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PRECIPITATION METHOD OF SEPARATING PLUTONIUM FROM CONTAMINATING ELEMENTS

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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 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 about 35 to about 46 and a heavy group with atomic numbers from about 51 to about 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 46; 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 production of plutonium as it is usually made by the bombardment of natural uranium with neutrons produced 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 and granted on March 19, 1957, as U. S. Patent No. 2,785,951.

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 plutonim 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 step 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 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 may be repeated.

While such a procedure functions to separate plu-

tonium from impurities, the very low concentrations of plutonium and fission products and large amount of solutions 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 is 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 completed in one operation would constitute a much desired improvement over the present existing methods.

In accordance with the present invention it has been discovered that this object may be achieved by the use of a hydroxide of a metal of group IV B of the periodic table as published in the book "Fundamental Chemistry," second edition, by H. G. Deming, John Wiley & Sons, Inc., as a scavenger for the removal of those radioactive uranium fission products which are carried with plutonium in a plus four valence state. The process of this invention consists broadly of the improvement in a process for recovering plutonium from radioactive uranium fission product contaminants in aqueous solutions by decontamination steps including by-product carrier precipitation, which comprises that novel step of introducing a pre-formed hydroxide of a metal of group IV B into an aqueous acidic solution containing plutonium in a higher oxidation state, radioactive uranium fission products contaminant, and a uranium fission products contaminant carrier precipitate, and thereafter separating the metal hydroxide and by-product precipitate.

The process of this invention may be used as a supplemental step in most carrier precipitation processes, and its use has been found to be especially desirable as a method of increasing the efficiency of such separation process as the bismuth phosphate process and the lanthanum fluoride process. The process of this invention has been found to increase the efficiency of the separation of radioactive fission products so greatly that substantially complete separations of the uranium fission products may be made in a single cycle precipitation, thus eliminating the necessity for the multi-cycle method of by-product precipitation that was necessary under the previously mentioned methods. The substantially complete precipitation of fission products achieved by use of the process of this invention removes the bulk of the remaining harmful radioactivity from solutions of plutonium and fission products, thus making it possible to decrease the amount of shielding necessary to screen operating personnel from radioactivity.

While the process of this invention is especially useful in the separation of plutonium from uranium fission products in that step of the bismuth phosphate-separation process which comprises precipitating phosphate insoluble fission products from a solution containing such products and phosphate-soluble plutonium ions, it also may be used in any other plutonium separation process wherein one of the steps comprises the precipitation, either directly or by carrier, of radioactive uranium fission products by use of an anion, or carrier, that will not precipitate the plutonium present.

Most other precipitation processes for the separation of plutonium contain as an essential part the step described above. Separation processes in which the step described above comprises an essential operation in the process include those in which the separation depends on the difference in solubility between plutonium compounds, wherein the plutonium is contained in the plus three and plus four valence states; the plus three and plus six valence states; as well as the plus four and plus six valence states. The last is exemplified by the bismuth phosphate process described above. Many carriers may be used in such precipitations either singly or in combination. As examples there may be mentioned the fluorides of lanthanum, cerium and other rare earths, thorium iodate, thorium oxalate, and bismuth phosphate. Thus, since this step is an integral part of most plutonium separation processes that have been previously used, it may be seen that the process of this invention will have a broad application as an improvement on various existing processes, since it can be used to great advantage with any known process employing the step described above.

The process of this invention is particularly advantageous since it may be used in the separation of plutonium wherein the plutonium and fission products are present in any concentrations. Thus, it may be used not only where the fission products are in such concentrations that they may be precipitated directly from solution, but it also may be used where the fission products are in such low concentrations that a carrier is used to precipitate the fission products out of solution.

While any preformed hydroxide of the metal group IV B of the periodic table may be used in this process, the hydroxides of zirconium and titanium have been found to be preferable for the separation of the radioactive fission products usually carried with plutonium when it is precipitated in a plus four valence state. Although the exact mechanism by which the metal hydroxide carries the uranium fission products from solution is not definitely known, it is believed that it may be due to any one of several factors or a combination of them. These factors include the surface adsorption of fission product ions and an exchange reaction whereby the radioactive fission products cations replace the cations of the hydroxide precipitate thus carrying the radioactive ions out of solution.

Where the preferred embodiment of this invention, which comprises the contacting of the plutonium fission products solution with the pre-formed metal hydroxide slurry, is used it is advisable to control the activity of the solution, since if the acidity is too great, the metal hydroxide will dissolve, and if the acidity is too low, the plutonium ion will precipitate as the hydroxide or will be carried out of solution by the hydroxide. The limits of acidity will vary somewhat with the concentrations of the ions in solution and with the specific metal hydroxide used. In general however it has been found that the hydroxide will remain in the solid state, if the acidity of the solution is not appreciably above 1 N, and that the plutonium will not precipitate, if the acidity is not appreciably below 0.5 N. Where the process of this invention is used as a step in the bismuth phosphate process of separation, it has been determined that the optimum acidity of the plutonium-uranium fission products solution is approximately 1 M nitric acid or equivalent of other suitable acids.

In order that the plutonium remain in solution when the plutonium-uranium fission products solution is contacted with the metal hydroxide, it is necessary that the plutonium ion be in a valence state greater than plus four. Therefore if the plutonium ion is contained in the plutonium-uranium fission products solution in the plus three or plus four valence state, it will be necessary to oxidize the plutonium to a higher valence state, prior to the introduction of the metal hydroxide. This oxidation may be accomplished by the use of sodium bismuthate or any other generally accepted oxidizing agent. When the process of this invention is used as a step in such generally used oxidation-reduction separation processes as the bismuth phosphate process, the oxidation of the plutonium to a valence state greater than four is a normal part of said processes, and thus the fulfillment of the condition of the process of this invention that the plutonium ion be in solution in a valence state greater than four will not entail any additional steps. Since the oxida-

tion of the plutonium is accomplished prior to the contacting of the plutonium-uranium fission product solution by the metal hydroxide, the method of oxidation will not affect the use of this invention.

The precipitate containing the fission products may be separated from the solution containing the plutonium by any generally used method, such as filtration or centrifugation.

The present invention may be further illustrated by the following specific example.

Example

A solution obtained by dissolving the phosphate precipitate of plutonium and fission products already containing bismuth in 10 normal nitric acid is diluted to 5 normal nitric acid and the plutonium is oxidized with 0.01 molar sodium bismuthate for one hour at 50° C. The oxidized solution is then diluted with water to a nitric acid concentration of 1 M, and phosphoric acid is added until the solution is 0.1 molar with respect thereto. This solution is digested for about thirty minutes at about 50° C. There after 100 grams per liter of zirconium hydroxide is added to the solution as the preformed zirconium hydroxide in an aqueous slurry, and the product is centrifuged to separate solids from the aqueous mixture. The plutonium in the mother liquor is then reduced and precipitated with bismuth phosphate in accordance with the procedure set forth above. The resulting precipitate contains only $\frac{1}{6500}$ of the original beta radioactivity and $\frac{1}{13,700}$ of the original gamma radiation compared to $\frac{1}{2750}$ and $\frac{1}{1140}$ of the beta and gamma activity when the bismuth phosphate separation is conducted without using the process of this invention.

While the example above illustrates the process of this invention with zirconium hydroxide as the metal hydroxide and the bismuth phosphate process as the general method of separation of plutonium, it is to be understood that this process is not to be limited to this example, but that it is capable of many modifications. Thus, the hydroxide used may be that of any metal of the IV B group, but preferably those which are similar in ionic structure to the uranium fission products such as zirconium and titanium.

This invention may also be used in any general process of separation which contains a step whereby insoluble fission products are precipitated from a solution containing soluble plutonium ions. Changes, therefore may be made without departing from the spirit and scope of the invention as described in the appended claims.

What is claimed is:

1. In a process for recovering plutonium from radioactive uranium fission products in aqueous solutions by decontamination steps including by-product carrier precipitation, the improvement which comprises introducing a preformed aqueous slurry of a hydroxide of a metal of group IV B into an aqueous acidic solution in which the acidity of the solution is between about 0.5 N and 1 N and which contains the plutonium in the hexavalent state, radioactive uranium fission products contaminant, and a by-product carrier precipitate and separating said metal hydroxide together with the by-product carrier precipitate.

2. In a process for recovering plutonium from radioactive uranium fission products in aqueous solutions by decontamination steps including by-product carrier precipitation, the improvement which comprises introducing a preformed aqueous slurry of zirconium hydroxide into an aqueous acidic solution containing plutonium in the hexavalent state, acid in a concentration of from 0.5 to 1 N, radioactive uranium fission products contaminant, and a by-product carrier precipitate and separating said zirconium hydroxide together with the by-product carrier precipitate.

3. In a process for recovering plutonium from radioactive uranium fission products in aqueous solutions by decontamination steps including by-product carrier precipitation, the improvement which comprises introducing a preformed aqueous slurry of a titanium hydroxide into an aqueous acidic solution containing plutonium in the hexavalent state, acid in a concentration of from 0.5 to 1 N, radioactive uranium fission products contaminant, and a by-product carrier precipitate and separating said titanium hydroxide together with the by-product carrier precipitate.

4. In a process for recovering plutonium from uranium fission products contaminant in an aqueous solution by forming a bismuth phosphate precipitate in a solution containing acid in a concentration of between 0.5 and 1 N, plutonium in a valence state greater than plus four and radioactive uranium fission products and removing the precipitate therefrom, the improvement which comprises introducing into the solution a preformed aqueous slurry of a group IV B metal hydroxide, and removing from the solution the metal hydroxide together with the bismuth phosphate carrier precipitate.

5. In a process for recovering plutonium from uranium fission products contaminant in an aqueous acidic solution by forming a bismuth phosphate precipitate in a solution containing plutonium in a valence state greater than plus four and radioactive uranium fission products and removing the precipitate therefrom, the improvement which comprises introducing into the acidic solution having an acidity between about 0.5 N and 1 N a preformed aqueous slurry of zirconium hydroxide, and removing the zirconium hydroxide together with the bismuth phosphate carrier precipitate from the solution.

6. In a process for recovering plutonium from uranium fission products contaminant in an aqueous acidic solution by forming a bismuth phosphate precipitate in a solution containing plutonium in a valence state greater than plus four and radioactive uranium fission products and removing the precipitate therefrom, the improvement which comprises introducing into the acidic solution having an acidity between about 0.5 N and 1 N a preformed aqueous slurry of titanium hydroxide, and removing the titanium hydroxide together with the bismuth phosphate carrier precipitate from the solution.

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