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METHOD OF CONCENTRATING FISSIONABLE MATERIAL

Louis B. Werner and Bernard A. Fries, Richland, Wash., and Glenn T. Seaborg, Chicago, Ill.

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Our invention relates to a process for the concentration of plutonium. More particularly, it is concerned with the concentration of the plutonium present in dilute decontaminated solutions thereof.

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 "Np" refer to a new element known as neptunium having an atomic number of 93.

Natural uranium is composed of two isotopes, namely, 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 third isotope, U^{239}, is produced having 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. During the neutron bombardment, fission of the U^{235} isotope present in natural uranium produces a number of highly radioactive fission fragments and decay products thereof all of which may be termed fission products. These fission products are composed of two distinct groups including a heavy group having atomic numbers of about 51 to 60 and a light group having atomic numbers of about 35 to 46. Such products make the mass extremely difficult to handle without danger of exposure of personnel to gamma radiation. Neutron bombardment is discontinued before the concentration of U^{239} and its products of decay increase since continued bombardment causes decomposition of the plutonium as rapidly as it is formed. Owing to this fact, plutonium is present in the bombarded uranium in small quantities, usually less than one percent by weight and frequently of the order of one or several parts per million parts by weight of uranium, the exact concentration depending on the density and length of neutron bombardment, and hence it is difficult to separate from the uranium or even to form a uranium concentrate of high plutonium content.

Plutonium obtained from neutron bombarded uranium metal is removed therefrom by dissolving the latter in a suitable acid, preferably nitric acid. Thereafter the plutonium is separated from uranium and the various fission products by means of any of several decontamination procedures. A method suitable for this purpose is that described and claimed in copending application U. S. Serial No. 478,570, filed March 9, 1943, by Stanley G. Thompson et al. In accordance with the procedure there described neutron irradiated uranium is dissolved in nitric acid, or preferably a mixture of nitric and sulfuric acids, after which a source of bismuth ion, usually in the form of bismuth nitrate, is added. Thereafter, phosphoric acid, or some other suitable source of phosphate ion, is introduced into the solution whereupon a precipitate of bismuth phosphate is produced carrying with it plutonium in a valence state not greater than 4 and a

relatively small proportion of the various fission products. The uranium and the bulk of the fission products are quite soluble under the conditions employed and remain in solution. The precipitate thus obtained is removed by filtration or other convenient means and the mother liquor discarded. The bismuth phosphate precipitate, which contains plutonium as the phosphate and some fission products, is dissolved in nitric acid and the solution further decontaminated by oxidizing the plutonium to a valence state greater than 4, usually the hexavalent state, and precipitating bismuth phosphate together with fission products from the soluble plutonium. However, since it is ultimately desired to obtain plutonium in as highly purified form as possible, other methods for the further separation of fission products therefrom must be employed.

Moreover, plutonium-containing solutions obtained in accordance with the general procedure outlined above are extremely dilute with respect to plutonium and hence in order to recover that element in appreciable quantities it becomes necessary to handle tremendous volumes of decontaminated solution.

An object of our invention is to furnish a procedure whereby the plutonium can be recovered from the original decontaminated solution in concentrations which are greatly increased over the low plutonium concentrations found in the previously decontaminated solutions.

Additional objects and advantages of our invention will be apparent from the description that follows.

We have now discovered a procedure by which the concentration of plutonium present in solutions of the above-mentioned type can readily be effected, and if fission products are present, a substantial separation of such products also may be recovered. Broadly, our invention involves the utilization of columbic oxide and a water insoluble compound of lanthanum such as the fluoride, oxalate, or hydroxide, or combinations thereof. Both columbic oxide and the lanthanum compounds will bring down plutonium from dilute solutions in the presence of the other. Thus, plutonium may be brought down with a lanthanum carrier and, the precipitate of plutonium and carrier may be dissolved in a smaller volume of solvent than that from which the carrier was precipitated to give a more concentrated solution of lanthanum, together with the plutonium removed by the lanthanum carrier. Thereafter, plutonium may be carried from the concentrated solution of lanthanum by adding thereto a columbium compound, preferably columbic oxide. This process may be repeated forming progressively more concentrated solutions until the concentration of plutonium is such that on solution the plutonium can be precipitated substantially completely without the aid of a carrier.

In a preferred embodiment, the process of our invention is carried out in accordance with the description which follows. A plutonium solution, preferably one which has been substantially freed from fission products, is obtained. For example, a bismuth phosphate carrier precipitate is formed in a solution containing plutonium in a valent state not greater than 4, and whose original fission product concentration has been reduced by a factor of about 10,000. Thus while we prefer to decontaminate the solution containing fission products by the bismuth phosphate carrier method described above, the particular process by which this decontamination is performed is immaterial in accomplishing our objects as long as the principal fission products are removed. The plutonium containing precipitate wherein the plutonium is present in a valence not higher than 4, is dissolved in nitric acid and to the resulting solution are then added in succession, and in approximately equal stoichiometric quantities, lanthanum nitrate and hydrofluoric acid, where-

upon lanthanum fluoride is precipitated carrying down with it plutonium probably as plutonium trifluoride and/or plutonium tetrafluoride. The precipitate thus obtained is then washed with dilute sodium hydroxide to remove any excess fluoride ions that may be present, after which the washed lanthanum fluoride precipitate is metathesized with an alkali metal hydroxide such as, for example, potassium or sodium hydroxides, to yield lanthanum hydroxide which is readily soluble in nitric acid. The lanthanum hydroxide precipitate is next washed with water to remove any fluoride ions that might be present, after which it is dissolved in concentrated nitric acid, preferably limiting the amount of solvent to produce a solution substantially smaller in volume than that of the initial plutonium solution. At this point, a source of zirconium ions may be added, if desired, to assist in the solution of the washed lanthanum hydroxide precipitate by forming a soluble zirconium-lanthanum fluoride complex with the fluoride ions, and/or with the lanthanum fluoride remaining therein. The undissolved precipitate remaining suspended in solution after the last mentioned step contains very little, if any, plutonium and may be separated and discarded. The pH of the solution is next adjusted to a value of between about 1 and 2 and then a quantity of columbic oxide is added while agitating. When sufficient columbic oxide has been introduced, agitation is stopped and the columbic oxide is permitted to settle or is centrifuged, carrying with it the dissolved plutonium. The resulting mass, consisting essentially of columbic oxide and associated plutonium, is washed with dilute sulfuric acid and then dissolved in a relatively small volume of hydro-fluoric acid, oxalic acid, or an alkali metal hydroxide to give a concentrated solution of columbium ions which generally is more concentrated as to plutonium.

Where a portion of the lanthanum is not removed by treatment of the columbic oxide precipitate with dilute sulfuric acid, this lanthanum precipitates as the fluoride or similar compound carrying with it the plutonium. In any event sufficient lanthanum is introduced into the solution to produce a precipitate which substantially completely removes the plutonium. This lanthanum fluoride precipitate is next washed with dilute sodium hydroxide metathesized with strong alkali, and then the metathesized product is washed with water. The product is next dissolved in a small volume of nitric acid to give a solution of plutonium whose volume may be of the order of 10,000 fold less than the volume of the original plutonium-containing solution. At this point in the process, the plutonium is converted in a known manner to a relatively insoluble compound such as the peroxide or the iodate thereby effecting separation thereof from the dissolved lanthanum by direct precipitation without carrier. Also in this connection it will be noted that, while the original solution employed is very low in fission product concentration, the solution ultimately obtained has been further decontaminated. Generally, the extent to which additional fission products have been removed from the solution thus treated may be represented by a decontamination factor of between about 100 and 1,000.

Our invention may be further illustrated by the following specific example:

Example

10 g. of lanthanum fluoride together with 100,000 counts per minute of plutonium were precipitated by the addition of hydrofluoric acid to 40 liters of a plutonium-containing solution whose original fission product concentration had been decreased to the extent of a factor of 10,000, and to which had been added lanthanum nitrate. After washing the resulting precipitate with 1 N sodium hydroxide to remove excess fluoride ions, it was reacted with four times its volume of 10 N potassium hydroxide for a period of about two hours at a temperature of between 75 and 100° C. in order to convert the lanthanum fluoride to lanthanum hydroxide. The precipitate thus obtained was next washed three times with water, the volume of each portion employed being about three times the volume of the precipitate. The washed precipitate was then dissolved in concentrated nitric acid in the presence of about 3 g. of zirconium nitrate to give a solution of 150 ml., the lanthanum concentration being 70 mg. per ml. The small quantity of undissolved precipitate which was removed at this stage contained relatively little plutonium and was discarded. The pH of the solution was then adjusted to a value of about 2 and thereafter columbic oxide was introduced in an amount equivalent to that which, if soluble, would yield a solution 0.005 M in columbic ion. Columbic oxide was then allowed to settle out of solution carrying with it the plutonium. This precipitate, which had a volume of 30 ml., was then washed four times with 100 ml. portions of 0.001 N sulfuric acid. It was next transferred to an acid resistant tube and hydrofluoric acid added thereto. That portion of the lanthanum which had not been extracted by washing the columbic oxide precipitate with dilute sulfuric acid, precipitated as the fluoride carrying with it the plutonium. This precipitate was washed with 1 N sodium hydroxide to remove excess fluoride ions, metathesized with 10 N potassium hydroxide, and then washed three times with water. The metathesized precipitate was next dissolved in concentrated nitric acid, the final volume of the solution which contained 81 percent of the plutonium originally present, being 4 ml.

The table appearing below shows the distribution of plutonium in terms of percent of total plutonium at various stages throughout the process, employing a solution containing sufficient plutonium to provide a concentration of 100,000 counts per minute.

	Percentage of Total recovered activity
Activity not precipitated by Cb_2O_5	3.4
1st Cb_2O_5 wash	4.7
2nd Cb_2O_5 wash	1.6
3rd & 4th wash	4.7
Percentage concentration not precipitated by second LaF_3 precipitation step	3.3
Supernatant from KOH metathesis and H_2O washes	0.9
Plutonium recovered in final solution	81.0
Plutonium in insoluble residue	0.9

It will be apparent to those skilled in the art that the process of our invention is susceptible of numerous alterations and modifications and that such changes can be made without departing from the scope thereof. For example, the process may be conducted in an alternate manner by first removing plutonium from this solution with columbic oxide and dissolving columbic oxide and plutonium in a suitable solvent such as oxalic acid to form a solution of smaller volume than that from which the plutonium was initially removed by the columbic oxide. Thereafter, this second solution may be treated with lanthanum as herein described to precipitate an insoluble lanthanum compound, such as lanthanum fluoride, oxalate or hydroxide, and to remove the plutonium from solution. This process may be repeated, alternately using columbic oxide and an insoluble lanthanum compound carrier and progressively forming a more concentrated solution of plutonium. While the process may be performed in a manner such that the carriers are precipitated in situ in the plutonium solution as previously described, this is unnecessary since the carrier precipitate may be preformed and introduced into the solution in which they are to be used, if desired. Moreover, while it is generally found preferable to subject to treatment solutions which have been previously treated for decontamination at least to a partial degree, from radioactive fission products, it is also possible to subject a solution of neutron irradiated uranium or any other solution of plutonium and radioactive fission products to treatment as herein contemplated without the use of any other puri-

fication or decontamination. Therefore, it is to be strictly understood that the above example is to be construed as merely illustrative and not limitative of our invention. In general, it may be said that our invention is to be considered generally applicable to the concentration and purification of dilute solutions of plutonium which may or may not contain fission products.

Our invention now having been described, what we claim is:

1. A process for the recovery of plutonium values in a concentrated form from a solution containing plutonium compounds which comprises adding to the resulting solution a soluble lanthanum compound, converting the lanthanum to a substantially water insoluble compound whereby plutonium values are carried down therewith, dissolving the resulting lanthanum carrier containing the plutonium values in a smaller volume of solvent than was utilized to dissolve the original solution containing plutonium, adding to the solution thus formed a source of columbium in the pentavalent state, precipitating the columbium as columbic oxide thereby carrying down plutonium values with it, dissolving the columbic oxide carrier and said plutonium values in a volume of solvent which is less than that of the solution from which said columbium oxide was precipitated, and repeating the above cycle to effect further purification and volume reduction.

2. In a process for the recovery of plutonium values in a more concentrated form from compositions containing plutonium compounds and a substantially water-insoluble lanthanum carrier, the steps which comprise dissolving said plutonium compounds containing lanthanum carrier, removing the plutonium values from the resulting solution with the aid of a columbic oxide carrier while maintaining the lanthanum carrier in solution, dissolving the columbic oxide carrier containing the plutonium values in a volume of solvent smaller than that represented by the original lanthanum carrier plutonium solution, and removing the plutonium values from the solution thus formed by means of a lanthanum carrier while maintaining the columbium values in solution.

3. In a process for the recovery of plutonium values in a concentrated solution containing plutonium compounds, the steps which comprise adding to the solution a soluble lanthanum compound, converting the lanthanum to a substantially water insoluble compound whereby the plutonium values are carried down therewith, dissolving the resulting lanthanum carrier containing said plutonium values in a smaller volume of solvent than was utilized to dissolve the original solution containing plutonium and carrier, adding to the solution thus formed a source of columbium in the pentavalent state, precipitating the columbium as columbium oxide thereby carrying down said plutonium values with it, and dissolving the columbium oxide carrier containing said plutonium in a volume of solvent which is less than that from which the columbium oxide was precipitated.

4. A process for the recovery of plutonium values in a more concentrated solution containing plutonium compounds, and a relatively low concentration of compounds of fission products, which comprises dissolving said plutonium values contained in a carrier precipitate, adding to the resulting solution a soluble lanthanum compound, converting the lanthanum to a substantially water insoluble compound, whereby said plutonium values are carried down therewith, dissolving the resulting lanthanum carrier containing said plutonium values in a smaller volume of solvent than was utilized to dissolve the original solution containing plutonium, adding to the solution thus formed a source of columbium in the pentavalent state, precipitating the columbium as a columbic oxide thereby carrying down said plutonium values with it, dissolving the columbic oxide carrier containing said plutonium values in a volume of solvent which is less than that of the solution from which said columbium oxide was precipitated, and repeating the above cycle to effect further purification and volume reduction.

5. A process for the recovery of plutonium values in a more concentrated form from a composition containing plutonium compounds, a carrier, and a relatively low concentration of compounds of fission products, which comprises dissolving said composition, adding to the resulting solution a soluble lanthanum compound, converting the latter to insoluble lanthanum fluoride whereby said plutonium values are carried down therewith, dissolving the resulting precipitate in a smaller volume of solvent than was utilized to dissolve the aforesaid composition, adding preformed columbic oxide to the solution thus formed, removing said columbic oxide and the plutonium values adsorbed thereon from said solution, dissolving the columbic oxide carrier containing said plutonium values in a volume of solvent which is less than that from which said plutonium values were precipitated and repeating the above cycle to effect further purification and volume reduction.

6. In a process for the recovery of plutonium values in a more concentrated form from a composition comprising plutonium compounds, lanthanum fluoride carrier, and a relatively low concentration of compounds of fission products, the steps which comprise dissolving said composition, adding to the resulting solution a soluble lanthanum compound, converting the latter to insoluble lanthanum fluoride whereby said plutonium values are carried down therewith, dissolving the resulting precipitate in a smaller volume of solvent than was utilized to dissolve the aforesaid composition, adding columbic acid to the solution thus formed whereby it precipitates as columbic oxide, removing said columibc oxide and the plutonium values adsorbed thereon from said solution, and dissolving the columbic oxide carrier containing said plutonium values in a volume of solvent which is less than that from which said columbic oxide was precipitated.

7. A process for the recovery of plutonium values in a more concentrated and purified form from a composition comprising a lanthanum fluoride carrier, plutonium compounds, and a relatively low concentration of compounds of fission products, which comprises converting said lanthanum fluoride to lanthanum hydroxide by metathesis with an alkali metal hydroxide, dissolving the lanthanum hydroxide thus formed in nitric acid, adding columbic acid to the resulting solution to form columbic oxide which precipitates carrying with it said plutonium values and fission product values, dissolving this precipitate in a volume of hydrofluoric acid smaller than the volume of the solution from which said columbic oxide was precipitated, forming in this solution a lanthanum fluoride carrier thereby removing said plutonium values from said solution, and repeating the above cycle to effect further purification and volume reduction.

8. A method of obtaining a concentrate of plutonium values which comprises contacting aqueous solution of plutonium compounds with a substantially water insoluble lanthanum compound whereby the plutonium values in the solution become associated with the lanthanum compound, removing the insoluble lanthanum compound together with the associated plutonium values, dissolving said plutonium values to form a second aqueous solution of smaller volume than the first named aqueous solution and removing said plutonium values from the second solution by contacting the second solution with columbic oxide.

9. A method of obtaining a concentrate of plutonium compounds which comprises contacting aqueous solution of plutonium values with columbic oxide whereby the plutonium values in the solution become associated with the columbic oxide, removing the insoluble columbic oxide together with the associated plutonium values, dissolving the plutonium values to form a second aqueous

solution of smaller volume than the first named aqueous solution and removing said plutonium values from the second solution by contacting the second solution with a substantially water-insoluble lanthanum compound.

10. A process for the recovery of plutonium values in a more concentrated and purified form from a composition comprising a lanthanum fluoride carrier, plutonium compounds, and a relatively low concentration of compounds of fission products, which comprises converting said lanthanum fluoride to lanthanum hydroxide by metathesis with an alkali metal hydroxide, dissolving the lanthanum hydroxide thus formed in nitric acid, adding columbic acid to the resulting solution to form columbic oxide which precipitates carrying with it said plutonium values and fission product values, dissolving this precipitate in a volume of oxalic acid smaller than the volume of the solution from which said columbic oxide was precipitated, forming in this solution a lanthanum fluoride carrier thereby removing the plutonium values from said solution, and repeating the above cycle to effect further purification and volume reduction.

11. A process for the recovery of plutonium values in a more concentrated and purified form from a composition comprising a lanthanum fluoride carrier, plutonium compounds, and a relatively low concentration of compounds of fission products, which comprises converting said lanthanum fluoride to lanthanum hydroxide by metathesis with an alkali metal hydroxide, dissolving the lanthanum hydroxide thus formed in nitric acid, adding columbic acid to the resulting solution to form columbic oxide which precipitates carrying with it said plutonium values and fission product values, dissolving this precipitate in a volume of potassium hydroxide smaller than the volume of the solution from which said columbic oxide was precipitated, forming in this solution lanthanum hydroxide carrier thereby removing the plutonium values from said solution, and repeating the above cycle to effect further purification and volume reduction.

12. A process for the recovery of fission products, and for the concentration of plutonium values, which comprises dissolving a carrier precipitate containing plutonium values and fission product values, adding to the resulting solution a soluble lanthanum compound, converting the lanthanum to a substantially water-insoluble compound whereby said plutonium values and a portion of said fission product values are carried down therewith leaving the balance of the fission product values in the solution in an uncontaminated state, dissolving the resulting lanthanum carrier containing said plutonium values and fission product values in a smaller volume of solvent than was utilized to dissolve the original solution containing plutonium values, adding to the solution thus formed a source of columbium in the pentavalent state, precipitating the columbium as a columbic oxide thereby carrying down said plutonium values with it and leaving the balance of the fission product values in solution in an uncontaminated state, and dissolving the columbic oxide carrier containing said plutonium values in a volume of solvent which is less than that of the solution from which said columbium oxide was precipitated.

No references cited.