

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As the temperature increases a point is reached at which the blue solution suddenly turns brown and brown fumes (NO_2) are liberated. At this point the entire solution foams up several times, each time with decreasing intensity. When foaming ceases the peroxide is completely dissolved.

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CONCLUSION AND DISCUSSION

The evidence gathered during the course of this investigation indicates that hydrogen peroxide is a superior reagent for use in the recovery of plutonium. The precipitation of plutonium peroxide has been shown to be one of the best, if not the best, methods available for the recovery of plutonium from almost all impurity elements. Under the conditions given herein, the precipitation of the peroxide is almost a specific reaction for plutonium - of all of the elements tested, uranium alone gave a precipitate under similar conditions, and even in the case of uranium, very good separations were realized when that element was present to the extent of no more than 5 to 10 o/o.

Aside from the fact that excellent separation is realized by the use of hydrogen peroxide, the method has the added advantage that no salts have been added during the process, and hence the supernatants from the precipitation is in a much more workable form then those obtained from other methods of recovery. Naturally there is a limit to how far the concentration of plutonium can be reduced in a peroxided supernatant because of the build-up of impurities in this solution. This, however, is true in all methods of recovery, and the peroxide method offers less difficulty from this than any other method.

Preliminary experiments would seem to indicate that a series of peroxide precipitations might be used as a purification method. However, experimental data are much too meager at this time to give more than a hint as to the possibilities of this method. Before any definite conclusions can be drawn the following questions must be answered:

1. What purity limits can be reached by repeated precipitations?
2. How many precipitations are necessary?
x How do purity limits compare with those obtained by other purification methods?

as those of other methods, are they sufficiently

5. Will the presence of the inevitable sulfate ion interfere with subsequent production steps?

6. Can the peroxide be converted directly to a form suitable for reduction in a manner similar to the oxalate?

7. Is metal made from peroxide purified plutonium staisfactory for weapon production and other use?

8. Can the process be engineered?

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