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PROCESS FOR SEPARATION OF HEAVY METALS

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The invention relates to the separation of transuranic elements such as element 93 and/or 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 and fission products, which are considered to be foreign products.

It is an object of the invention to obtain element 94 in a purified state by a convenient process which is suitable for use on both a commercial and laboratory scale and which is particularly adapted for concentrations of element 94 such as are obtained from neutron-irradiated uranium where fission products and other substances resulting from a neutron bombardment of uranium are present.

It is a further object of the invention to provide a process for the separation of plutonium from substances of the type present in neutron-irradiated uranium while such pultonium is in its higher oxidation state.

It is a more specific object of the invention to provide a process in which plutonium in its higher oxidation state is removed from solution by a complex acetate of uranium, a divalent metal and sodium or other alkali metal.

Further 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. References herein to any of the elements is to be understood as denoting the element generically, whether in its free state or in the form of a compound, unless indicated otherwise by the context.

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

Neutron irradiation of uranium produces $_{92}U^{239}$ 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 other products such as UX_1 and UX_2. The amount of 93^{239} and 94^{239} combined is generally minute, rarely in excess of 0.1 percent by weight of the uranium and more often approximately 0.02 percent by weight or less. 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 of 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 34 to 48; and a heavy group with atomic numbers from 50 to 63. 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, Y, Zr, Cb, and Ru of the group of atomic numbers from 34 to 48; and Te, I, Xe, Cs, Ba, La, and Ce from the group of atomic numbers from 50 to 63, inclusive.

Plutonium is believed to have at least two oxidation states. In its lower oxidation state, that is, in its reduced state, plutonium is substantially water insoluble either as a phosphate or as a fluoride, and is believed to have a valence of 4. In its higher oxidation state, that is, its oxidized state, the plutonium is water-soluble to a substantial degree as a phosphate and as a fluoride and is believed to have a valence of 6. In its oxidized state, plutonium forms a plutonyl ion, probably having the formula PuO_2^{++}. Hereinafter, the plutonium in its reduced state or fluoride-insoluble state is designated as Pu^r, and plutonium in its higher oxidation state or fluoride soluble state is designated as Pu^o. In its reduced state, Pu^r is carried from solution by a lanthanum fluoride precipitate while Pu^o is not. The present invention makes possible the removal of plutonium from solution while the plutonium is in its fluoride and phosphate soluble state.

It has been found that plutonium in its higher oxidation state forms insoluble complex acetates in the presence of alkali metal ions, particularly sodium ions, and divalent ions, such as ions of magnesium or other metal and as hereinafter designated. In its lower oxidation state, however, plutonium remains in solution under similar conditions.

The invention resides in separating plutonium while in its higher oxidation state from fission products either by precipitating the plutonium as a complex acetate while maintaining the fission products in solution or (where the plutonium content is low) by carrying the plutonium out of solution by precipitating sodium magnesium uranyl acetate or similar complex acetate which carries or adsorbs the plutonium to a high degree even though the plutonium concentrations may be below the solubility point of sodium plutonyl acetate. To separate the plutonium from uranium, which precipitates with the plutonium as a complex acetate when the latter is in its higher oxidation state, the uranium may be precipitated as a complex acetate while the plutonium is in its reduced state.

Where fission products and uranium are present with plutonium, the plutonium may be separated from these substances by precipitating the uranium and plutonium in their higher oxidation states as complex acetates while the fission products remain in solution and subsequently dissolving the precipitate, after its removal from the solution, containing the fission products, reducing the plutonium, and precipitating or removing the uranium by suitable means such as by precipitating it as a complex acetate while the plutonium remains in solution. If desired, the uranium may be removed from the plutonium and fission products by precipitating the uranium as a complex acetate, while the plutonium in the reduced state and fission products remain in solution, and subsequently oxidizing the plutonium and precipitating it as a complex acetate, while the fission products remain in solution. The precipitates are removed from the solution by any suitable means such as filtration, centrifugation, or the like.

In changing the oxidation state of plutonium from its

reduced state (Pu^r) to its oxidation state (Pu^o), any suitable oxidizing agent may be used, such as dichromate ion ($Cr_2O_7^{--}$), ceric ion (Ce^{+4}), or the like. In reducing the plutonium from its higher oxidation state (Pu^o) to its reduced state (Pu^r), reducing agents, such as sulphur dioxide or hydrogen peroxide, have been found to be satisfactory.

The invention is particularly adapted to the separation of plutonium and/or uranium as sodium magnesium plutonium acetate and sodium magnesium uranyl acetate, respectively. However other alkali metals and other divalent metals capable of combining to precipitate a complex uranyl acetate of an alkali and a divalent metal may be used for this purpose. Thus sodium ions and lithium ions have been found to be especially suitable for use in the precipitation step. The divalent ions may be ions of magnesium, nickel, cobalt, zinc, manganese, copper, or cadmium. The plutonyl ions appear to combine with the acetate ions to form a complex acetate, such complex acetate being precipitated by the alkali metal ions and divalent ions in accordance with the following formula:

$$A^+ + B^{++} + 3(PuO_2Ac_3)^- + 9H_2O \rightarrow AB(PuO_2Ac_3)_3.9H_2O$$

in which A may be sodium or lithium and in which B is an ion of a divalent element of the group consisting of magnesium, nickel, cobalt, zinc, manganese, copper and cadmium or other metal capable of forming with an alkali metal an isoluble uranyl acetate complex.

When the plutonium is present in low concentrations in the solution, a carrier may be used to aid in separating it from the solution. It has been found that uranium in the form of a complex uranyl acetate carries plutonium and is particularly advantageous, for, as previously noted, uranium in its higher oxidation state is precipitated as a complex uranyl acetate by sodium ions and magnesium or zinc or other divalent ions in a manner similar to that in which the plutonium is precipitated. Where the plutonium is treated first in its reduced state to separate the uranium and some of the fission products from the plutonium and the remainder of the fission products, it has been found desirable in the subsequent separation of the plutonium from the remaining fission products to add small amounts of uranyl ion to the solution to form the insoluble sodium magnesium uranyl acetate which carries the plutonium.

Example 1

Uranyl nitrate hexahydrate, which has been bombarded by slow neutrons until it contains about 200 mg. of plutonium per ton of uranium, is dissolved in water and the quantities of uranyl nitrate hexahydrate, water and HNO_3 used in preparing the solution are such that the UO_2^{++} ion concentration is about 0.5 M and the H^+ ion concentration is about 0.2 M. Sufficient $K_2Cr_2O_7$ is added to this solution to obtain a $Cr_2O_7^{--}$ ion concentration of about 0.1 M. The solution is heated to about 75° C. and the temperature is maintained at this value for about 30 minutes in order to ensure substantially complete oxidation of the 94 and 93 content thereof to the higher valence state. After the heating operation, the solution is cooled to about room temperature and then $NaAc.3H_2O$ and $MgAc_2.H_2O$ are added to the solution in such amounts as to give a Mg^{++} ion concentration of about 1.0 to 1.5 M and Na^+ ion concentration of about 2.5 to 5.0 M, after the formation of the precipitate. This treatment causes the uranium present to be precipitated substantially completely as the complex sodium magnesium uranyl acetate, and substantially all of the 94 and 93 present is caried with this precipitate. The precipitate is filtered out and washed two or three times with small amounts (10–25 cc.) of a wash solution which is 3 M in $NaNO_3$, 1 M in $NaAc.3H_2O$, 1 M in $MgAc_2.4H_2O$, and 0.5 M in HAc. The filtrate and wash contain the major portion of the fission products and may be discarded or set aside for separate treatment for recovery of the fission products if desired.

The precipitate, after washing, is dissolved in HNO_3 of such a quantity and concentration that the resultant solution is about 0.5 M in UO_2^{++} ion and 0.2 M in H^+ ion. This solution is next treated with sufficient $NaHSO_3$ to make the solution about 0.05 to 0.1 M in $NaHSO_3$. This reduces the 94 and 93 to the lower-valent (fluoride-insoluble) state; the reduction is complete in about ten minutes at room temperature under these conditions. The uranium is not reduced by this treatment. The UO_2^{++} ion is substantially completely precipitated away from the reduced 94 and 93 by addition to the solution of $NaAc.3H_2O$ and sodium nitrate and $MgAc_2.4H_2O$ in amounts sufficient to establish the concentrations mentioned for the first sodium magnesium uranyl acetate precipitation. The precipitate is removed by filtration and is washed two or three times with small amounts (10–25 cc.) of the wash solution before mentioned. The filtrate and wash waters are combined and contain in the reduced condition substantially all of the 94 and 93. To this combined solution concentrated HNO_3 is added in an amount to make the total HNO_3 concentration about 0.2 M. Then potassium dichromate is added in sufficient amount to make the solution about 0.15 M in $Cr_2O_7^{--}$ ion. This solution is heated at about 75° C. for about 30 minutes in order to oxidize the 94 and 93 to the higher-valent (fluoride-soluble) state. After cooling the solution to room temperature an amount of uranium in the form of uranium acetate equivalent to about 1/20 of the amount initially present is added to the solution. Sufficient $NaAc.3H_2O$ and $MgAc.4H_2O$ is added so that the total Na^+ ion concentration is about 4 M and the total Mg^{++} ion concentration is about 1.5 M. Under these conditions the UO_2^{++} ion is substantially completely precipitated and carries with it substantially all of the 94 and 93. The precipitate is separated from the supernatant liquid by filtration and is washed two or three times as before described. The precipitate contains substantially all of the 94 and 93 originally present in the starting material, is substantially free of the fission products and is concentrated with about 1/20 of the amount of uranium originally present.

By repeating the cycle of operations above described, namely, dissolving the precipitate, reducing the 94 and 93, precipitating the uranium and separating it away from the reduced 94 and 93, then treating the filtrate to oxidize the 94 and 93, then adding an amount of uranium equal to about 1/20 of that present in the preceding cycle, precipitating the uranium as the complex sodium magnesium uranyl acetate, removing the precipitate which carries the oxidized 94 and 93 from the supernatant liquid and redissolving in nitric acid of less volume than that used in the previous cycle, it is possible to obtain substantially all of the 94 and 93 originally present in a concentrated form as a final preparation with a small amount of uranium and almost entirely free of radioactive fission products.

Example 2

The process of Example 1 is repeated.

A precipitate is formed which comprises uranium, plutonium, and element 93 in the form of sodium magnesium complex acetates as above described. After being removed from the solution by filtration, the precipitate is dissolved in nitric acid, and the plutonium and element 93 are reduced with sulphur dioxide. The uranium remains in its higher oxidation state. A lanthanum salt, such as lanthanum chloride, and hydrofluoric acid are added to form lanthanum fluoride which is thrown down, carrying with it the plutonium, probably in the form of insoluble plutonous fluoride. An analysis of the lanthanum fluoride precipitate indicated that 60 percent of the plutonium and 64 percent of element 93 are carried from the original solution by the sodium magnesium

uranyl acetate. A negligible amount of uranium is carried down by the lanthanum fluoride.

In accordance with a further modification substantially all of the uranium may be precipitated initially from solution as sodium magnesium uranyl acetate or similar complex acetate while the Pu is in its reduced state. Thereafter the plutonium may be oxidized and concentrated as described in Example 1.

The precipitation and carrying method, as it is generally carried out, separates element 93 (neptunium) 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 period of time. Thus, in several 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. In most cases, the separation of plutonium and neptunium is carried out after substantially all of the fission products, including cerium, have been removed by the above described process from the plutonium and neptunium. As an example of such separation, the neutron-irradiated uranium may be 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 in amount sufficient to establish a concentration of 0.1 M of BrO_3^- may be added to the solution containing H_2SO_4 in a concentration of 1 M 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 selectively without oxidation of 94, provided the solution is permitted to stand at room temperature for not longer than thirty minutes and provided no cerium is present. 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 as acetate ions which in the presence of sodium ions and divalent metallic, such as magnesium, ions will precipitate element 93 while permitting plutonium to remain in solution, or by the addition of 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 suitable means such as filtration, centrifugation, or the like.

In accordance with a further modification of the invention other plutonium salts of organic acids may be prepared, particularly salts of carboxylic acids. Thus while the invention is particularly concerned with the recovery of plutonium and the production of complex plutonyl acetates, salts of other acids such as propionic, butyric, acrylic, chloracetic, methacrylic and propiolic acids may be prepared. These salts may be prepared as complex salts such as sodium plutonyl chloroacetate or propionate or sodium magnesium plutonyl chloroacetate or propionate or as more simple salts such as plutonyl or plutonous chloroacetate, 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.

I claim:

1. In a process for the separation of plutonium from fission products, the step which comprises contacting a solution containing fission products and plutonium in its higher state of oxidation with an alkali metal positive divalent metal uranyl acetate in which the positive divalent metal is a member of the group consisting of Mg, Ni, Co, Zn, Mn, Cu and Cd.

2. The process of separating plutonium from a solution containing that element in its higher state of oxidation, which comprises contacting said solution with an alkali metal positive divalent metal uranyl acetate in which the positive divalent metal is a member of the group consisting of Mg, Ni, Co, Zn, Mn, Cu and Cd.

3. In a process for the separation of plutonium from a solution containing that element in its higher state of oxidation, the step which comprises forming in said solution an alkali metal positive divalent metal uranyl acetate by producing a mixture of alkali metal ions, positive divalent metal ions, uranyl ions, and acetate ions, said positive divalent metal being a member of the group consisting of Mg, Ni, Co, Zn, Mn, Cu and Cd.

4. In a process for the separation of plutonium from a solution containing hexavalent uranium and plutonium, the step which comprises contacting said solution with a mixture of sodium and magnesium acetates.

5. In a process for the separation of plutonium from a nitric acid solution of neutron irradiated uranium, the step which comprises contacting said solution containing plutonium in its higher state of oxidation with an alkali metal positive divalent metal uranyl acetate in which the positive divalent metal is a member of the group consisting of Mg, Ni, Co, Zn, Mn, Cu and Cd.

6. In a process for the separation of plutonium from a solution comprising neutron irradiated uranium, the step which comprises contacting said solution containing plutonium in its higher state of oxidation with sodium magnesium uranyl acetate.

7. In a process for the separation of plutonium from a solution comprising uranium, plutonium, and fission products wherein the uranium is in its higher valent state and the plutonium is in its lower valent state, the step which comprises contacting said solution with alkali metal ions, positive divalent metal ions and acetate ions, said positive divalent metal being a member of the group consisting of Mg, Ni, Co, Zn, Mn, Cu and Cd.

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