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PLUTONIUM RECOVERY PROCESS

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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 94 and to the compounds thereof, unless the context indicates clearly that the plutonium is referred to in its metallic state.

Uranium is composed of three isotopes, namely, U^{234}, U^{235} and U^{238}, the latter being present in excess of 99 percent of the whole. When U^{238} is subjected to the action of slow or thermal neutrons, a fourth isotope, U^{239}, is produced; it has a half-life of 23 minutes and undergoes beta decay to Np^{239} which decays further by beta radiation with a half-life of 2.3 days to yield plutonium. In addition to the formation of 94^{239}, there are simultaneously produced other elements of lower atomic weight known as fission fragments. These fission fragments are composed of elements having atomic numbers from about 32 to 64. The elements of this group, as originally produced, are considerably overmassed and undercharged, and hence are highly unstable. By beta radiation, however, they quickly transform themselves into isotopes of these various elements having longer half-lives. The resulting materials are commonly known as fission products.

The various radioactive fission products have half-lives ranging from a fraction of a second to thousands of years. Those having very short half-lives may be substantially eliminated by aging the material for a reasonable period before handling. Those with very long half-lives do not have sufficiently intense radiation to endanger personnel protected by moderate shielding. On the other hand, the fission products having half-lives ranging from a few days to a few years have dangerously intense radiations which cannot be eliminated by aging for practical storage periods. These products are chiefly radioactive isotopes of Sr, Y, Zr, Nb, Ru, Te, I, Cs, Ba, La, Ce, and Pr.

It may be readily seen that plutonium, produced as generally set forth above, is contaminated with considerable quantities of uranium and fission products. In fact, the plutonium constitutes only a very minor portion of the irradiated mass, i. e., less than one percent thereof. In view of such a low concentration of plutonium in the irradiated metal, it becomes apparent that the procedure employed to recover that element must be highly efficient in order to be at all practicable.

There have been devised a number of procedures for the removal and concentration of plutonium from extremely dilute solutions thereof. In general, such methods involve the formation of various insoluble compounds in said dilute solutions capable of carrying plutonium in the reduced state. The carrier precipitate and plutonium thus obtained are then dissolved and the plutonium is oxidized to the hexavalent state in which state of oxidation it is soluble in the presence of said carrier. Under these conditions, the plutonium remains in solution and the fission products are removed when the carrier is added. Thereafter, the dissolved plutonium is reduced to a valence state in which it is carriable by the aforesaid carrier and removed from solution in the form of a carrier precipitate which may again be dissolved and the plutonium purified further, if considered necessary or desirable, by repeating the above cycle. A carrier precipitate which carries plutonium is usually referred to as a "product" precipitate while a carrier precipitate which removes elements other than plutonium, leaving the plutonium in the solution, is usually referred to as a "by-product" precipitate.

It is an object of this invention to provide a convenient and efficient method of recovering plutonium from impurities commonly associated therewith in a neutron-irradiated uranium mass.

A further object of this invention is to provide a suitable method of recovering plutonium from an aqueous basic solution containing uranium, plutonium, and other products of neutron-irradiation of uranium.

Broadly, this invention involves treating a solution, obtained by dissolving neutron-irradiated uranium in an inorganic acid, with a suitable oxidizing agent whereby the plutonium present is oxidized to the hexavalent state. The acidity of this solution is then adjusted in the presence of carbonate ions, so that a solution having a pH greater than 6.8 is obtained. This treatment effects the complexing of the uranyl and plutonyl ions present. A by-product carrier precipitate is then formed in the solution by contacting the solution with a source of a cation which will form an insoluble carbonate in the solution. Lanthanum has been found to be particularly suitable, but other members of the ceric group of rare earths may be employed. This precipitate acts as a carrier for radioactive lanthanum, and other fission products present, particularly barium, zirconium, and niobium, and these products are separated from the solution with the by-product precipitate. The hexavalent plutonium contained in the solution is then treated with a reducing agent which has a potential such that it will reduce the plutonium present, but not the uranyl ion. A product carrier precipitate is then formed in the solution and separated therefrom, carrying with it the trivalent and tetravalent plutonium, but leaving the hexavalent uranium, zirconium, niobium, and cerium ions in solution. Bismuth hydroxide forms a particularly suitable product carrier. The product carrier precipitate obtained in this manner may then be dissolved and the plutonium oxidized to the hexavalent state, after which it may be readily separated from the carrier by converting the latter to an insoluble compound.

In one embodiment of this invention a uranyl nitrate hexahydrate solution prepared by dissolving neutron-irradiated uranium in concentrated nitric acid and diluting with water, so that the uranyl nitrate hexahydrate is present in about a 20 to 40% ratio by weight, is treated with an oxidizing agent having a potential more negative than −1.11 volts whereby the plutonium present is converted to the hexavalent state. Oxidizing agents which have been found to be particularly suitable include sodium bismuthate, ceric ion, and dichromate ion. Following oxidation, the plutonyl and uranyl ions present are complexed by decreasing the acidity of the solution to a pH of greater than 6.8, and preferably to a pH of between 9 and 11, in the presence of carbonate ions. This is usually accomplished by treating the solution with a soluble alkali metal carbonate solution. Of the common alkali metal carbonates, it has been found that Na_2CO_3 gives the best results, since sodium uranyl carbonate is more soluble than the potassium uranyl carbonate. Where the uranyl ion is contacted with an alkali metal carbonate, such as sodium carbonate in a

solution with a pH less than 6.8, it has been found that an insoluble sodium uranyl carbonate will precipitate and although this may be redissolved by increasing the pH of the solution, it has been found desirable to avoid the formation of the precipitate if possible. The uranyl nitrate hexahydrate solution is therefore usually added to the carbonate solution, rather than the reverse, since by this procedure the uranyl and plutonyl ions are contacted by the carbonate ions in a solution having a pH greater than 6.8 at all times.

A by-product carrier precipitate is then introduced into the solution. The precipitate may be added as a preformed precipitate but is preferably formed in the solution. A particularly suitable by-product carrier is basic lanthanum carbonate. This may be formed in solution by contacting the solution with a soluble lanthanum salt. The amount of lanthanum required to form a precipitate varies somewhat with the acidity of the solution. It has been found, however, that where the pH of the solution is greater than 9, a precipitate of basic lanthanum carbonate will form where the concentration of the lanthanum ion is at least one gram per liter of lanthanum ion. Other members of the ceric group of rare earths will form suitable carrier precipitates under the same conditions as lanthanum, and since radioactive lanthanum and cerium are present, the concentrations of these elements already present in the solution may be taken into consideration in forming the carrier precipitate. This precipitate of lanthanum basic carbonate is a very effective carrier for fission products which are not complexed by the carbonate ion at the pH at which this precipitate is formed. Radioactive lanthanum and barium are carried quantitatively by this precipitate at carbonate concentrations given below. A substantial portion of the radioactive zirconium and niobium present is also removed by this precipitate. It has been found that a carbonate complexed solution having a pH between 9 and 11 furnishes the best conditions for decontamination with this precipitate. The carbonate concentration should not be greater than approximately 3 M, however, since the lanthanum-ceric group rare earth carbonates tend to redissolve in solutions containing carbonate ion in greater quantities. The lanthanum basic carbonate precipitate may be separated from solution by centrifugation, filtration or decantation. For the most efficient operation of this process it may be also desirable to wash the precipitate after separation and combine the wash water with the supernatant solution.

Following the separation, the supernatant solution containing carbonate complexed uranyl and plutonyl ions is treated with a reducing agent which will reduce the plutonyl ions present but will not affect the uranyl ions. Such reducing agents include hydroxylamine, hydrazine, sodium sulfite, and hydrogen peroxide. Good results have been obtained by using 0.1 M hydroxylamine sulfate reducing agent and digesting the solution at 50° C. for one hour. It is immaterial whether the plutonium is reduced to the trivalent or tetravalent state, since plutonium in either state is carried effectively by the product carrier precipitate which is removed in the step which follows. In this step of the process a product carrier precipitate is formed in, and separated from, the solution. A suitable plutonium carrier may be formed by adding a soluble bismuth salt, such as bismuth nitrate, to the solution in quantities sufficient to attain in the solution at least 3.5 mg./cc. of Bi^{+3}, then digesting the precipitate of bismuth hydroxide thus formed at an elevated temperature, such as 50° C., for an hour. This precipitate carries the tetravalent plutonium quantitatively from the solution but it does not remove the uranyl ion or the radioacive fission products, such as barium, niobium, and zirconium. The completeness of the carrying of the reduced plutonium ions depends somewhat upon the bismuth concentration, the temperature, and the time. It has been found that with a bismuth concentration of 5 mg./cc. of solution and a digestion period of two hours at 75° C. the tetravalent plutonium present is carried 100% with the bismuth hydroxide precipitate formed. If the bismuth concentration is 3.5 mg./cc. and the digestion period reduced to one hour at 50° C., 92 to 99% of the plutonium carried, but if the bismuth concentration is reduced to 2.5 mg./cc. with a digestion at 40–50° C. for one hour, only 16–20% of the tetravalent plutonium is carried with the precipitate. Since these three factors, the bismuth concentration, the time and the temperature of digestion, are interdependent, any one may be varied by varying the others correspondingly. The bismuth hydroxide precipitate may be separated from the solution by any of the usual methods.

Following the separation of the bismuth hydroxide plutonium carrier precipitate from the solution, the precipitate can be dissolved in a small quantity of acid. The plutonium may then be separated from the carrier in any of several different ways. For example, the plutonium may be oxidized to the hexavalent state and the bismuth separated from the solution by forming an insoluble precipitate of bismuth hydroxide or bismuth phosphate. An alternate method is to oxidize the plutonium to the hexavalent state and precipitate the plutonium from the solution as an insoluble hexavalent plutonium compound such as plutonium hydroxide or plutonium uranyl acetate.

It will be apparent that the procedure set forth above has considerable advantage over other separation methods inasmuch as all precipitates involved can be readily dissolved in comparatively small quantities of acid, thus effecting not only a separation of plutonium from contaminating elements but also a concentration of the plutonium.

Another embodiment of our invention is concerned with an alternate method of separating the plutonium from the uranyl ion following the by-product precipitation of basic lanthanum carbonate as described above. By this alternate method the solution containing uranyl and plutonyl ions, following the basic lanthanum carbonate by-product carrier precipitation, is acidified with an acid, such as nitric acid. Sufficient acid should be used so that the hydrogen ion concentration of the solution is greater than 1 N. The acidification should be carried out in a closed container, since the fumes which are given off during the acidification are very poisonous. Plutonium contained in the acid solution is then reduced to a lower oxidation state and a carrier precipitate of bismuth phosphate formed in the solution. This bismuth phosphate precipitate is a carrier for tetravalent plutonium but not for uranyl ion and the plutonium may thus be separated from the solution. The plutonium may then be separated from the bismuth phosphate carrier by the same method as described above for separating plutonium from the bismuth hydroxide carrier.

Now that this invention has been described it may be further illustrated by the following specific example.

EXAMPLE

A neutron-irradiated uranium mass containing about one part plutonium and one part fission products to 4250 parts of uranium was dissolved in nitric acid to give a 40% uranyl nitrate hexahydrate solution and a nitric acid concentration of about 0.2 N. The solution was made 0.01 N in potassium permanganate and digested for one hour at 60° C., thereby oxidizing all of the plutonium to the hexavalent state. The oxidized solution was added to a saturated sodium carbonate solution so that the final pH of the combined solutions was between 9.5 and 11. Lanthanum nitrate was added to the solution to give a concentration of La^{+3} of one gram per liter. A precipitate of basic lanthanum carbonate formed and the solution was digested for one hour at 75° C. The basic lanthanum carbonate precipitate was separated by centrifugation, and the precipitate washed

once with water. The supernatant solution and the wash water were combined, and the plutonium contained therein reduced by making the solution 0.1 M in hydroxylamine sulfate and digesting for one hour at 50° C. The solution was maintained at 50° C. and bismuth nitrate added to the solution over a thirty-minute period to give a final Bi^{+3} ion concentration of 3.5 g./l. The plutonium carrier precipitate of bismuth hydroxide thus formed was digested for one hour at 50° C. and then separated from the solution by centrifugation. Radiometric analysis showed that less than 1% of the plutonium was lost with the basic lanthanum by-product precipitate, and that better than 99% of the plutonium was carried with the bismuth hydroxide product carrier precipitate. The decontamination effected by the process is shown by the following table.

Table

DECONTAMINATION THROUGH CARBONATE EXTRACTION CYCLE

Fission activity	Percent fission activity carried with basic lanthanum carbonate by-product precipitate	Percent fission activity carried with bismuth hydroxide product precipitate
	Percent	*Percent*
La	98.2	
Ba	95.0	1.5
Cb	86.5	1.8
Zr-Nb	54.5	1.5

It will be apparent to those skilled in the art that various modifications of the present invention exist. In general, it may be said that any process for the separation of plutonium from uranium and other impurities normally associated therewith, based upon the precipitation of impurities from carbonate complexed hexavalent plutonium solutions and the precipitation of plutonium from carbonate complexed uranyl solutions, is to be considered within the scope of the present invention.

What is claimed is:

1. In a process for the recovery of plutonium from neutron-irradiated uranium, the steps which comprise oxidizing the plutonium contained in an aqueous solution of a salt of neutron-irradiated uranium to the hexavalent state, reacting the solution with an alkali metal carbonate whereby the hexavalent plutonium ions are complexed with carbonate ions, forming a by-product carrier precipitate in the solution which will carry contaminants but not hexavalent plutonium ions and separating it therefrom, reducing the plutonium ions contained in the solution to an oxidation state less than +5, forming a product carrier precipitate in the solution which will carry the trivalent and quadrivalent plutonium present but not the contaminants and separating it therefrom.

2. In a process for the separation of plutonium from neutron-irradiated uranium, the steps which comprise oxidizing plutonium contained in an aqueous solution of uranyl nitrate hexahydrate to the hexavalent state, reacting the solution with an alkali metal carbonate whereby the hexavalent plutonium ions present are complexed with the carbonate ions, contacting the solution with a by-product carrier precipitate which will carry contaminants but not carbonate complexed plutonium ions, and separating it therefrom, reducing the plutonium ions contained in the solution to an oxidation state less than +5, forming a product carrier precipitate in the solution which will carry the trivalent and quadrivalent plutonium ions present but not the contaminants, and separating it therefrom.

3. In a process for the recovery of plutonium from neutron-irradiated uranium, the steps which comprise oxidizing plutonium contained in an aqueous solution of uranyl nitrate hexahydrate to the hexavalent state, alkalifying the solution with sodium carbonate to a pH greater than 6.8, contacting the solution with an insoluble ceric sub-group rare earth carbonate and separating it therefrom, reducing the plutonium ions contained in the solution to a valence state less than +5, introducing a bismuth hydroxide product carrier precipitate into the solution, and separating it therefrom.

4. In a process for recovery of plutonium from neutron-irradiated uranium, the steps which comprise oxidizing plutonium contained in an aqueous solution of uranyl nitrate hexahydrate to a hexavalent state, alkalifying the solution with sodium carbonate to a pH of between 9 and 11, forming a by-product carrier precipitate in the solution by contacting the solution with a source of lanthanum ions and separating the precipitate thus formed from the solution, reducing the plutonium ions contained in the solution to an oxidation state less than +5, forming a plutonium carrier precipitate in the solution by introducing a source of bismuth ions into the solution, and separating the precipitate thus formed from the solution.

5. In a process for the recovery of plutonium from neutron-irradiated uranium, the steps which comprise oxidizing plutonium contained in an aqueous solution of uranyl nitrate hexahydrate to the hexavalent state, adjusting the acidity of the solution to a pH of between 9 and 11 in the presence of carbonate ions, treating the solution with a soluble lanthanum salt in quantity sufficient to form a precipitate separating the precipitate thus formed from the solution, reducing the plutonium contained in the solution to a valence state less than +5, introducing a soluble bismuth salt into the solution to give a concentration of greater than 2.5 g./l. of Bi^{+3} ions, digesting the solution at a temperature greater than 40° C., and separating the product carrier precipitate thus formed.

6. In a process for the recovery of plutonium from neutron-irradiated uranium, the steps which comprise oxidizing the plutonium contained in an aqueous solution of uranyl nitrate hexahydrate to the hexavalent state, alkalifying the solution with a soluble carbonate to a pH of greater than 6.8, forming a by-product carrier precipitate in the solution which will carry contaminants but not hexavalent plutonium ions, and separating it therefrom, acidifying the solution to a hydrogen ion concentration of greater than 1 N, reducing the plutonium ions in solution to a valence less than +5, forming a bismuth phosphate plutonium carrier precipitate in solution, and separating it therefrom.

7. In a process for the recovery of plutonium from neutron-irradiated uranium, the steps which comprise oxidizing plutonium contained in a uranyl nitrate hexahydrate solution to the hexavalent state, adjusting the alkalinity of the solution to a pH of between 9 and 11 in the presence of carbonate ions, forming a basic lanthanum carbonate by-product carrier precipitate in the solution and separating it therefrom, reducing the plutonium ions contained in solution to an oxidation state less than +5, acidifying the solution with nitric acid to an acidity of greater than 1 N HNO_3, introducing a soluble bismuth compound and a soluble phosphate compound into the solution, and separating the product carrier precipitate of bismuth phosphate thus formed from the solution.

8. The method of separating hexavalent plutonium from fission products, which comprises alkalifying a solution of hexavalent plutonium and said products to a pH of between 9 and 11 with a soluble carbonate, introducing a soluble lanthanum compound into the solution whereby a by-product carrier precipitate of basic lanthanum carbonate is formed, and separating it therefrom.

9. The method of separating hexavalent plutonium from fission products, which comprises adjusting the acidity of a solution of hexavalent plutonium and said products to a pH of between 9 and 11 in the presence of carbonate ions, forming a precipitate of lanthanum basic carbonate in the solution, and separating it therefrom.

10. The method of separating plutonium from uranium,

which comprises forming an aqueous solution of uranyl nitrate hexahydrate and hexavalent plutonium, reducing the plutonium present to an oxidation state less than +5, alkalifying the solution to a pH of greater than 6.8 in the presence of carbonate ions, forming a product carrier precipitate of bismuth hydroxide in the solution, and separating it therefrom.

11. The method of separating plutonium from uranium, which comprises adjusting the acidity of a solution containing uranyl nitrate hexahydrate and hexavalent plutonium to a pH of between 9 and 11 by introducing a soluble alkali metal carbonate into the solution, reducing the plutonium to a valence state of less than +5, introducing a soluble bismuth salt into the solution to give a concentration of bismuth ions of greater than 2 g./l. of solution, digesting the bismuth hydroxide plutonium carrier precipitate thus formed at a moderately elevated temperature, and separating the plutonium carrier precipitate from solution.

No references cited.