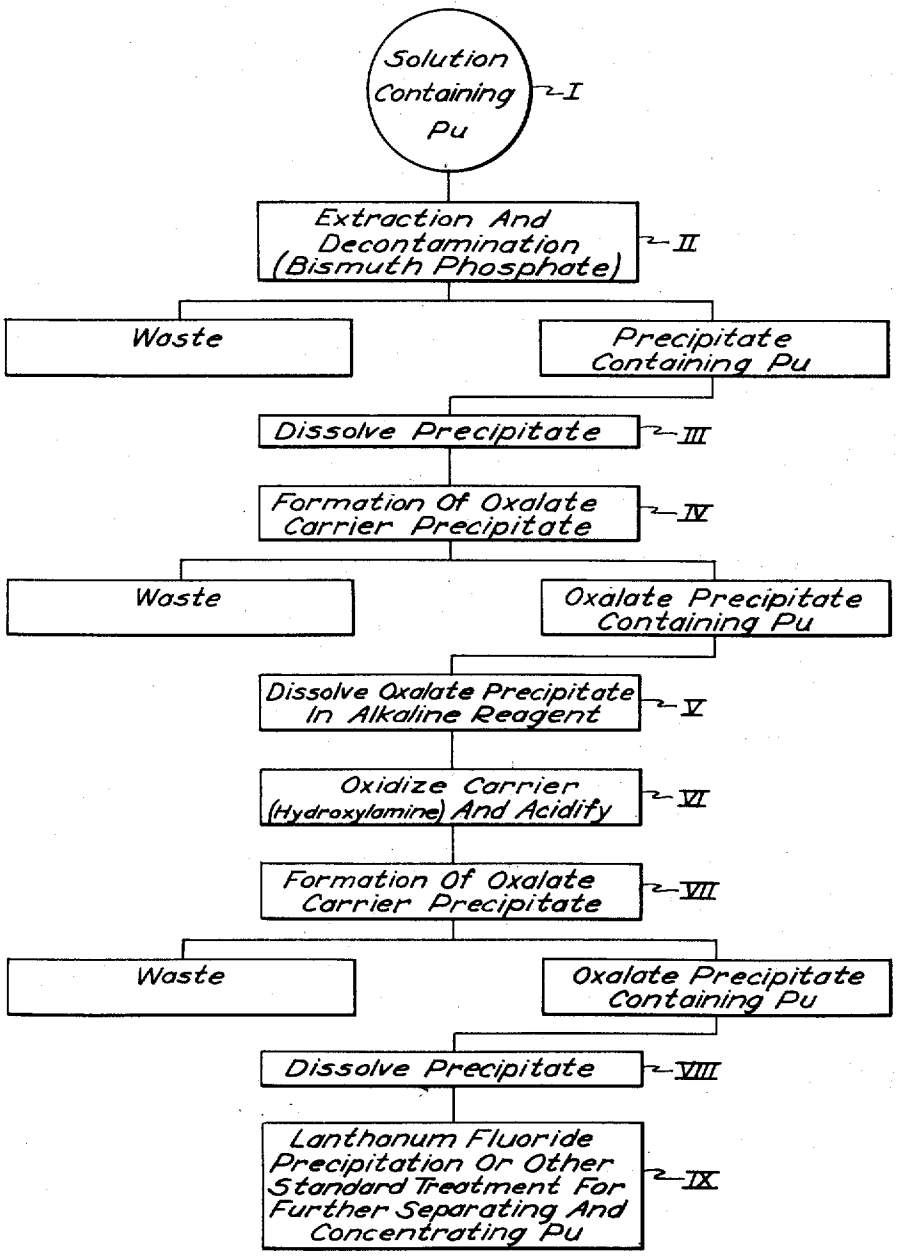
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CONCENTRATION OF P_u USING OXALATE TYPE CARRIER

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INVENTOR.
David M. Ritter
BY Robert P.S. Black
Robert A Saunders

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CONCENTRATION OF Pu USING OXALATE TYPE CARRIER

David M. Ritter and Robert P. S. Black, Oak Ridge, Tenn., assignors to the United States of America as represented by the United States Atomic Energy Commission

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This invention relates in general to methods for processing materials containing the element of atomic number 94, known as plutonium, and specifically to a method for separating the plutonium from extraneous matter such as substances of the kind present in neutron irradiated uranium as exemplified by uranium and especially fission products, and the like radioactive contaminants. More particularly, this invention concerns a separatory and concentration procedure involving the use of an oxalate carrier wherein certain improved steps may be employed in treating the carrier.

As described herein, the isotope of element 94 having a mass of 239 is referred to as 94^{239} and is also called plutonium, symbol Pu. In addition, the isotope of element 93 having a mass of 239 is referred to as 93^{239}. Reference herein to any of the elements or the term plutonium value 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.

Elements 93 and 94 may be obtained from uranium by various processes which do not form a part of the present invention including irradiation of uranium with neutrons. 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.

Naturally occurring uranium contains a major portion of $_{92}U^{238}$, a minor portion of $_{92}U^{235}$, and small amounts of other substances such as UX_1 and UX_2. When a mass of such uranium is subjected to neutron irradiation, particularly with neutrons of resonance or thermal energies, $_{92}U^{238}$ by capture of a neutron becomes $_{92}U^{239}$ which has a half life of about 23 minutes and by beta decay becomes 93^{239}. The 93^{239} has a half life of about 2.3 days and by beta decay becomes 94^{239}. Thus, neutron irradiated uranium contains both 93^{239} and 94^{239} but by storing such irradiated uranium for a suitable period of time, the 93^{239} is converted almost entirely to 94^{239}.

In addition to the above-mentioned reaction, the reaction of neutrons with fissionable nuclei such as the nucleus of U^{235} results in the production of a large number of radioactive fission products. As it is undesirable to produce a large concentration of these fission products which must, in view of their high radioactivity, be separated from the 94^{239} and further as the weight of radioactive fission products present in neutron irradiated uranium is proportional to the amounts of 93^{239} and 94^{239} formed therein, it is preferable to discontinue the irradiation of the uranium by neutrons when the combined amount of 93^{239} and 94^{239} is equal to approximately 0.02 percent by weight of the uranium mass. At this concentration of these substances, the concentration of fission elements which must be removed is approximately the same percentage.

A number of processes have already been proposed for accomplishing the separation and concentration of Pu. Certain of these processes are generically known as the "bismuth phosphate" process and the "wet fluoride"

process. These processes are the invention of others and the details of the processes are described in copending applications, as for example application Serial No. 519,714, now Patent No. 2,785,951, to be referred to hereinafter, which gives complete details relative to the bismuth phosphate process. Still another type of procedure is the "oxalate method" wherein the precipitate which carries Pu is an oxalate compound. Consequently, all of the details of operation of the aforementioned processes are not described herein.

While the aforementioned processes have been used successfully, the present invention provides certain variations in these processes for obtaining additional advantages. That is, by the present invention utilizing many of the same steps which have been previously worked out, but supplemented and altered in certain respects the advantage of easier reaction may be obtained as will be described.

The term decontamination as used herein refers in particular to the separation or removal of radioactive material from the Pu, or materials containing the Pu. The meaning of the term carrier precipitate and other similar terms will be apparent as the description proceeds.

This invention has for one object, to provide a new method for the separation and recovery of plutonium.

Another object is to provide a method of separating plutonium by a procedure wherein in certain steps different reagents than have heretofore been used are employed.

A still further object is to provide a process for separating Pu wherein elimination of extraneous materials such as fission products may be better accomplished.

Still another object is to provide a novel process for separating the Pu which lends itself to the use of and to coupling with steps already known or practiced.

Another object is to provide a separatory process for the recovery of Pu which may employ many of the materials used in existing processes and which may be carried out in existing equipment without change, or with a minimum of equipment change.

Still another object is to provide a process for the recovery of Pu which may be applied to solutions containing Pu either in relatively small or large amounts.

Another object is to provide a separatory and concentration process for Pu containing materials involving the use of both oxalate and bismuth phosphate carriers.

Still another object is to provide a method of obtaining an acid solution of materials that resist direct dissolution in acid.

Other objects will appear hereinafter.

For a further understanding of the invention, reference will later be made to the attached drawing forming a part of the present application. In this drawing, a diagrammatic representation of one embodiment of the invention is given in the form of a flow sheet.

We have found that Pu in admixture with various extraneous material may be separated and concentrated by the use of the series of steps involving the utilization of a bismuth phosphate treatment followed by an oxalate treatment. These treatments are in accordance with known practice. However, we have found that the combination of steps may be rendered simpler and more efficient by interposing the improvement features described herein such as a different type of dissolution procedure or optionally the use of different type oxidizing agents and other variations as set forth in detail. By the utilization of these features, not only are the advantages previously obtained in the processes still obtainable, but easier and simplified operation as well as savings in time are effected.

The bismuth phosphate process is set forth in applica-

tion Serial Number 519,714, now Patent No. 2,785,951, filed January 26, 1944, Thompson and Seaborg, and reference is made to that application for full disclosure of such process, details thereof being omitted from the present disclosure except where necessary to an understanding of the present invention. As set forth in said application, it has been discovered that plutonium has more than one oxidation state, including a lower oxidation state or states principally the tetravalent state referred to herein as $Pu^{(r)}$ in which the element is characterized by forming insoluble phosphates and fluorides and a higher oxidation state or states principally the hexavalent state referred to as $Pu^{(o)}$ in which the element forms soluble phosphates and fluorides. (In general, similar remarks apply to processes of treating Pu by oxalate processes; that is, $Pu^{(r)}$ is characterized by forming insoluble oxalate, while $Pu^{(o)}$ forms soluble oxalate.) Thus, the solubility of plutonium in the presence of phosphate ions is changed by changing the oxidation state of the plutonium. As foreign product, such as uranium and uranium fission products, which are normally encountered as contaminants in plutonium production, form substances which are in part insoluble and in part soluble in the presence of phosphate ions, the process contemplates alternately separating, by precipitation, plutonium in its phosphate insoluble "lower oxidation" state from the phosphate soluble foreign products, and with the plutonium in its higher oxidation (phosphate soluble) state, separating the plutonium from foreign products which are in a phosphate insoluble state. However, where the plutonium is present in relatively low concentrations, as, for example, 10 milligrams per liter, as is often encountered, it is below its limit of solubility, as phosphate, in the solution, so that the addition of phosphate ions will normally not cause the bulk of the plutonium to be thrown down as a precipitate. In such case it has been found desirable to use suitable substances which will be converted into insoluble phosphate carriers by phosphate ions and will thereupon carry the plutonium phosphate out of solution. In this regard, bismuth phosphate, in particular, has been found to be a very effective carrier for this purpose. Bi^{+3} ions may be introduced into the solution (e.g. a 1 N HNO_3 solution) by the addition of bismuth nitrate or other bismuth compound, preferably as an acid solution; usually, 10 to 25 mg. of Bi^{+3} per 10 cc. of solution is sufficient to precipitate with phosphate ions and carry substantially all of the plutonium out of solution. An excess of phosphoric acid is added to the solution to precipitate the bismuth and plutonium as insoluble phosphates; a phosphoric acid concentration in the solution of approximately 0.4 M to 0.8 M is usually satisfactory. Alternatively, the Bi^{+3} may be introduced into the solution already containing the the phosphoric acid. Preferably, the solution may be heated for approximately an hour at about 75° C. to promote substantially complete precipitation. To insure the presence of plutonium in said reduced state during the carrier precipitation, it may be desirable to initially add small amounts of a reducing agent, e.g. ferrous salts, to the solution. The resulting bismuth phosphate precipitate carrying plutonium values is then separated from the solution by such means as filtration, centrifugation, or the like, and the separated precipitate many then be dissolved in an excess of a concentrated acid, e.g. 10 N nitric acid.

The aforementioned processes are conducted under acid conditions. It has heretofore been customary to dissolve the oxalate carrier precipitate in an acid, such as nitric acid, to obtain the aforesaid acid conditions. However, it has been observed that the oxalate precipitate dissolves with difficulty and that dissolution consumes a relatively long period of time.

We have discovered, as will be described in detail hereinafter, that possibly this difficulty may be due to carryover of bismuth ions or some similar materials from the preceding steps in the process. We have found that this difficulty of redissolution of oxalate precipitate carrying Pu may be readily overcome by utilizing certain alkali reagents for dissolving the oxalate precipitate. Not only is the dissolution of oxalate precipitate materially facilitated by the use of such solvents, but as will be further described in detail, under the alkaline conditions of such dissolution, it is possible to utilize as oxidizing agents materials not hitherto regarded as capable of such use. The resultant alkaline solutions of the oxalate precipitates may then be readily rendered acidic and subjected to further treatment.

In general, the operation of our process for the separation and recovery of Pu from extraneous materials is as follows: Materials which have undergone neutron bombardment and otherwise processed to contain Pu are given conventional preliminary treatments and finally a $BiPO_4$ plutonium product precipitation is carried out. The $BiPO_4$ precipitate carrying Pu is dissolved in acid, the solution treated with oxalic acid and, optionally, with KCl. Uranous oxalate is precipitated carrying Pu by adding a source of U^{++++} in H_2SO_4 solution. The uranous oxalate precipitate is dissolved in a soluble carbonate solution or in alkali oxalate solution, in accordance with the present invention, and the solution is oxidized. Hydroxylamine may be used to effect oxidation in the alkaline solution. The oxidized solution is neutralized with acid. Thereafter HNO_3, HCl and H_2SO_4 may be added, and a second uranous oxalate product precipitation effected. This second precipitate may be dissolved in HNO_3 and further treated as desired as by lanthanum fluoride precipitation to concentrate the product.

A still further understanding of the general application of our process may be had by reference to the attached flow sheet. The source from which the plutonium is to be separated and recovered is indicated at I. This source is subjected to standard extraction and decontamination procedure such as the bismuth phosphate procedure as indicated at II. The precipitate of bismuth phosphate carrying Pu obtained from the foregoing procedure may be dissolved in acid in the conventional manner at III. Likewise, the formation of an oxalate precipitate for carrying Pu may be carried out at IV in accordance with conventional procedure. However, the oxalate precipitate carrying Pu resulting from precipitation at IV presents difficulty of dissolution.

In accordance with the present invention, at V, special dissolution procedure is applied. If desired, special oxidation procedure in accordance with the present invention may be applied at VI.

The foregoing operations produce a solution to which may now be applied a standard oxalate precipitation operation at VII. The oxalate precipitate carrying Pu from VII may be redissolved at VIII by conventional solvents such as nitric acid. Thereafter at IX standard operations for further separating and concentrating Pu may be applied.

As apparent from the foregoing by the interposing of the steps of the present invention, the use of an oxalate type of process with a phosphate type of process is facilitated. We have provided a procedure by which an acid solution of a carrier precipitate which resists direct acid dissolution may be obtained.

The new combination of steps including the aforementioned features of dissolution and optional oxidizing are set forth in further detail in the following example. As already indicated, certain steps are individually old, or are not per se regarded as the invention of the herein named inventors. However, the combination of steps set forth below and particularly the steps relative to dissolution of certain Pu containing oxalate precipitates in alkali reagents, and the oxidation and acidification of the resultant solutions are believed to be novel. Referring now

to a more detailed example, the steps making up the several operations are set forth below.

Example

The materials containing Pu which had undergone neutron treatment were dissolved and conventional preliminary treatment applied. The solution from the preceding step was reduced by any of the several reducing procedures. For example, hydrogen peroxide, ferrous salts and the like may be used as described in application Ser. No. 519,714, now Patent No. 2,785,951, aforementioned. The standard $BiPO_4$ precipitation procedure was carried out on the solution in (r) condition to obtain a Pu containing product precipitate. The foregoing steps are embraced under operations I to III inclusive of the flow sheet.

Referring now to the steps pertaining in particular to this invention, the bismuth phosphate precipitate containing Pu from the preceding treatments was further processed as follows: About 1350 ml. of solution were prepared by dissolving the $BiPO_4$ precipitate in 7 N HCl. The solution contained approximately 150 grs. Bi^{+++} per liter. The solution was then treated to contain .4 M of oxalic acid and about .1 M of KCl. The addition of the latter is optional. Uranous oxalate was precipitated by adding approximately a gram of U^{++++} as a .05 M solution in .1 N H_2SO_4. This addition was made over a period of ½ hr. at room temperature. The mixture was digested for about 1 hr. An oxalate precipitate carrying Pu was separated.

If it is attempted to dissolve the aforementioned oxalate precipitate in HNO_3, it requires several hours heating at 75° C. before the precipitate starts to dissolve. On the other hand utilizing our invention employing alkaline reagents exemplified by alkali metal carbonates and alkali metal oxalates, the precipitate dissolves in a few minutes, as indicated in the next step.

The aforementioned uranous oxalate precipitate carrying Pu was readily dissolved in 4.2 ml. of 50% K_2CO_3 solution. The carrier in the resultant solution was oxidized by adding .66 ml. of 30% H_2O_2 solution. We have also found that hydroxylamine may be used as an oxidizing agent in lieu of the peroxide. We have found hydroxylamine has the property of acting as an oxidizing agent in the aforementioned alkaline environment, but does not oxidize in acid solution. It will be observed here that the function of the oxidation is to convert the uranous oxalate to uranyl oxalate. In other words, the oxidizing agent merely functions to change the oxidation state of the carrier. The Pu is not oxidized.

After oxidation had been accomplished, there was added 2.9 ml. of 16 N HNO_3 to neutralize the K_2CO_3. Then the following additions were made: 3.7 ml. further of HNO_3; 4.5 ml. (12 N) HCl; .84 ml. (36 N) H_2SO_4. The resultant solution was made up to 30 cc. volume by adding water. A second uranous oxalate precipitate, carrying Pu was obtained in the aforementioned solution by making an addition of U^{++++} over a period of approximately ½ hr. in the amount of 2 grams per liter in a manner comparable to the procedure set forth above for forming the first oxalate precipitate. This second precipitate was separated and dissolved in HNO_3 and further treated in a conventional manner by lanthanum fluoride precipitation, to further concentrate the product.

While the process has been described in particular as being carried out utilizing the uranous oxalate type of carrier, our invention is not limited specifically to this carrier. There are various other oxalate types of carriers known to carry Pu such as thorium oxalate and lanthanum oxalate. Our invention may be used in a similar manner for facilitating operation in other instances where the carrier resists acid dissolution.

As described above, it is possible that the resistance to dissolution of such oxalate carriers may be caused by certain metallic ions carried along from preceding steps in the process. However, by using the alkaline solvents described herein, it has been found that dissolution may be rapidly accomplished and also that the desired acid conditions for further precipitation may be obtained.

It will be further observed that although the alkali dissolution conditions are employed for placing the first of the oxalate carrier precipitates in solution that in subsequent dissolution steps applied to oxalate precipitates, the dissolution may be directly accomplished with conventional solvents such as nitric acid as may be noted in the preceding example. However, if desired, all oxalate carrier dissolution steps may be carried out using our alkaline solvents.

Any of the soluble forms of the alkali reagents referred to herein such as sodium, potassium and ammonium salts may be used. The particular amount of or strength of reagent used is not a limitation on our invention. In general, in processes of the type described, since reduction of volumes and concentration is desired, the use of the smallest amount of alkaline reagent consistent with good dissolution would preferably be employed. However, this does not preclude the use of larger amounts of reagents or diluted reagents as the process may be operated with excesses.

While the solution treated in the example described herein contained a small amount of Pu this is not a limitation as our process may be carried out on solutions containing various amounts of Pu from, for example, tracer amounts to 200 grams per liter. The precipitates may be separated by centrifuging or filtering and other conventional techniques may be employed in carrying out the process.

It is to be understood that all matter contained in the above description and examples shall be interpreted as illustrative and not limitative of the scope of this invention, and it is intended to claim the present invention as broadly as possible in view of the prior art.

We claim:

1. In a process for the recovery of plutonium values from an aqueous solution containing the same comprising precipitating uranous oxalate therein to thereby carrier precipitate said plutonium values from solution therewith, the improved method for subsequent processing which comprises contacting the resulting oxalate carrier precipitate with an aqueous solution of a reagent chosen from the group consisting of the carbonates and oxalates of alkali metals and ammonium to thereby dissolve the oxalate precipitate together with said plutonium values carried therein, thereupon incorporating in the resulting solution an oxidant selected from the group consisting of hydroxylamine and hydrogen peroxide to thereby oxidize dissolved uranous ions to the uranyl oxidation state, thereafter acidifying the solution, and providing a source of uranous ions therein thereby precipitating uranous oxalate to thereby carrier precipitate said plutonium values from solution therewith.

2. The process of claim 1 wherein said alkali metal carbonate is specifically potassium carbonate.

3. The process of claim 1 wherein said oxidant is specifically hydroxylamine.

4. The process of claim 1 wherein said oxidant is specifically hydrogen peroxide.

5. In a process for the recovery of plutonium values from an aqueous solution containing the same comprising precipitating bismuth phosphate therein to thereby carrier precipitate said plutonium values from solution therewith, then dissolving the resulting carrier precipitate to obtain an aqueous solution of said plutonium values, and thereafter precipitating in the obtained solution uranous oxalate to thereby carrier precipitate said plutonium values from solution therewith, the improved method for subsequent processing which comprises contacting the resulting uranous oxalate carrier precipitate with an aqueous solution of potassium carbonate to thereby dissolve the oxalate precipitate together with

said plutonium values carried therein, thereupon incorporating hydrogen peroxide in the resulting alkaline solution to oxidize dissolved uranous ions to the uranyl oxidation state, thereafter acidifying the resulting solution with an acid selected from the group consisting of nitric, hydrochloric, and sulfuric acids, and providing a source of uranous ions therein thereby precipitating uranous oxalate to thereby carrier precipitate said plutonium values from said solution therewith.

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