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CARBONATE METHOD OF SEPARATION OF TETRAVALENT PLUTONIUM FROM FISSION PRODUCT VALUES

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This invention is concerned with an improved method of separating plutonium from certain contaminating elements.

The word "plutonium" as hereinafter used in the specification and claims refers to the element of atomic number of 94 and to the compounds thereof, unless the context indicates clearly that plutonium is referred to in its metallic state.

Plutonium is the transuranic element of atomic number 94, which has recently been discovered. Plutonium is normally produced by the bombardment of a uranium mass with neutrons in a chain neutronic reactor of the pile type. In a pile-type neutronic reactor, the U^{235}, which is present with other isotopes of uranium, fissions liberating neutrons. The reaction of these neutrons with atoms of U^{238} forms U^{239} which is radioactive with a half-life of 23 minutes and decays with the emission of beta particles to form Np^{239} which in turn decays by beta emission with a half-life of 2.3 days to form Pu^{239}.

Neutrons also react with the U^{235} to form radioactive fission products and neutrons. The fission of a U^{235} atom usually results in the formation of two fission products: (1) a light element with an atomic number between about 35 and 45, and (2) a heavy element with atomic number between about 50 and 60. The reaction in the neutronic reactor is ordinarily stopped when the plutonium and fission products are present in only very small concentrations. This is done primarily to prevent building up of a dangerous concentration of the extremely radioactive fission products.

The problem of separating the plutonium from the uranium mass is therefore highly important. The methods of separation must be very efficient because of the small concentrations of plutonium and the method must be simple enough that it may be operated by remote control because of the presence of the radioactive fission products. One of the most efficient methods of separation now known is the precipitation method which is based upon the fact that plutonium has at least two valence states and that the compounds which plutonium forms in its various valence states vary widely in solubility. In the methods normally used plutonium is reduced to a valence state of not greater than +4 in which state it forms certain insoluble compounds which may then be separated from those contaminating elements present which do not form insoluble compounds under such conditions. Plutonium may then be redissolved and oxidized to a higher valence state in which state it may be separated either by precipitation of plutonium in that state or by precipitation of the contaminating elements that had been carried with it.

The principal object of this invention is to provide a method of separating quadrivalent plutonium from an aqueous solution by formation of a novel composition of plutonium which is insoluble in a neutral solution.

An additional object of this invention is to provide a novel method of separating plutonium from an aqueous solution in which the plutonium is present in very dilute concentration.

Still another object of this invention is to provide a new and improved method of separating plutonium from contaminants which comprise compounds of the cerium group of the rare earth metals.

We have discovered that plutonium may be separated from a solution in which the plutonium ions are present in the +4 valence state by forming a precipitate of a new composition of matter, plutonium carbonate, and separating the plutonium carbonate from the solution. Thus, plutonium may be separated from a solution in which it is present in the +4 valence state by contacting said solution with a soluble carbonate salt, adjusting the acidity of the solution so that it is approximately neutral, i. e., having the acidity between approximately pH 5.5 and 7.5 and separating the precipitate of plutonium carbonate thus formed.

The precipitate of plutonium carbonate is light tan or white in color and is characteristically flocculent. The precipitate is relatively insoluble in water and experiments have shown that its solubility in 0.2 M NaAc—0.2 M Na_2CO_3 at room temperature is 0.01 gram per liter. Solubilities of the carbonate in various solvents have been determined and are as follows (the solubility is given in milligrams of quadrivalent plutonium per liter of solution: H_2O, 43 mg.; 1 M Na_2CO_3, 72 mg.; 2.5 M Na_2CO_3, 140 mg. Excellent separation of plutonium may be obtained by this process either with centrifugation or filtration because of the flocculent form of the precipitate and the relative insolubility of the compound. The tan precipitate of plutonium carbonate may be rapidly converted to the green plutonium hydroxide by hydrolyzation. It is relatively stable, however, in 1 M NaAc and it is, therefore, desirable to make the solution, from which the plutonium is to be precipitated, approximately 1 M in NaAc, prior to forming the precipitate. The composition of the carbonate formed by quadrivalent plutonium has not been finally determined, but it is believed to have a composition of $Pu(CO_3)_2$ or $PuOCO_3$. Water of crystallization may be present in the compound depending upon conditions of formation.

While plutonium forms a quite insoluble precipitate with carbonate ion when the carbonate ion is present in stoichiometric proportions, an excess of the carbonate ion apparently complexes plutonium, thus greatly increasing the solubility of the plutonium carbonate as shown by the solubility data furnished in the preceding paragraph. The presence of uranyl ions in the solution also tends to prevent the formation of the quadrivalent plutonium carbonate. The reason for this action of the uranyl ion has not been precisely determined but it is believed to be either a complexing of the quadrivalent plutonium ion by the uranyl ion or a tendency of the uranyl ion to act as a holdback carrier.

The plutonium carbonate may be formed by the addition of any soluble carbonate to the solution containing the Pu^{+4} ion in which the acidity of the solution is maintained within the pH range of approximately 5.5 to 7.5. Thus, any of the alkali carbonates such as sodium, ammonium, or potassium carbonates may be used. It may also be desirable to use a soluble bicarbonate salt but if a bicarbonate salt is used the acidity must then be readjusted to bring it within the neutral range.

The separation of plutonium from an aqueous solution by the process of this invention has several great advantages over other methods. One of these advantages is that a precipitate of plutonium carbonate may be readily dissolved in a very small quantity of an appropriate solvent, and thus the plutonium concentration may be greatly increased. Because of this, the process of our invention may be advantageously employed to concen-

trate the plutonium after its separation by the usual oxidation-reduction methods of plutonium separation. The plutonium carbonate may be either dissolved in an acid solution or may be dissolved by the addition of an excess carbonate.

The other great advantage of separating plutonium by the process of this invention is that plutonium carbonate may be redissolved in acid with the evolution of carbon dioxide thus removing from solution the anion used to precipitate the plutonium. This is a considerable advantage, since the anions used in many other plutonium separation processes form corrosive compounds and often further complicate the steps which follow the separation of plutonium from solution.

Now that this embodiment of our invention has been described, it may be illustrated by the following example.

Example I

A 0.1 solution of $Pu(NO_3)_4$ was prepared by dissolving plutonium in dilute nitric acid. Sodium acetate was then added to make the solution about 0.2 M, and 0.5 M sodium carbonate solution was then rapidly added to the solution in quantity sufficient to make the solution about 0.2 M in sodium carbonate. A light tan flocculent precipitate formed in the solution. This precipitate was separated from the solution by centrifugation. The separation of plutonium was practically quantitative as tests of the precipitate disclosed that its solubility was 0.01 grams per liter.

Another embodiment of this invention is concerned with the separation of plutonium present in solution in quantities so minute that it cannot be precipitated directly from the solution. When plutonium is formed by the reaction of neutrons with a uranium mass contained in a neutronic reactor, the plutonium is often present in the uranium in very small proportions often less than .01% and sometimes less than .0001%.

In order to separate plutonium from a solution of such a low concentration that a plutonium compound will not precipitate directly, it is necessary to employ an auxiliary insoluble "carrier" to effect removal of the plutonium from the solution. The insoluble carrier may be introduced into the solution as pre-formed, finely divided solid, but is preferably precipitated directly in the solution from which the plutonium is to be carried. The mechanism of the carrying of plutonium from solution is not fully understood but it is believed to be effected in some cases by incorporation of plutonium ions into the carrier crystal lattice, in some cases by surface adsorption of plutonium ions and in other cases by a combination of both. The carrying procedure may be effected by any of the known techniques for effecting adequate contact of liquids with soluble solids. In the case of preformed carriers, the finely divided solid may be agitated with the solution or the solution may be continuously passed through beds of the carrier. As previously pointed out, however, the preferred procedure is to precipitate the carrier directly in the plutonium solution. This may be effected in the plutonium solution. This may be effected by adding the ions in any order but it is generally preferred to add the cation first and then the anion.

We have discovered that plutonium in the +4 valence state will be effectively carried from an approximately neutral aqueous solution by the use of a cerium-group rare earth carbonate carrier, thus, Pu^{+4} present in minute amounts may be separated from an aqueous solution by contacting the solution with an insoluble cereic-rare-earth-group carbonate such as lanthanum carbonate or cerium carbonate or preferably by the formation of a cerium-rare-earth-group carbonate precipitate in the plutonium-containing solution and the separation of the cerium-rare-earth-group carbonate precipitate together with the entrained plutonium carbonate from the solution by any suitable method.

By the preferred method a soluble rare earth salt such as the lanthanum halide or nitrate is added to the aqueous solution containing the plutonium in the +4 state. A soluble carbonate salt is then added to the solution. The alkali metal carbonates and bicarbonates and ammonium carbonate and bicarbonate salts have been found to be suitable sources of carbonate ion. It is preferable to add the carbonate ion in approximately stoichiometric proportions since a plutonium carbonate complex tends to form in an excess carbonate solution. Where sodium acid carbonate is used as a source of the carbonate ions, addition of the sodium acid carbonate to make the solution 0.25 M has been found to give satisfactory precipitations.

The acidity of the solution should be maintained not substantially below a pH of 5.5 nor substantially above 7.5 in order to effect maximum carrying. Uranyl ions also tend to prevent the formation of a carbonate of quadrivalent plutonium so it is desirable to remove all uranyl ions from solution prior to the formation of the lanthanum carbonate carrier. The carrier precipitate may be separated from the solution readily by any of the ordinary methods such as filtration, decantation or centrifugation.

The separation of plutonium from solution with the cerium sub-group carbonate carrier may be illustrated by the following example:

Example II

To a solution containing Pu^{+4} in tracer quantity was added 0.5 mg. of lanthanum nitrate. The solution was then made 0.25 M in $NaHCO_3$ by the addition of $NaHCO_3$. The acidity of the solution was then adjusted so that the hydrogen ion concentration was 10^{-6} M. The precipitate of lanthanum carbonate, thus formed, was separated from the solution by centrifugation, washed several times and the amount of plutonium present in the precipitate determined by counter analysis of the radioactivity present. It was found that plutonium was carried 81% with 7% of the plutonium remaining in solution and 12% unaccounted for.

Another modification of our invention is concerned with the separation of plutonium from the cerium subgroup of rare earth metals. Desirability of separating plutonium from the cerium group of rare earth metals ordinarily arises either from the use of a cerium group carrier precipitate for plutonium carbonate as described above, or the separation of plutonium from radioactive contaminating fission products. In the production of plutonium by reacting natural uranium in a neutronic chain reactor certain fission elements are by-products of the reaction. These include the cerium group of the rare earth metals. Of this group La^{140}, cerium of 20-day and 200-day half-lives, and praseodymium are particularly troublesome because the gamma rays given off by these elements are very hazardous to personnel handling the separation process. The basis for the separation of plutonium from the cerium rare earth group is our discovery that plutonium, which forms an insoluble carbonate in the presence of stoichiometric proportions of carbonate ion in aqueous solution, redissolves upon the addition of excess carbonate ions in distinction to the cerium group of rare earths whose carbonates remain insoluble in the presence of a considerable excess of carbonate ion. Thus, the plutonium may be readily separated from a plutonium carrier comprising a cerium rare earth group carbonate by introducing the cerium group carbonate plutonium carrier into a solution containing carbonate ion in a concentration less than that required to dissolve the cerium group carbonate. Where lanthanum carbonate is used as the carrier, it has been found that plutonium carbonate will dissolve leaving the lanthanum carbonate as a precipitate when a lanthanum carbonate carrier is introduced into a solution with molarity of the carbonate ion between about 1 and

3. If the molarity of the carbonate is greater than about 3, lanthanum carbonate will dissolve slowly at room temperature with the rate of dissolution increasing with higher temperatures or higher molarity. This method of separating plutonium from the cerium rare earths may be illustrated by Examples 3 and 4.

Example III

About 3 mg. of lanthanum nitrate was added to a solution containing plutonium in the +4 oxidation state and the solution was made 1 M in sodium carbonate; the resulting precipitate was removed from the solution by centrifugation. Analysis by counting the radioactivity present disclosed that only 1% of the activity came down with the lanthanum carbonate precipitate.

Example IV

0.5 mg. of lanthanum carbonate carrier containing plutonium in tracer quantities was introduced into a solution containing potassium carbonate in 1 M concentration. At the end of 30 minutes the precipitate which remained undissolved was separated from the supernatant liquid by filtration. Analysis disclosed that the solution contained 93% of the plutonium carbonate. The precipitate contained 3% of the plutonium carbonate and all of the lanthanum carbonate while 4% of the plutonium was unaccounted for.

An alternate method of separating plutonium from the cerium rare earths is the addition of a uranyl ion to a solution containing plutonous and cerium rare earth group ions followed by the forming of a cerium rare earth group carbonate. This alternate method is illustrated by Example 5.

Example V

To a solution containing Pu^{+4}, La^{+3}, and CO_3^{-2} ions was added potassium carbonate to make the solution 0.5 M in potassium carbonate. The precipitate of lanthanum carbonate formed was digested for 90 minutes at room temperature and then separated by filtration. Analysis of the precipitate disclosed that 13% of the plutonium was carried with the precipitate and 87% of the plutonium remained in solution.

While there have been described certain embodiments of our invention, it is to be understood that it is capable of many modifications. Changes, therefore, may be made without departing from the spirit and scope of the invention as described in the appended claims in which it is the intention to claim all novelties in the invention as broadly as possible.

What is claimed is:

1. A method of separating tetravalent plutonium values from lanthanum-group rare earth values which form carbonates insoluble in a carbonate solution contained in an aqueous acid solution, comprising adjusting the pH value of said solution to between 5.5 and 7.5, adding carbonate anions to said solution in an approximately stoichiometric amount with regard to plutonium and rare earths present whereby Pu (IV) carbonate and rare earth carbonates precipitate, separating said carbonate precipitate from the solution, contacting said carbonate precipitate with an aqueous carbonate solution of a concentration of between 1 and 3 M whereby said Pu (IV) carbonate is dissolved, and separating said rare earth carbonates-containing precipitate from said plutonium-containing solution.

2. The process of claim 1 wherein said carbonate anions are added in the form of a water-soluble carbonate.

3. The process of claim 1 wherein said carbonate anions are added in the form of a water-soluble bicarbonate.

4. The process of claim 1 wherein said aqueous acid solution contains sodium acetate in a concentration of between 0.2 and 1 M.

5. A method of separating tetravalent plutonium values from rare earth fission product values which form carbonates insoluble in a carbonate solution contained in an aqueous nitric acid solution, comprising adjusting the pH value of said solution to between 5.5 and 7.5, adding carbonate anions to said solution in an approximately stoichiometric amount with regard to plutonium and fission products present, incorporating a cerium-group rare earth carbonate precipitate in said solution whereby said Pu (IV) values and said fission product values are carried on said rare earth carbonate precipitate, separating said rare earth carbonate carrier precipitate fom the solution, contacting said carier with an aqueous carbonate solution of a concentration of between 1 and 3 M whereby said Pu (IV) carbonate is dissolved, and separating said fission product carbonates-containing carrier from said plutonium-containing solution.

6. The process of claim 5 wherein the carrier precipitate is lanthanum carbonate.

7. The process of claim 5 wherein the carrier precipitate is cerium carbonate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,767,044	Hill et al.	Oct. 16, 1956
2,768,871	Brown et al.	Oct. 30, 1956

OTHER REFERENCES

Babor et al.: General College Chemistry, p. 426 (1940), publ. by Thomas Y. Crowell Co., N. Y.