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PROCESS FOR THE SEPARATION OF HEAVY METALS

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FIG. 1.

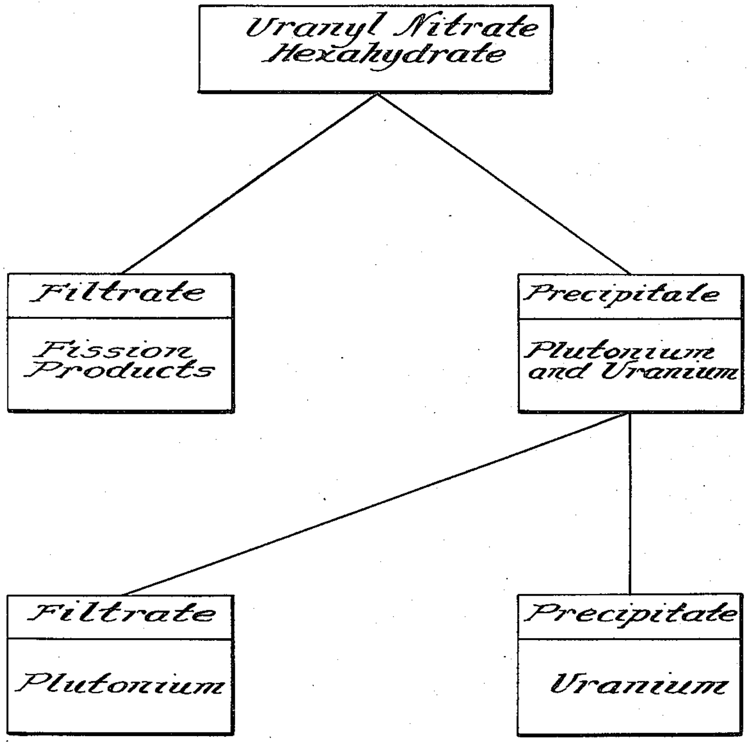

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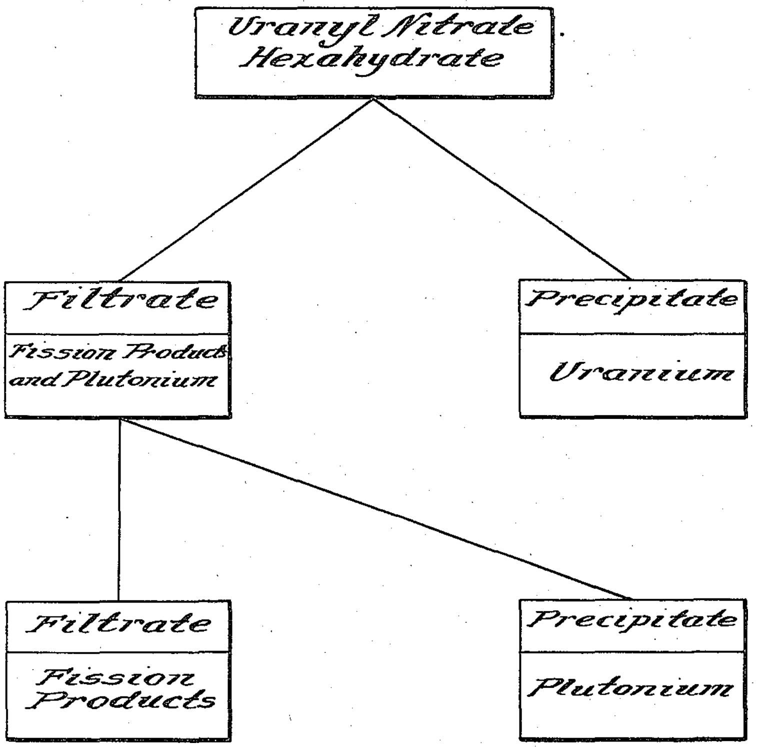
FIG. 2.



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PROCESS FOR THE SEPARATION OF HEAVY METALS

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10 Claims. (Cl. 260—429.1)

This invention relates to the separation of element 94 from other substances, and more particularly, to the separation of element 94 from various substances of the kind present in neutron irradiated uranium, such as uranium, fission products, and the like.

It is an object of the invention to obtain element 94 in a concentrated state by a process in which advantage is taken of the solubility characteristics of element 94 and the substances from which it is to be separated, particularly with respect to different oxidation states of element 94. It is a further object of the invention to provide a process suitably adapted for concentrations of element 94 such as are obtained from neutron irradiated uranium where foreign substances such as uranium, fission products, and the like are present. A further object is to provide a method by which plutonium may be removed from a solution by precipitation of a complex salt of sodium or similar alkali metal, acetic acid and uranium or plutonium. Other objects and advantages will be apparent from the following detailed description.

As described herein, the isotope of element 93 having a mass of 239 is referred to as 93^{239} and the isotope of element 94 having a mass of 239 is referred to as 94^{239}. Element 94 may also be spoken of as plutonium, symbol Pu.

Neutron irradiated uranium may be prepared by reacting uranium with neutrons from any conventional neutron source, but preferably the neutrons used are obtained from a chain reaction of neutrons with uranium.

Sodium plutonyl acetate precipitated by the process herein described forms as a pink crystalline precipitate of low solubility in dilute weak acid solution but which is soluble or at least decomposable in strong acids such as nitric acid. The crystals of sodium plutonyl acetate are isotropic tetrahedral crystals which measure about 1 to 10 microns from one edge to the opposite point. The solubility of sodium plutonyl acetate decreases with increased sodium ion and in general is less soluble than sodium uranyl acetate.

In the drawings, Fig. 1 diagrammatically represents a process embodying the invention, and Fig. 2 similarly represents a modified process.

Neutron irradiation of uranium produces 92^{239} which has a half-life of 23 minutes and by beta decay becomes 93^{239}. This element has a half-life of 2.3 days and by beta decay becomes 94^{239}. Neutron irradiated uranium contains 93^{239}, 94^{239} and a large number of radioactive fission products produced by reaction of neutrons on fissionable atoms, such as U^{235} which is present in uranium from natural sources. It also contains minor amounts of products of the natural radioactive decay of uranium isotopes, such as UX_1 and UX_2. The amount of 93^{239} and 94^{239} combined is generally minute, such as, for example, approximately 0.02 percent by weight. By storing the neutron irradiated uranium for a suitable period of time, the 93^{239} is converted almost entirely to 94^{239}. The fission products are present in the neutron irradiated uranium generally to an extent up to about 0.02 percent by weight. Because the fission products in general are highly radioactive, it is preferred that these materials be removed.

The fission products consist of a large number of elements which may be classified into two groups: a light group with atomic numbers from 35 to 45; and a heavy group with atomic numbers from 51 to 60. The fission products with which we are particularly concerned are those having a half-life of more than three days since they remain in the neutron irradiated reaction mass in substantial quantities at least one month after reaction. These products are chiefly 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}, Cs (many years half-life), 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.

Plutonium is found to have at least two states of oxidation. In its lower state of oxidation the plutonium is substantially insoluble in water as a phosphate or fluoride and is believed to have a valence of 4. In its higher state of oxidation, the plutonium is water soluble as a phosphate or fluoride and is believed to have a valence of 6. This oxidized plutonium is capable of forming a plutonyl ion having the probable structure PuO_2^{++}. Frequently plutonium in its reduced or fluoride insoluble state is designated as Pu^r and plutonium in its oxidized or fluoride soluble state is designated as Pu^o.

In accordance with the present invention it has been found that plutonium (element 94) may be removed from an aqueous solution by precipitation of a complex acetate. For example, when the plutonium is in its higher state of oxidation it may be precipitated as a sodium plutonyl acetate. Moreover it may be carried down from solution by precipitation of sodium uranyl acetate which adsorbs or carries the plutonium from solution. Likewise sodium uranyl acetate may be precipitated or otherwise formed in a finely divided or easily distributable form and this product introduced into the plutonium solution for removal of the plutonium.. It has been found that plutonium in its lower oxidation state or reduced state will not be precipitated or carried to a substantial degree under similar conditions. In precipitating plutonium in its higher oxidation state with an alkali metal as a complex acetate, the plutonium is separated to a substantial degree from fission products since they remain in solution. Moreover the above separation process may be used to separate plutonium in its reduced state from uranium by precipitation of the uranium as an alkali metal uranyl acetate while the plutonium remains in solution. Where both of the above separation processes are used, it is contemplated that they may be carried out as shown in Fig. 2 in which the plutonium and fission products are first separated from the uranium and then from each other, or as shown in Fig. 1 in which the plutonium and uranium are first separated from the fission products and then from each other.

While various suitable oxidizing agents may be used to change the oxidation of plutonium in its reduced state (Pu^r) to its higher oxidation state (Pu^o), it has been found that dichromate ions ($Cr_2O_7^{--}$) are particularly suitable for this purpose. Reducing agents such as sulfur dioxide, hydroxylamine, or hydrogen peroxide have been found to be satisfactory for converting plutonium from its higher oxidation state (Pu^o) to its reduced state (Pu^r). Usually this reduction is conducted in the presence of a small quantity of acid such as sulphuric acid.

In separating the plutonium from the fission products by precipitation of the plutonium in its higher oxidation state as a complex acetate, acetate ions are introduced into the solution in any convenient form, such as by sodium acetate, preferably following the addition of acetic acid in order to adjust the acetic acid/acetate ion ratio to such a value that the danger of precipitating any salt other than the desired complex salt is substantially completely eliminated. To precipitate the plutonyl acetate complex, an excess of sodium ions are introduced into the solution in the form of a sodium salt. Preferably, sodium nitrate may be used for introducing sodium ions and sodium acetate for introducing acetate ions. It is believed that the plutonyl ions combine with the acetate ions to form a complex acetate, the complex being prepicitated by the alkali metal ions in accordance with the following formula:

$$R^{+}+(PuO_2Ac_3)^{-}\rightarrow RPuO_2Ac_3$$

in which R is an alkali metal such as sodium, potassium or lithium. It has been found that a substantial excess of sodium ions facilitates the precipitation of the plutonium as a complex acetate.

Where the plutonium is present in the solution in low concentrations and it is desired to precipitate the plutonium in its higher oxidation state, a carrier may be used to aid in taking the plutonium out of the solution. It has been found that uranium in the form of an alkali metal uranyl acetate precipitate may be used for this purpose. The uranium in its higher oxidation state is precipitated as a complex uranyl acetate by alkali metal ions, such as sodium ions, in a manner similar to that in which the plutonium is precipitated. Frequently, the uranium is used as a carrier even where the plutonium is present in relatively high concentrations as its use increases the yield of plutonium separated from the fission products.

Where a solution of neutron irradiated uranium is treated first with the plutonium in its higher oxidation state, the presence of uranium in the solution makes unnecessary the addition of further amounts of uranium for use as a carrier. In the precipitation of the plutonium as a complex acetate, a portion of the uranium is likewise precipitated and by substantial precipitation of the uranium the plutonium is carried out of the solution containing the fission products. Where a solution of neutron irradiated uranium, however, is first treated to precipitate an alkali uranyl acetate with the plutonium in its reduced state so as to obtain a substantially uranium-free solution containing the plutonium and fission products, subsequent precipitation of the plutonium in its higher oxidation state to separate it from the fission product is facilitated by the addition of small amounts of uranium to carry the plutonium from the solution. The addition of uranium as a carrier makes necessary a further separation step if the plutonium is to be obtained free of the uranium. There is an advantage, however, in such addition inasmuch as the resulting precipitate may be dissolved in a small amount of solvent such as nitric acid, thereby greatly increasing the concentration of plutonium in the solution. The addition of small amounts of uranium for concentration of the plutonium may advantageously be employed where the plutonium has been obtained free from fission products and uranium irrespective of whether the plutonium was first treated in its reduced state or in its oxidized state.

This process may be conducted to effectively concentrate the plutonium by use of a plurality of successive plutonium precipitations. Thus plutonium may be precipitated from aqueous solution by precipitation of sodium uranyl acetate, the precipitate redissolved in a smaller volume of acid solution, the plutonium reduced, the uranium separated from the solution leaving the reduced plutonium in solution, the plutonium oxidized and the process repeated a number of times using a progressively smaller quantity of solution to dissolve the uranium-plutonium precipitate and progressively smaller portions of uranium to effect the precipitation.

For example a uranium nitrate solution containing plutonium as Pu^o may be treated with sodium and acetate ions to precipitate sodium uranyl acetate and to carry the plutonium down with the precipitate. This precipitate may be dissolved in a minimum of nitric acid and the plutonium reduced to the Pu^r state by means of a reducing agent such as hydroxylamine hydrochloride or a sulphite such as sodium bisulphite which leaves the uranium in hexavalent state. Thereafter the uranium may be largely precipitated as sodium uranyl acetate and the plutonium reoxidized to the Pu^o state. The solution containing the Pu^o may then be treated with a smaller amount of uranium, usually not over 10 percent of the initial uranium concentration and sufficient sodium and acetate ions supplied to the solution to precipitate the uranium and plutonium. This precipitate may be dissolved in a minimum of nitric acid and the process repeated until the desired concentration of plutonium has been secured.

The following examples are illustrative:

Example 1

Uranyl nitrate hexahydrate containing 0.00000005 percent Pu by weight was dissolved in water and nitric acid added so that the resulting solution contained 0.55 mole per liter of $UO_2(NO_3)_2 6H_2O$ and 0.87 mole per liter of HNO_3. To this solution was added sufficient sodium dichromate, $Na_2Cr_2O_7$ to make the solution 0.087 mole per liter in dichromate ion. This was then heated at 75° C. for 30 minutes after which solid sodium acetate was added in such amount as to give a ratio of 6 moles of $NaAc.3H_2O$ to every mole of $UO_2(NO_3)_2.6H_2O$. This caused the uranyl ion (UO_2^{++}) to be precipitated as the insoluble sodium uranyl acetate and the plutonyl ion PuO_2^{++} to be precipitated probably as sodium plutonyl acetate or at least to be carried out of solution by the precipitation of sodium uranyl acetate. The precipitate was removed by filtration and washed with a solution which was about 0.5 mole per liter in $NaAc.3H_2O$, 0.5 mole per liter in HAc and 1.5 moles per liter in $NaNO_3$. The filtrate contained substantially all of the fission products and negligible amounts of plutonium and uranium.

The mixed complex acetate was dissolved in nitric acid to give a solution which was 0.87 mole per liter in UO_2^{++} and 3.4 moles per liter in HNO_3 (mole ratio of nitric acid to UO_2^{++} was 4 to 1). Sodium acid sulphite in such amount as to give a mole ratio of 1 mole of $NaHSO_3$ to 5.5 moles of UO_2^{++} was then added to bring about reduction of the Pu^o to Pu^r. This reduction is complete in about 10 minutes. The UO_2^{++} was again precipitated leaving Pu^r in solution by adding $NaAc.3H_2O$ in such quantity as to give a mole ratio of 6 moles of $NaAc.6H_2O$ to one mole of UO_2^{++} ion. The precipitate of sodium uranyl acetate was removed by filtration and was washed with a solution which was 0.5 mole per liter in $NaAc.H_2O$, 0.5 mole per liter in HAc and 1.5 moles per liter in $NaNO_3$. Over 90 percent of the plutonium remained in solution in the filtrate which contained but negligible amounts of fission products and uranium.

Example 2

A solution of uranyl nitrate hexahydrate containing 0.00000005 percent Pu by weight was adjusted to be 0.55 M in UO_2^{++} ion and 0.2 M in H^+ (HNO_3) ion. This solution was treated with hydroxylamine hydrochloride so that it is 0.1 M in NH_3OH^+ ion to put the Pu in the reduced form Pu^r ion leaving uranium substantially unreduced. $NaAc.3H_2O$ was then added in quantity sufficient to give a Na^+ concentration of 1.5 M. Sodium uranyl acetate then precipitated from this solution. The precipitate was washed with a small volume of wash solution made up of $NaNO_3$, $NaAc.3H_2O$, and HAc in such proportion as to have the following concentrations: Na^+ 1.5 M, Ac^- .2 M, and HAc.2 M. The wash water was added to the filtrate containing the reduced Pu. The filtrate and wash was then treated with nitric acid and sodium dichromate in such quantity as to make the solution 0.2 M and H^+ (HNO_3) and 0.1 M. in $Cr_2O_7^=$ ion. After heating for about 30 minutes at 75° C. the Pu was in the higher state of valence, namely PuO_2^{++} ion. Uranyl nitrate hexahydrate was added to the extent of $\frac{1}{20}$ of the amount originally present and this solution was treated with $NaNO_3$ and $NaAc.3H_2O$ in such quantity as to maintain concentrations in the supernatant solution of Na^+ 5.0 M, Ac^- 0.2 M, and HAc 0.5 M, whereby the complex uranyl and plutonyl acetates are precipitated. The $NaNO_3$ was used in order to raise the Na ion concentration level to a high value in order to ensure substantially complete precipitation of the plutonyl complex. The precipitate was filtered out and washed with two small portions of a wash containing $NaNO_3$, $NaAc.3H_2O$, and HAc in the following concentrations: Na^+ 5.0 M, Ac^- 0.2 M, and HAc 0.35 M, and both filtrate and wash were discarded. The filtrate and wash, containing substantially all of the fission products and negligible amounts of plutonium, was discarded.

The precipitate contained substantially all of the plutonium, the added uranium, and 0.17 percent of the fission products. The precipitate was dissolved in a minimum of nitric acid as in Example 1, and hydroxylamine hydrochloride (NH_3OHCl) was added to reduce the plutonium. An excess of sodium acetate was added to precipitate the uranium as sodium uranyl acetate as above described. The precipitate was removed from the solution by filtration and washed with three 50 ml. portions of wash solution containing 1.5 M Na^+, 0.2 M Ac^-, and 0.2 M HAc. The precipitate containing substantially all of the added uranium and negligible amounts of plutonium and fission products was discarded.

The filtrate and wash contained the remainder of the plutonium and a small percentage of the fission products. The plutonium was again precipitated with sodium acetate and uranyl nitrate as before using about $\frac{1}{20}$ of the amount of uranium previously used. The major portion of the plutonium was collected in the precipitate while the fission products largely remained in solution.

Where the negligible amount of fission products at the end of the first cycle is not objectionable, the precipitate may be further treated to separate the plutonium from the uranium that was added for use as a carrier. In such case, the precipitate may be dissolved in nitric acid and the plutonium reduced with NH_3OHCl. An excess of sodium acetate may then be added to precipitate the uranium while maintaining the plutonium in solution. The sodium uranyl acetate may be removed from the solution by filtration.

Where the concentration of plutonium in the solution has reached fairly high levels and it becomes desirable to separate the plutonium and uranium, this may be done by removing the uranium as sodium uranyl acetate while maintaining plutonium in the reduced state in solution. The plutonium if in sufficient concentration may be obtained in solid form by being oxidized and precipitated as a complex acetate without the addition of uranium. The plutonium may be obtained in solid form also by evaporating the solution containing the reduced plutonium or by the use of a precipitant that converts the plutonium to an insoluble plutonous compound such as a phosphate, fluoride, or the like.

Example 3

0.43 microliter of a solution of uranyl nitrate hexahydrate containing 0.0413 microgram of Pu, 117 micrograms of uranium containing 0.1 mol per liter of $Na_2Cr_2O_7$ and 0.1 mol per liter of HNO_3 was heated at 130° C. for 1 hour in a sealed capillary, sodium acetate and nitric acid were added and the volume was adjusted to form a solution containing 0.4 mole per liter of HAc, 0.2 mole per liter of acetate ion and 1.5 moles per liter of sodium ion and sufficient water was added to increase the volume of the solution to one microliter.

The precipitate was separated by centrifugation and washed with three portions of water each portion being about 0.14 microliter in volume.

The precipitate was dissolved in nitric acid to form a solution containing about 0.2 mole per liter of nitric acid and 0.55 mole per liter of UO_2^{++} and hydroxylamine hydrochloride was added in amount sufficient to establish a concentration of 0.1 mole per liter of NH_3OH^+. After the solution was allowed to stand sodium acetate and acetic acid were added in amount sufficient to form a solution 0.9 microliter in volume and containing 0.2 mole per liter of acetate ion, 1.9 moles per liter of HAc, 1.5 moles per liter of sodium ion and 0.1 mole per liter of NH_3OH^+. The precipitate was removed and washed with three portions of water each 0.14 microliter in volume. The combined wash water and the filtrate contained 89 percent of the plutonium and negligible amounts of fission products and uranium.

The precipitation method, as it is generally carried out, separates element 93 as well as plutonium from the foreign substances, such as uranium, fission products, and the like. Since element 93 undergoes beta decay to plutonium with a half-life of only 2.3 days, the process may be carried out with only a negligible amount of element 93 present if the reaction mass is stored for a suitable length of time. Thus, in approximately sixteen days over 99 percent of element 93 is converted to plutonium and at the end of approximately thirty days over 99.9 percent of element 93 has been converted to plutonium through beta decay.

Where it is desired to proceed without storing the neutron irradiated uranium for substantial conversion of element 93 to plutonium by beta decay, element 93 may be separated from plutonium by taking advantage of the different oxidation characteristics of the two elements both of which possess a higher and a lower valent state. In an example of such separation, the neutron irradiated uranium is dissolved as by nitric acid and element 93 and plutonium are maintained or converted to their reduced state by the addition of a reducing agent such as sulphur dioxide. Potassium bromate may then be added to the solution to oxidize element 93 while permitting the plutonium to remain in its reduced state. It has been found that the addition of 0.5 gram of potassium bromate to 30 cc. of solution containing tracer amounts of element 93 and plutonium will oxidize all of the element 93, leaving 94 unoxidized provided the solution is permitted to stand at room temperature for not longer than thirty minutes and provided no cerium is present. Cerium which may be present as a fission product should be removed before such a separation is attempted. Where element 93 has been obtained in its oxidized state with plutonium remaining in its reduced state, the two may be separated by precipitants such by precipitation of sodium uranyl acetate in the solution whereby the neptunium is carried with the precipitate probably as alkali metal neptunyl acetate, i. e., sodium neptunyl acetate. Where the concentration of neptunium is sufficiently high, sodium neptunyl acetate or its equivalent may be precipitated without addition of uranium to form sodium uranyl acetate. In accordance with a further modification, the solution may be treated with phosphate ions which will precipitate plutonium while permitting element 93 to remain in solution. The particular precipitate obtained can be separated from the solution by any conventional means such as filtration, centrifugation, or the like.

In accordance with a further modification of the invention other plutonium salts particularly plutonyl salts of organic carboxylic acids may be prepared. Thus while the invention is particularly adapted to the recovery of plutonium from aqueous media by formation of an alkali metal plutonyl acetate, the process may also be used for production of other plutonium salts such as sodium plutonyl propionate, sodium plutonyl mono-chloracetate or salts of other organic acids such as chloracetic acid, propionic acid, butyric acid, etc.

The above detailed description is given for purposes of illustration and the invention is to be limited only by the scope of the appended claims.

We claim:

1. In a process for the separation of plutonium from uranium, the step which comprises contacting a solution containing uranium and plutonium in their hexavalent states and fission products with an alkali metal acetate whereby the uranium is precipitated as an alkali metal uranyl acetate which carries the plutonium therewith.

2. Process of claim 1 in which alkali metal acetate is sodium acetate.

3. In a process for the separation of plutonium from uranium, the steps which comprise contacting a solution of neutron irradiated uranium wherein the uranium is in a hexavalent state of oxidation and the plutonium is in a state of oxidation not greater than +4 with an alkali metal acetate to precipitate the uranium as the corresponding alkali metal uranyl acetate, removing the latter from the solution, oxidizing the plutonium to the hexavalent state, and thereafter contacting the solution containing the oxidized plutonium with an alkali metal acetate to precipitate the plutonium as the corresponding alkali metal plutonyl acetate.

4. In a process for separating plutonium from uranium, the step which comprises contacting a solution containing uranium in the hexavalent state of oxidation and plutonium in a state of oxidation not greater than +4 with an alkali metal acetate whereby the uranium is precipitated from the solution as an alkali metal uranyl acetate.

5. The process of claim 3 in which the solution of neutron irradiate uranium is prepared by dissolving the latter in nitric acid.

6. A method of concentrating plutonium which comprises contacting an aqueous solution containing hexavalent plutonium ions with a substantially insoluble alkali metal uranyl acetate whereby the plutonium becomes associated with the alkali metal uranyl acetate precipitate, removing the precipitate and thereafter dissolving the precipitate in acid to produce a solution more concentrated than the original with respect to plutonium, reducing the latter, contacting the resulting solution with an alkali metal acetate to form the corresponding insoluble alkali metal uranyl acetate, oxidizing the dissolved plutonium to the hexavalent state and thereafter contacting the resulting solution with a smaller quantity of an alkali metal uranyl acetate to remove the plutonium in a more concentrated form.

7. The process of claim 6 in which the alkali metal uranyl acetate is sodium uranyl acetate and the alkali metal acetate is sodium acetate.

8. In a method for the separation of plutonium from neptunium, the steps which comprise forming a solution containing neptunium in its hexavalent state of valence while maintaining the plutonium in a valence state not greater than +4 and contacting said solution with an alkali metal acetate.

9. The process of claim 8 in which the alkali metal acetate is sodium acetate.

10. A method of separating plutonium from uranium where the plutonium is present in very low concentrations comprising forming an aqueous nitric acid solution thereof, reducing the plutonium to a valence state not greater than +4, contacting the solution with an alkali metal acetate to form insoluble alkali metal uranyl acetate, separating the alkali metal uranyl acetate from the solution, oxidizing the plutonium to the +6 valence state, adding uranium nitrate to the solution, the amount of uranium added being much less than that precipitated from the solution in the preceding stage, contacting the solution with an alkali metal acetate to form insoluble alkali metal uranyl acetate and alkali metal plutonyl acetate, separating these acetates from the solution, reducing the plutonium to a valence state not greater than +4, contacting the solution with an alkali metal acetate whereby the uranium is precipitated as insoluble alkali metal uranyl acetate, and separating the alkali metal uranyl acetate.

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