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# SEPARATION OF FISSION PRODUCTS FROM PLUTONIUM BY PRECIPITATION

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This invention relates to a method for the decontamination of plutonium solutions. More specifically it is concerned with a method for the separation of plutonium from radioactive uranium fission products present in a solution containing said products and plutonium.

The designation "plutonium" or "element 94" as used throughout the present description refers to the transuranic element having an atomic number of 94. The expression "$94^{239}$" means the isotope of element 94 having an atomic weight or mass of 239. Similarly, the terms "element 93" or "neptunium" refer to the transuranic element having an atomic number of 93.

It is now known that the transuranic elements 94 and 93 and also elements of lower atomic weight known as fission products may be produced by the bombardment of uranium with neutrons. Natural uranium contains a large proportion of the isotope $U^{238}$ and a smaller proportion (about $\frac{1}{139}$ of 238) of the isotope $U^{235}$. The reaction of $U^{238}$ with slow neutrons produces the isotope $U^{239}$ which undergoes beta decay with a half-life of 23 minutes to $93^{239}$ which in turn decays with a half-life of 2.3 days to $94^{239}$.

The slow neutrons also react with $U^{235}$ to produce nuclear fission and two fragments called fission fragments. These fission fragments are in general highly radioactive and undergo beta disintegration, with gamma radiation, into chains of two groups, a light group of elements with atomic numbers from 35 to 46 and a heavy group with atomic numbers from 51 to 60. These elements either alone or combined as compounds are known as fission products.

The half-lives of the various intermediate nuclei of these fission products range from fractions of a second to a year or more with several of the important species having half-lives of the order of a month or so. The dangerous radioactivity of fission products having a very short half-life may be eliminated by suitable aging of a few days. This aging period also serves to permit the transformation of the greater part of the $92^{239}$ to $93^{239}$, and of the $93^{239}$ into $94^{239}$. The fission products of very long half-lives have a minimum of radioactivity, but the fission fragments of intermediate half-lives, of the order of a month or so, for example: $Sr^{89}$, Y (57 day half-life), Zr, Cb, and Ru of the group of atomic numbers from 35 to 45; and $Te^{127}$, $Te^{129}$, $I^{131}$, $Xe^{133}$, Ba (12 days half-life), $La^{140}$, and Ce of 20 day and 200 day half-lives, from the group of atomic numbers from 51 to 60 inclusive, make the mass extremely difficult to handle without danger of exposure of personnel to gamma radiation. A prime object of the decontamination of plutonium is to remove these radioactive fission products so that the plutonium may be handled without the massive shielding necessary to protect operating personnel from radioactivity. Consequently it has been found convenient to measure the extent of decontamination of plutonium by measuring the amount of radioactivity present after the separation has been effected.



In the customary production of plutonium by the bombardment of natural uranium with neutrons by a chain reaction in a uranium lattice reactor, the reaction is usually stopped when the concentration of the plutonium is still very small in relation to the $U^{238}$, usually less than 1 percent by weight and often less than one or several parts per million parts of $U^{238}$. Consequently the percentage of fission products is also very small, for example of the order of 0.02 percent of the mass by weight. The separation of the plutonium from the mass of uranium and from the fission products is therefore a very difficult process, not only because of the extremely minute concentrations, but also because of the dangerous radioactivity of the fission products present.

The separation of plutonium has been the subject of much investigation and as a result of such research, four general types of chemical separation methods have been developed: recovery based on different volatilities of plutonium compounds and corresponding fission product compounds, absorption, solvent extraction, and carrier precipitation methods. While some degree of success has been attained with each method, the precipitation method has been found to be preferable. One embodiment of this method is the procedure employing bismuth phosphate as a carrier for plutonium which depends on the fact that plutonium in a valence state of four forms an insoluble phosphate and is carried down with the bismuth phosphate, but in a valence state greater than four is soluble in a solution containing the phosphate ion. This process is described and claimed in co-pending application U.S. Serial No. 519,714, filed January 26, 1944, by Stanley G. Thompson and Glenn T. Seaborg granted as U.S. Patent No. 2,785,951 on March 19, 1957.

In accordance with the procedure therein described, neutron-irradiated uranium is dissolved in nitric acid or preferably a mixture of nitric and sulfuric acids. The acidic solution thus formed contains uranium ions in the hexavalent state, plutonium ions in the tetravalent state and the various fission products ions. If the plutonium is present in sufficient concentration, it may be precipitated directly from solution as the phosphate. Usually however the concentration of plutonium is so low that a precipitate of a plutonium compound will not form by itself and it is necessary to employ an auxiliary insoluble "carrier" such as bismuth phosphate to effect removal of the plutonium from the solution. This precipitation is called the product precipitation. The carrier is believed to act either by the incorporation of plutonium ions into the carrier crystal lattice, by surface adsorption of plutonium ions, or by a combination of both. Certain of the uranium fission products ions in the solution, chiefly the zirconium and columbium, are isomorphic with the plutonium ions and will be precipitated or carried out of solution with the plutonium. The uranium ions and the bulk of the fission products ions are quite soluble under the conditions employed and remain in solution. The phosphate precipitate containing the plutonium and isomorphic radioactive fission products is dissolved in nitric or other suitable acid and the plutonium ions are oxidized to the hexavalent state with sodium bismuthate, sodium dichromate, or other suitable oxidizing agents. Thereafter the fission products are precipitated either directly or by carrier technique with bismuth phosphate and the hexavalent plutonium ions remain in solution. This precipitation step is called the by-product precipitation. The hexavalent plutonium ions in solution may then be reduced with hydrogen peroxide, ferrous ammonium sulfate, or like reducing agents to the tetravalent state and the process repeated.

While such a procedure functions to separate plutonium from impurities, the very low concentrations of plutonium and fission products and large amount of solu-

tions used make a quantitative separation by this method very difficult and require that the oxidation-reduction cycle be repeated until the yield is satisfactory and the radioactivity reduced so that the product may be handled without excessive shielding. The disadvantages of this procedure are especially noticeable in connection with the separation of plutonium from the phosphate-insoluble radioactive fission products, such as zirconium and columbium, since these elements tend to be closely associated with plutonium and are strong gamma emitters. It is, therefore, apparent that any method whereby the removal of the aforementioned radioactive fission products could be substantially increased in one cycle would constitute a much desired improvement over the present existing methods.

A principal object of this invention is to provide an improvement on plutonium separation processes employing a by-product carrier precipitation step, whereby the separation of radioactive fission product contaminants, in said by-product carrier precipitation step, can be substantially increased in a single decontamination cycle.

In accordance with the present invention it has been discovered that this object may be achieved by the use of a scavenger precipitate of mixed cerium and zirconium compounds. It has been found that in the plutonium separation processes in which a carrier such as a bismuth phosphate or lanthanum fluoride precipitate is used to carry radioactive fission products from a solution containing these products and plutonium ions in an oxidized state, a much higher factor of separation may be obtained by the use of a mixed by-product carrier precipitate of zirconium and cerium compounds, supplemental to the main by-product carrier precipitate. The process of this invention broadly comprises an improvement in by-product carrier precipitation from an aqueous solution containing said contaminants and plutonium in an oxidation state such that it will not form insoluble compounds with the by-product carrier used in said process, said improvement residing in a supplemental by-product carrier precipitation of compounds of cerium and zirconium and separating said precipitate.

The process of this invention may be used as an improvement on any separtion process wherein one of the steps comprises the precipitation, either directly or by carrier, of radioactive fission products by use of an anion or carrier precipitate that will not precipitate or carry the plutonium ion present. A separation process of this type is the bismuth phosphate process described above. In that process the first product precipitate of bismuth phosphate, which has carried with it plutonium in a plus four valence state and contaminants such as radioactive zirconium and columbium, is dissolved in nitric acid and the plutonium oxidized to the plus six state. In this valence state the only common insoluble plutonium compound is the hydroxide (basic nitrates, sulfates, chlorides, etc.). A bismuth phosphate precipitate is then formed in the acidic solution and separated therefrom. This precipitate, which will hereafter be referred to as the main by-product carrier precipitate, carries with it contaminants such as radioactive zirconium and columbium, but the hexavalent plutonium ion will remain in solution. The plutonium ion may then be reduced to the plus four state and precipitated from the solution with a bismuth phosphate carrier. The complete operation of plutonium oxidation, by-product carrier precipitation, plutonium reduction, and product carrier precipitation is referred to as a decontamination cycle, and may be repeated until satisfactory decontamination is obtained. In the normal bismuth phosphate process, numerous cycles are necessary since the decontamination factor is quite low. By the process of this invention, however, the decontamination factor may be increased by approximately a factor of fifteen to thirty for beta radiation, and twenty-five to fifty for gamma radiation, thus reducing the number of decontamination cycles necessary, and greatly increasing the overall efficiency of the separation process with which it is used.



Although single scavenging agents have been used in some separation processes and do constitute an improvement over the normal separation process, it has been found that by the use of the process of this invention the decontamination factor is increased by 1.5 for beta radiation and 2–5 for gamma radiation over that obtained with a single scavenging agent.

As used with the bismuth phosphate separation method, the process of this invention comprises the addition, to the solution containing plutonium ions in a hexavalent state and radioactive fission products contaminants, of zirconium and cerium compounds which are soluble in the acidic solution. The bismuth phosphate precipitate is then formed in the solution in the usual manner, and since both cerium and zirconium phosphates are insoluble, the two types of cations will form precipitates with the phosphate ions present and may be separated from the solution with the main by-product carrier precipitate of bismuth phosphate. It is believed that the greatly increased factor of decontamination obtained by the use of the process of this invention is due to a combination of several factors, including the surface adsorption of radioactive fission products ions; an exchange reaction whereby the radioactive fission products cations replace the zirconium and cerium cations of the supplemental by-product carrier, thus carrying the radioactive ions out of solution; and by an incorporation of radioactive fission product ions into the carrier crystal lattice. It will be seen that the last factor is only applicable where the supplemental by-product carriers are formed in the solution. While this is the preferable method, and both cerium and zirconium are usually added in a form that will be soluble in the acidic solution so that the supplemental by-product carrier precipitate will be formed at the same time as the main by-product carrier precipitate and be separated with it, it is possible and in some cases desirable to add either the cerium or zirconium or both to the solution as a preformed precipitate. It should also be noted that the supplemental by-product carrier precipitate may be separated from the solution prior to, or following the separation of the main by-product carrier precipitate, although the usual practice is to separate the supplemental precipitate with the main by-product carrier precipitate. The precipitate may be separated from the solution by any generally used method, such as filtration, centrifugation, or decantation.

When the zirconium and cerium salts are to be formed in solution, the cerium and zirconium ions may be added to the solution in any convenient form soluble in the acidic solution. In the bismuth phosphate process, $(NH_4)_2Ce(NO_3)_6$, and $Zr(OH)_4$ have been found to be suitable cerium and zirconium compounds. The quantities used are not rigidly fixed and will depend somewhat upon the separation process with which this invention is used; whether the supplemental precipitate is to be formed in solution; and whether the supplemental precipitate is to be removed from the solution with, or separately from the main by-product carrier precipitate. In the bismuth phosphate process where the supplemental precipitate is formed in the solution and separated with the main carrier precipitate, the amount of scavenging precipitate used has varied from 2.5 to 0.05 grams per liter of solution, with approximately 1.5 grams per liter of solution giving the best results.

The following example illustrates the use of the process of this invention with the bismuth phosphate process of plutonium separation:

## EXAMPLE

Neutron-irradiated uranium containing plutonium and radioactive fission products in small amounts was dissolved in nitric acid and a bismuth phosphate product

carrier precipitate formed in solution and separated therefrom. The product precipitate obtained was then dissolved in nitric acid and oxidized with $NaBiO_3$ and made .001 M in $K_2Cr_2O_7$. This oxidized solution was then separated into equal portions of 158 cc. each. Portion A was diluted to 944 cc., heated to 75° C., and 6.4 ml. of 85 percent $H_3Po_4$ was added to the solution over a 10 minute period. The mixture was then agitated at 75° C. for one-half hour and 1.5 gm. of freshly prepared $Zr(OH)_4$ was added in a slurry and the mixture then agitated for another one-half hour. Two grams of $(NH_4)_2Ce(NO_3)_6$ were added and the mixture was again agitated for one-half hour at 75° C. The supplemental and main by-product precipitate formed was then centrifuged off and washed with approximately 100 cc. of 0.3 M $H_3Po_4$—1 N $HNO_3$ and dissolved in HCl for analysis. The plutonium ions in the product solution were then reduced to the plus four state by the addition of 11.72 grams of ferrous ammonium sulfate to the mother liquor. 34 ml. of 85 percent $H_3Po_4$ and 15 ml. of 150 mg./ml. of $Bi^{+3}$ were added, and the resulting product precipitate was separated thus completing the decontamination cycle. The product precipitate was then carried through a second decontamination cycle identical in procedure with the first. The second portion of the original solution was used as a control and carried through two decontamination cycles identical with those just described, except that cerium and zirconium scavengers were not added to the solutions. The results of this test are tabulated below.

*Table I.—Use of* Ce *and* Zr *scavengers with* $BiPo_4$ *process*

| Fraction | Run 1 (With Zr and Ce Scavengers), counts per minute | | Run 2 (Control), counts per minute | |
|---|---|---|---|---|
| | Beta | Gamma | Beta | Gamma |
| 1st Product Precipitate | 4,688,250 | 350 | 15,970,500 | 10,150 |
| 1st By-product Precipitate. | 45,700,000 | 139,868 | 41,650,000 | 117,100 |
| 2nd Product Precipitate | 70,350 | 74.5 | 770,700 | 1,624 |
| 2nd By-product Precipitate. | 4,535,008 | 336 | 14,014,684 | 10,016 |

The overall decontamination factors for one decontamination cycle are shown below:

*Table II*

| | Run 1 | Run 2 (control) |
|---|---|---|
| Beta | 840 | 76 |
| Gamma | 1,754 | 80 |

It will be noted that in Table II the decontamination factors for a single decontamination cycle only are shown. Other experiments on the use of the process of this invention with the bismuth phosphate separation process, similar to the one described above, but in which the product was carried through several decontamination cycles showed the following results:

*Table III.—Decontamination factor (overall)*

| | Use of $Zr(OH)_4$ and $Ce^{+4}$ Scavengers | Control |
|---|---|---|
| I | | |
| Beta | 3,600 | 320 |
| Gamma | 4,000 | 190 |
| II | | |
| Beta | 2,315 | 105 |
| Gamma | 4,450 | 69 |

While the process of this invention has been illustrated with the bismuth phosphate process which depends on changes in valence of the plutonium ion between the plus four and plus six states, the use of the process of this invention is not limited to this process with bismuth phosphate. Thus it may be used with processes employing such carriers as the fluorides of lanthanum, cerium, and other rare earths, thorium iodate, and thorium oxalate. This process is also applicable to separation processes based upon the changes in solubilities of plutonium in the plus three and plus four valence states, or in the plus three and plus six valence states. Thus since the proces of this invention may be used in such a wide variety of separation processes, it will be seen that it will have a broad application with any separation process employing a by-product carrier precipitation step.

What is claimed is:

1. In a process for separating plutonium from fission products in aqueous nitric acid solution by decontamination steps including by-product carrier precipitation, the improvement which comprises adding to an aqueous solution containing said fission products and plutonium in a valence state greater than plus four a nitric-acid-soluble ceric compound, a nitric-acid-soluble zirconium compound, and a carrier cation, coprecipitating said zirconium, ceric and carrier ions, and removing the mixed precipitate formed, the quantity of said cerium and zirconium precipitates being between 0.05 and 2.5 grams per liter of solution.

2. In a process for separating plutonium from fission products in an aqueous nitric acid solution by forming a bismuth phosphate precipitate in a solution containing said fission products and plutonium in a valence state of plus six and removing said precipitate therefrom, the improvement which comprises adding to the solution nitric-acid-soluble compounds of cerium IV and zirconium whereby a supplemental precipitate of cerium and zirconium phosphate forms, the quantity of said cerium and zirconium precipitates being between 0.05 and 2.5 grams per liter of solution, and removing said supplemental precipitate.

3. In a process for separating plutonium from fission products in aqueous solution by decontamination steps including by-product carrier precipitation, the improvement which comprises introducing into an aqueous solution containing said fission products and plutonium in the hexavalent state of oxidation from 0.05 to 2.5 grams per liter of solution of a supplemental by-product carrier precipitate comprising phosphates of cerium IV and zirconium, and removing the by-product carrier precipitate and the supplemental by-product carrier precipitate.

4. In a process for separating hexavalent plutonium from fission products contained in aqueous solution by decontamination steps including by-product carrier precipitation, the improvement which comprises adding to said aqueous solution from 0.05 to 2.5 grams per liter of solution of a supplemental by-product carrier precipitate of cerium IV and zirconium phosphates, and removing said supplemental by-product precipitate together with the by-product carrier precipitate.

5. In a process for separating hexavalent plutonium from fission products contained in an aqueous nitric acid solution by forming a bismuth phosphate precipitate in said solution, the improvement which comprises adding to said solution ceric ammonium nitrate and zirconium hydroxide to form a concentration of from 0.05 to 2.5 grams per liter of a supplemental precipitate of phosphates of cerium and zirconium, and removing said supplemental precipitate together with the by-product carrier precipitate.

6. The process of claim 5, wherein about 1.5 grams of zirconium hydroxide and 2 grams of ceric ammonium nitrate are added per one liter of solution.

7. A process of separating plutonium values from fission product values present on a bismuth phosphate carrier, comprising dissolving said carrier in nitric acid, oxidizing the plutonium values to the hexavalent state,

adding phosphoric acid to said solution, adding zirconium hydroxide and ceric ammonium nitrate to said solution whereby a mixed carrier precipitate containing fission products forms, separating said mixed precipitate from the solution, reducing the plutonium values in the solution to the tetravalent state, forming a bismuth phosphate carrier precipitate in said solution, and separating said bismuth phosphate carrier precipitate containing said tetravalent plutonium values from said solution.

8. The process of claim 7 in which the zirconium hydroxide and the ceric ammonium nitrate are added in a quantity to yield a total zirconium and ceric precipitate concentration of between 0.05 and 2.5 grams per liter of solution.



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