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THORIUM OXALATE-URANYL ACETATE COUPLED PROCEDURE FOR THE SEPARATION OF RADIOACTIVE MATERIALS

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The present invention relates to the separation and recovery of radioactive products of nuclear reactions. More particularly, it is concerned with a method for the separation of plutonium and other transuranic polyvalent actinide rare earth elements, and of radioactive fission products from neutron-irradiated uranium.

When uranium is irradiated with neutrons in a nuclear reactor, a very small portion of the U^{235} atoms fission and produce fission products which comprise approximately the elements having atomic numbers from 32 to 64. A very small portion of the U^{238} atoms present upon irradiation with neutrons are converted by neutron capture and radioactive decay into plutonium. Thus, after a period of irradiation with neutrons, the uranium will contain a small amount of plutonium and a small amount of radioactive fission products. These fission products are highly useful in scientific and medical applications. Moreover, the usefulness of plutonium is well known. The separation of plutonium and the fission products from the neutron-irradiated uranium is, however, impractical by normal chemical separation methods because of the intense radioactivity associated therewith and because of the extremely minute portions of fission products and plutonium usually present. Therefore novel methods have had to be found to carry out these separations.

It is an object of the present invention to provide a process for the separation of plutonium from neutron-irradiated uranium.

It is an additional object of the present invention to provide a process for the recovery of radioactive fission products from neutron-irradiated uranium.

Other objects and advantages of the present invention will be apparent from the description that follows.

I have discovered that plutonium and fission products may be recovered from a nitrate solution of neutron-irradiated uranium in a high degree of purity by a series of carrier precipitations in which the plutonium in the tetravalent state and certain of the fission products are carried with a thorium oxalate carrier. The zirconium-type fission products are then removed from the thorium oxalate carrier by dissolving the thorium oxalate carrier and then reprecipitating the thorium oxalate carrier and associated plutonium and fission products other than zirconium-type elements under such conditions that the zirconium-type elements remain in solution as oxalate complexes. The rare earth-type and alkaline earth fission products are then removed from the thorium oxalate carrier by the step of dissolving the thorium oxalate carrier and precipitating a rare earth oxalate carrier in the solution under conditions such that the thorium is not precipitated. Finally the plutonium is separated from the thorium oxalate solution by oxidizing the plutonium to the hexavalent state and separating it from the thorium-containing solution with a sodium uranyl acetate carrier.

The process is quite flexible and, while the steps of the process are usually employed in the foregoing order where it is desired to completely separate plutonium and fission products from neutron-irradiated uranium, numerous variations of the process may be effected. For example, fission products may be separated from neutron-irradiated uranium from which the plutonium has previously been removed, by carrying out the first three steps of the above process. Certain steps of the process may be repeated one or more times in order to increase the separation of a particular fission product, and variations in the order of the zirconium-type fission product precipitation and lanthanide rare earth-type fission product precipitation steps may also be made.

As the first step in the employment of the present process in the recovery of fission products and/or plutonium from neutron-irradiated uranium, the uranium is dissolved in a suitable solvent, such as a mineral acid, and preferably nitric acid, to give an acidified solution of, for example, uranyl nitrate hexahydrate. The dissolution of the uranium in nitric acid insures that the uranium atoms are present in the solution in the hexavalent state. Under certain conditions of acidity and oxalate concentration uranyl oxalate will precipitate so that, in order to avoid the precipitation of uranium oxide during the separation of plutonium fission products with a thorium oxide carrier, it is necessary to avoid the conditions under which uranyl oxalate will precipitate. It has been found that uranyl oxalate precipitation may be avoided by precipitating the thorium oxalate from an acidic solution, while avoiding the presence of a large excess of oxalate ions and conducting the carrying at room temperature with agitation. In carrying out the process of the present invention it has been found most desirable to employ solutions having oxalate ions not substantially in excess of 0.02 M and preferably from about 0.001 to 0.02 M, for example about 0.015 M. Ordinarily, with oxalate concentrations in excess of 0.02 M the solubility product of uranyl oxalate is exceeded.

Inasmuch as it is known that thorium oxalate is quite soluble in neutral solutions, it is essential that the initial acidity of the plutonium-containing solutions should be maintained within a range of from about 0.05 to 4.0 N. In this connection it should be noted that with relatively high acidities correspondingly lower concentrations of excess oxalate should be employed. This precaution should be observed since the solubility of thorium oxalate increases substantially in solutions having a nitric acid concentration appreciably above 1.0 N, whereas the solubility of uranyl oxalate remains for the most part unaffected by increased acidity. Thus, in regard to the optimum acidity range, it may be said that in the majority of instances a value of around 1 N is considered most desirable.

In agreement with the above observations, there has been found to exist a definite correlation between the percent plutonium carried and the percentage of thorium precipitated as thorium oxalate. For example, it has been shown that precipitation of 99 percent of the thorium in solution as oxalate carried 98.8 percent of the plutonium present in solution, whereas in instances in which only 70 percent of the thorium oxalate precipitated just 63 percent of the plutonium was removed.

In carrying out the process of the present invention any soluble thorium compound may be employed as a source of thorium ions; however, in general, thorium nitrate is preferable since it does not introduce an anion which might be considered objectionable at any stage in the present separation process. The molar concentration of thorium ions may vary rather widely and for the most part is controlled only by the concentration of oxalate ion present. However, it will ordinarily be found that thorium ion concentrations ranging from between about 0.01 and 0.03 M are most satisfactory. In employing thorium oxalate as a carrier in accordance with the pres-

ent invention it is generally preferable to form such compound in the plutonium containing solution by adding a source of oxalate ions such as oxalic acid, potassium oxalate, or ammonium oxalate to a solution which contains both the plutonium and thorium. Satisfactory carrying or adsorption can also be secured by adding a suitable source of thorium ions to the oxalate-containing solution, or, if desired, preformed thorium oxalate, may be added to remove the plutonium. In most instances, however, it has generally been found that the quantity of plutonium carried is somewhat less when thorium is added to a plutonium solution containing oxalate ions.

In this connection it should also be pointed out that plutonium in order to be carried from solution in accordance with the present invention must be present in the ionic form and in a valence state not above +4, for example +3 or +4. If the plutonium ions are allowed to form a stable complex, satisfactory carrying cannot be effected in view of the relatively high solubility thereof and hence conditions which favor the formation of such complexes are to be avoided. In preventing the occurrences of these soluble plutonium complexes, care should be exercised to avoid the presence of anions of slightly ionized acids where the acidity of the plutonium-containing solution is relatively low, i.e., where it has a pH of between 1.5 and 4.0. The adverse effect of such ions can be avoided, however by increasing the acidity of the solution with a suitable highly ionized acid such as, for example, nitric acid.

Where solutions are encountered in which the plutonium is in a valence state greater than +4 or a non-carriable state, it may be readily converted to a carriable form by reduction with hydrovyl ammonium chloride or hydroxyl ammonium acetate. Reduction can also be effected by utilizing such materials as sulfur dioxide, oxalate ions and the like.

Following the step of removing the thorium oxalate carrier precipitate from the uranium-containing solution, the thorium oxalate carrier precipitate which contains plutonium and the bulk of the fission products is dissolved by contacting the precipitate with a solution containing an excess of oxalate ions. A solution which has been found effective in dissolving the carrier precipitate is an approximately 0.3 M ammonium oxalate solution. Other oxalate salts and other molarities, however, may be used. To effect complete dissolution it has been found desirable to digest the precipitate in the solution for a short period of time, for example, from 15 minutes to 2 hours, at a temperature from room temperature to 85° C.

The next step in the process is the separation of zirconium and niobium, sometimes referred to as the zirconium-type fission products, from the oxalate solution. This is effected by acidifying the solution with a strong acid in an amount sufficient to provide a slight excess acidity over the amount required to convert the ammonium oxalate to oxalic acid. By this method a thorium oxalate carrier precipitate is formed containing plutonium and the rare earth and alkaline earth fission products, but the zirconium and niobium fission products remain in solution as oxalate complexes. Although nitric acid may be used to effect the acidification, it has been found that better carrying of the plutonium by the thorium oxalate precipitate is effected when sulfuric acid is used in an amount sufficient to give an excess of sulfuric acid in the final solution of between about 0.5 and 2 N. It is also desirable to digest the precipitate at an elevated temperature of, for example, 75° for from about ½ to 4 hours in order to insure the best separation. Following the separation of the carrier precipitate from this solution the precipitate is again dissolved in an excess oxalate solution as before. It may be pointed out here that this step of separating zirconium-type fission products may be repeated as often as necessary to attain the separation factor desired,

The dissolution of the thorium oxalate carrier in a solution containing excess oxalate ions is carried out in a manner similar to the preceding dissolution of the oxalate carrier. This dissolution, however, should be carried out in a solution at an elevated temperature, for example 75 to 85° C., because a dissolution at the elevated temperature will insure that the plutonium ions are in the tetravalent state in the solution. This is important in the next step of the process, which is a separation of lanthanide rare earths and alkaline earths by means of a rare earth oxalate precipitate. Of course, if for some reason the dissolution should be carried out at a lower temperature, a suitable oxidizing agent may be added to the solution to insure that the plutonium is present in the tetravalent state. A source of rare earth ions such as cerous nitrate is then added to the solution in quantities sufficient to make the solution between about 0.0075 and 0.150 M in Ce^{+3} ion. This is equivalent to about 1 or 2 mg. of Ce^{+3} per ml. of solution. The rare earth oxalate carrier precipitate will carry from the solution substantially all the rare earth and alkaline earth fission products present with a separation factor of approximately 100, with the exception of yttrium which is only partially carried by this precipitate. The separation factor, of course, may be increased by repeating this step.

Following this rare earth separation step, the plutonium is converted from the tetravalent to the hexavalent state. This is suitably accomplished by acidifying the oxalate solution containing the thorium and plutonium ions and introducing a strong oxidizing agent such as dichromate or bismuthate ion into the solution. It has been found that in a 4 N nitric acid solution 0.3 M dichromate ion will oxidize all the plutonium present within a reasonable time. The oxidation is carried out in a solution maintained at an elevated temperature for from about 2 to 4 hours. This procedure not only effects the oxidation of the plutonium but also destroys the oxalate ion in the solution. The hexavalent plutonium is separated from this solution by means of an alkali metal uranyl acetate carrier precipitate. This precipitate substantially quantitatively removes the plutonium, but leaves the thorium, yttrium, and any other alkaline earth or rare earth fission products in the solution. A preformed carrier precipitate may be used, but more efficient separations are usually obtained with a carrier formed in situ. Since a solution containing plutonium and thorium is usually a nitric acid solution, the uranyl ion is ordinarily introduced into the solution as uranyl nitrate, although, of course, other uranyl salts may be used. The acetate ions and sodium ions are usually introduced into the solution in the form of sodium acetate salt. It has been found that a more complete precipitation is effected in the presence of an excess of the alkali ions, for example sodium ions, and these are normally supplied by the addition of a sodium salt such as sodium nitrate. The precipitate is normally stirred in the solution for a short time, for example ½ hour, before separation of the precipitate from the solution. The precipitate may then be washed with a sodium acetate-acetic acid solution. If it is found desirable to increase the separation factor, the precipitate may be dissolved in nitric acid and a second precipitation then carried out in the same manner as the preceding one.

The following example is illustrative.

Example

Neutron-irradiated uranium was dissolved in nitric acid and the concentration was then adjusted so that 1 liter of the solution was 0.5 M in $UO_2(NO_3)_2$, 1.0 M in HNO_3, 2×10^{-4} M in plutonium, and contained a total amount of fission products approximately equal to the plutonium content of the solution. To this solution was then added thorium nitrate to make the solution

0.015 M in $Th(NO_3)_4$ and acetic acid to 0.045 M concentration, and the solution was stirred for 2 hours at 50° C. and 2 hours at room temperature. The carrier precipitate of thorium oxalate thus formed was separated from the solution by filtration and then washed with 30 ml. of a 0.015 M acetic acid-0.5 M sulfuric acid solution. The precipitate was then dissolved in 950 ml. of a 0.3 M $(NH_4)_2C_2O_4$ solution by stirring the mixture for ½ hour at 75° C. To this solution was then added sufficient 5.0 N H_2SO_4 to convert the $(NH_4)_2C_2O_4$ to $H_2C_2O_4$ and to make the final solution 0.1 N in H_2SO_4. This solution was then stirred for 1 hour at 75° C. and 1 hour at room temperature. By this step a thorium oxalate carrier precipitate was formed, probably having the formula $Th_2(C_2O_4)_5(NH_4)_2 \cdot 7H_2O$. This precipitate, which carried the plutonium and rare earth and alkaline earth fission products, was then separated from the solution. The zirconium and niobium fission products remained in the solution in the form of zirconium and niobium oxalate complexes. The thorium oxalate carrier precipitate was then washed with 30 ml. of a 0.015 M $H_2C_2O_4$-1.0 N H_2SO_4 solution and the wash discarded. The precipitate was then dissolved in 950 ml. of 0.3 M $(NH_4)_2C_2O_4$ in the same manner as in the preceding dissolution step. To this solution was added 1.0 gram of Ce^{+3} in the form of solid $Ce(NO_3)_3$, thus forming a cerous oxalate carrier precipitate. This precipitate was digested for 1 hour at 75° C. and then separated from the solution, carrying with it the bulk of the rare earth and alkaline earth fission products. To the supernatant solution was then added 48 ml. of 2.5 M $Na_2Cr_2O_7$, 102 ml. of 16 N HNO_3 and 246 ml. of water. This made the resulting solution 0.3 M in $Na_2Cr_2O_7$ and 4 N in nitric acid. This solution was then heated at 75° for 4 hours, thus destroying the oxalate ion and oxidizing the plutonium ions present to the hexavalent state. The solution was then cooled, and 35 ml. of 2.0 M $UO_2(NO_3)_2$ and 424 grams of $NaNO_3$ were added to the solution and the solution diluted to 800 ml. with H_2O. Following the dilution step 498 ml. of 4.0 M NaAc solution was added and the solution then still further diluted with 102 ml. H_2O. A sodium uranyl acetate carrier precipitate formed, and the mixture was stirred for ½ hour at room temperature; then the precipitate was separated from the solution and washed twice with 50 ml. of a solution 5.0 M in Na^+ ions, 0.2 M in acetate ions and 0.4 M in acetic acid. Following dissolution of the precipitate, 40 ml. of 8 M HNO_3, 858 ml. of 7 M $NaNO_3$ solution, 23.4 ml. of glacial acetic acid and 80.5 ml. of 4.0 M NaAc solution were added to the solution to form a second sodium uranyl acetate carrier precipitate. This precipitate was then separated from the solution and the plutonium separated from this precipitate by conventional methods.

The process of the present invention is capable of numerous modifications. For example, the first three steps of the process may be employed to separate fission products from a solution of neutron-irradiated uranium from which the plutonium has been previously removed. The process may also be used to separate mixtures of uranium and non-radioactive elements having atomic numbers 32 to 64. Furthermore the process may be used to recover other transuranic polyvalent actinide rare earths such as neptunium, and fission products from neutron-irradiated uranium. While not all chemical reactions of plutonium and neptunium are the same, those involved in the present process are sufficiently similar that neptunium will be separated in the same manner as plutonium if neptunium rather than plutonium is present in the solution of neutron-irradiated uranium. It is also to be understood that separations may be made in all cases with preformed carrier precipitates, although carriers formed in situ are usually preferable. Other modifications may also be made, and in general it may be said that the use of any equivalents or modifications of procedure which would naturally occur to those skilled in the art are included in the scope of the present invention.

The present invention is a continuation-in-part of the copending application of John Gofman, S.N. 752,831, filed June 5, 1947, granted on January 6, 1959, as U.S. Patent No. 2,867,640 and entitled "Oxalate Process for Separating Element 94" and the specification of that application is incorporated herein by reference.

What is claimed is:

A method of recovering fission products from neutron-irradiated uranium which comprises treating an acidic solution of uranium containing fission products including zirconium with a thorium oxalate carrier precipitate, separating the carrier precipitate and associated fission products from the solution, dissolving said carrier precipitate in an aqueous oxalate solution, acidifying the resultant solution to an access of acidity not greater than about 2 N whereby a thorium oxalate carrier precipitate containing lanthanide rare earths and alkaline earth metals is formed, separating the thorium oxalate carrier precipitate from the solution which contains soluble zirconium oxalate complex, dissolving the precipitate in an aqueous oxalate solution at an elevated temperature, treating the resultant solution with a lanthanide rare earth oxalate carrier precipitate, and separating from the solution said rare earth carrier precipitate together with associated lanthanide rare earth and alkaline earth element fission products associated therewith.

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