United States Patent Office

3,005,681
Patented Oct. 24, 1961

3,005,681

PROCESS FOR SEPARATING PLUTONIUM (IV) VALUES FROM URANIUM AND FISSION PRODUCT VALUES, e.g., ZIRCONIUM AND COLUMBIUM, UTILIZING A LANTHANUM OXALATE CARRIER PRECIPITATE

Raymond W. Stoughton, Oak Ridge, Tenn., assignor to the United States of America as represented by the United States Atomic Energy Commission

No Drawing. Filed Jan. 16, 1946, Ser. No. 641,627
3 Claims. (Cl. 23—14.5)

The present invention relates to recovery and concentration of transuranic elements. More particularly, it is concerned with a method for the separation of plutonium from solutions containing impurities commonly associated with that element.

An object of this invention is to provide an efficient method for the separation of transuranic elements from uranium, fission products and other contaminants associated therewith.

It is a further object of this invention to provide a method capable of effecting a substantially complete separation of plutonium from objectionable fission products such as radioactive columbium and zirconium.

An additional object of this invention is to provide a new class of carriers for plutonium which are readily filterable and easily dissolved, thereby substantially aiding in an efficient and relatively rapid recovery of that element.

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

It is known that plutonium can be produced in small quantities by the bombardment of natural uranium with neutrons. The designation "plutonium" or "element 94" as used throughout the present description refers to the transuranic element having an atomic number of 94. The expression "94^{239}" means the isotope of element 94 has an atomic weight or mass of 239. Similarly, the terms "element 93" or "Np" refer to the new element known as neptunium having an atomic number of 93.

Uranium is composed of three isotopes, namely, U^{234}, U^{235} and U^{238}, the latter being present in excess of 99 percent of the whole. When U^{238} is subjected to the action of slow or thermal neutrons, a fourth isotope, U^{239}, is produced having a half-life of 23 minutes and undergoes beta decay to Np^{239} which decays further by beta radiation with a half-life of 2.3 days to yield plutonium. In addition to the formation of 94^{239}, there are simultaneously produced other elements of lower atomic weight known as fission fragments. These fission fragments are composed of two distinct element groups, i.e., a light and heavy element group. The light group contains elements having atomic numbers of between about 35 and 46 while the heavier group is composed of elements of atomic numbers varying between about 51 and 60. The elements of these groups as originally produced are considerably overmassed and undercharged, and hence are highly unstable. By beta radiation, however, they quickly transform themselves into isotopes of these various elements having longer half-lives. The resulting materials are commonly known as fission products.

The various radioactive fission products have half-lives ranging from a fraction of a second to thousands of years. Those having very short half-lives may be substantially eliminated by aging the material for a

reasonable period before handling. Those with very long half-lives do not have sufficiently intense radiation to endanger personnel protected by moderate shielding. On the other hand, the fission products having half-lives ranging from a few days to a few years have dangerously intense radiations which cannot be eliminated by aging for practical storage periods. These products are chiefly radioactive isotopes of Sr, Y, Zr, Cb, and Ru of the light group and Te, I, Cs, Ba, La, Ce, and Pr of the heavy group.

It may be readily seen that plutonium produced as generally set forth above is contaminated with considerable quantities of uranium and fission products. In fact, the plutonium constitutes only a very minor portion of the irradiated mass, i.e., less than one percent thereof. In view of such a low concentration of plutonium in the irradiated metal, it becomes apparent that the procedure employed to recover that element must be highly efficient in order to be at all practicable.

There have been devised a number of procedures for the removal and concentration of plutonium from extremely dilute solutions thereof such as for example the bismuth phosphate carrier method described and claimed in co-pending application U.S. Serial No. 519,714, filed January 26, 1944 by Glenn T. Seaborg et al., now U.S. Patent 2,785,951, issued March 19, 1957. In general, such methods involve the formation of various insoluble compounds in said dilute solutions capable of carrying plutonium in the reduced state. The carrier precipitate and plutonium thus obtained are then dissolved and the plutonium oxidized to PuO_2^{++} in which state of oxidation it is soluble in the presence of said carrier. Under these conditions, the plutonium remains in solution and the fission products are removed when the carrier is added. Thereafter, the dissolved plutonium is reduced to a valence state in which it is carriable by the aforesaid carrier and removed from solution in the form of a carrier precipitate which may again be dissolved and the plutonium purified further if considered necessary or desirable by repeating the above cycle.

While such a procedure functions to separate a substantial portion of the fission products and other impurities from plutonium, certain of the fission products such as zirconium and columbium are extremely difficult to separate completely therefrom by the above method since these elements tend to be closely associated with plutonium in its carriable state and as a result are found to be present in plutonium precipitates after removal of the other common impurities has been effected.

It has been discovered that the above and other objects may be readily accomplished by the utilization of a substantially water insoluble oxalate as a carrier for plutonium in its reduced state. Broadly, the invention involves contacting a solution containing plutonium with an insoluble oxalate preferably in the presence of an excess of oxalate ions, thereafter recovering the plutonium containing precipitate and processing said precipitate in a known manner to obtain the plutonium therefrom.

A preferred embodiment of the present invention comprises the utilization of the aforesaid insoluble oxalate as a follow-up carrier in combination with procedures using other carriers which tend to bring down fission products such as zirconium and columbium along with

the carrier precipitate containing plutonium. Such conditions are encountered when plutonium is removed from a solution of neutron irradiated uranium by means of carriers such as zirconium phosphate, columbium oxide, bismuth phosphate, lanthanum fluoride and the like. With carrier precipitates capable of removing zirconium and columbium along with plutonium in its reduced state, separation of the plutonium from the two former elements can be effected by first dissolving said precipitate in oxalic acid or a solution of a suitable soluble oxalate, adding a soluble compound whose cation forms an insoluble oxalate to the resulting solution and thereafter introducing if necessary, sufficient oxalate ion to effect precipitation of the oxalate thus formed. Under these conditions columbium and zirconium, if the latter is present, form soluble stable oxalate complexes thereby effecting a substantially complete separation of columbium and zirconium from the plutonium which precipitates with the insoluble oxalate formed in solution.

An outstanding advantage obtained in employing the carriers of the present invention resides in the fact that the anion portion thereof is readily destroyed by means of heating an aqueous mixture of said carrier and a suitable oxidizing agent such as for example nitric acid, sodium dichromate, sodium bismuthate, or the like, thereby causing the cation of the carrier to combine with an anion which results in the formation of a compound much more soluble than the oxalate carrier. It is apparent that such a property makes possible a relatively efficient and convenient means for effecting a substantial concentration of element 94 in a single operation. Furthermore, it will readily be recognized by those skilled in the art that such a means of effecting concentration of plutonium can be accomplished by using other carriers, such as the insoluble tartrates, citrates, etc. whose anion is readily destroyed under similar conditions.

One of the distinct advantages afforded by using the oxalates of the present invention is that such carriers, in general, are much more soluble in the common mineral acids than carriers previously used such as columbic oxide, bismuth phosphate etc. With carriers of the latter type large volumes of concentrated acid and long digestion periods are required whereas the oxalates employed in the process of this invention require short digestion periods and only relatively small volumes of acid thereby resulting in the procurement of a highly concentrated solution of plutonium. For example, by using uranous oxalate as a carrier for plutonium after the standard bismuth phosphate process has been employed to separate the plutonium from the bulk of the fission products present, it has been found that a plutonium concentration factor of about 80 can be achieved inasmuch as uranous oxalate can be dissolved in a much smaller volume of acid than bismuth phosphate. In employing uranous oxalate as a carrier, however, it has been found that the presence of ferric ions has somewhat of an adverse effect on the removal of plutonium by said carrier when the aforesaid ions are present in concentrations of around 0.1 M and above.

It has been further observed that in employing uranous oxalate as a carrier in combination with procedures involving the use of bismuth phosphate as a carrier that at any given ferric ion concentration the carrying of element 94 by uranous oxalate decreases as the bismuth phosphate concentration increases. This effect, however, is only slight with ferric ion concentrations of the order of about 0.05 M but is rather noticeable at concentrations of around 0.1 M as shown by the table below. In obtaining the data appearing in the table the plutonium was removed from a solution 5 N in hydrochloric acid, 0.1 N in potassium chloride and containing tetravalent uranium in concentration of 1 mg./ml. and plutonium in a concentration of 0.04 mg./l. by adding thereto sufficient oxalic acid to render the resulting solution 0.4 M therein.

TABLE I

Bi^{+3} as $BiPO_4$, mg./ml.	Fe^{+3} Molarity	Pu carried, Percent
50	0.05	94
50	0.05	94
100	0.05	87
100	0.05	89
140	0.05	88
140	0.05	84
50	0.10	86
50	0.10	88
100	0.10	58
100	0.10	69
140	0.10	39
140	0.10	55

While the utilization of insoluble oxalates as carriers of plutonium in accordance with the present invention may be effectively applied to any plutonium-containing solution, such carriers are particularly useful for the removal of that element from solutions formed by dissolving neutron irradiated uranium in a suitable acid such as, for example, hydrochloric acid or nitric acid.

In employing an insoluble oxalate to remove plutonium from such solutions it is recommended that alternate carriers be used at the various oxidation levels of the plutonium inasmuch as the oxalate ion tends to at least partially reduce that element from its higher valent states to a valence of +4 and hence an insoluble oxalate when employed to carry fission products from a solution containing plutonium in a higher valent state would partially reduce said element to a valence of +4 owing to the excess oxalate ion present and, as a result, a portion of the plutonium would be carried down with the fission products. To avoid the occurrence of such a loss a suitable carrier other than an insoluble oxalate which does not in any way tend to reduce hexavalent plutonium to the tetravalent state may be utilized. Examples of satisfactory carriers for fission products and which have no effect on the valent state of plutonium are thorium iodate, bismuth phosphate, lanthanum fluoride, and the like.

In general, it has been found that the acid concentration of the solutions, from which the plutonium is removed, has very little effect on the carrying efficiency of the insoluble oxalates as employed in accordance with this invention. However, for maxium carrying efficiency the time of contact of the oxalate with the plutonium containing solution should, in general, be about ten minutes. Carrying is also facilitated by periodic agitation of the mixture.

It has been further observed that the carrying of plutonium from solutions, in which that element is present in low concentrations, is generally improved by the presence of a suitable alkali metal ion such as potassium, sodium, or the like. This phenomenon has been found to occur particularly in instances where uranous oxalate was utilized as the carrier. Normally, in order to secure noticeably improved results alkali metal ion concentrations of the order of between about 0.01 M and 0.1 M should be used.

As examples of suitable oxalate carriers in addition to uranous oxalate previously disclosed there may be mentioned bismuth oxalate and the alkaline earth metal and rare earth metal oxalates such as, for example, the oxalates of calcium, barium, strontium, lanthanum, thorium, cerium, and the like. In employing these carriers it is generally preferable to form such compounds 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 the cation that forms an insoluble oxalate. Satisfactory carrying can also be secured by adding the desired cation to the oxalate-containing solution or, if desired, the preformed insoluble oxalate, per se, may be added and the plutonium removed thereby. In most instances, however, it has generally been observed that the

quantity of plutonium separated is somewhat less when the desired cation 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 valent state not above +4. If the plutonium ions are allowed to form a stable complex, it has been found that satisfactory carrying can not 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 occurrence 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., from a pH of between about 1.5 and 4.0. The adverse effect of such anions can be avoided, however, by increasing the acidity of the solution through the addition of a suitable highly ionized acid such as nitric acid, hydrochloric acid or the like.

Where solutions are encountered in which the plutonium is in a valent state greater than +4, or a noncarriable state, it will generally be found that it may be readily converted to a carriable form by reduction with hydroxylamine chloride or hydroxylamine acetate. Reduction can also be effected by utilizing such materials as sulphur dioxide, oxalate ions, and the like.

The present invention may be further illustrated by the following specific examples.

Example I

To a dilute solution of tetravalent ionic plutonium, 0.8 M with respect to nitric acid and 0.018 M with respect to lanthanum nitrate, there was added an equal volume of 0.8 M oxalic acid while agitating the mixture. The resulting slurry was then agitated for an additional ten minutes at room temperature, after which the precipitate of lanthanum oxalate and associated plutonium was separated by centrifuging On the basis of determinations of alpha radiation from aliquot portions of the initial plutonium solution and the final supernatant solution, using standard counter tube techniques, the amount of plutonium carried by the lanthanum oxalate precipitate is 96% of that in the initial solution.

The following example demonstrates the ability of bismuth oxalate to carry plutonium from nitric acid solutions and also the effect of the acidity of such a solution on the percentage of plutonium carried.

Example II

A bismuth phosphate precipitate containing plutonium was dissolved in sufficient 60 percent nitric acid to produce a solution having the normality indicated in the table below. Bismuth oxalate was then precipitated by adding enough oxalic acid to make the solution 0.12 M with respect to oxalic acid. After agitating the resulting mixture the solution was allowed to remain in contact with the precipitate for approximately ten minutes. Thereafter the mixture was centrifuged and the percent plutonium carried on the bismuth oxalate determined in accordance with the method used in Example I. The quantity of plutonium carried in each instance is shown in the table below.

TABLE II

HNO_3 Normality	Bi mg./ml.	Percent Pu carried
1	2.5	93.9
3	2.5	92.0
1	1.0	92.3
3	1.0	87.6

Example III

To a solution containing uranyl nitrate hexahydrate in a concentration of 10 percent, plutonium in the tetravalent state and a solution containing 6 mg. potassium oxalate per ml., was added, a U^{+4} solution containing 3.6 mg. of that ion per ml. The resulting mixture was then allowed to digest at room temperature for about one hour after which the precipitate thus formed was separated by centrifugation. By practicing this procedure 99 percent of the plutonium was carried.

It may be seen from the foregoing description and examples that the ultilization of insoluble oxalates as carriers for plutonium in accordance with the present invention may be readily adapted to a variety of procedures embodying the use of said oxalates alone or in combination with other suitable carriers. Furthermore, although the present invention has been illustrated with particular reference to the concentration and decontamination of plutonium and is especially useful for this purpose, it should be understood that such invention is equally applicable to the concentration and decontamination of neptunium having a valent state not greater than +4 or of mixtures of neptunium and plutonium. All of the procedures disclosed above may be applied to dilute solutions of neptunium or to dilute solutions of neptunium and plutonium as well as aged solutions containing only plutonium.

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.

What is claimed is:

1. A process of recovering plutonium values from an aqueous plutonium (IV) salt solution, comprising adding lanthanum nitrate to said solution, adding a water-soluble oxalate-anions-containing substance to said solution at room temperature whereby a lanthanum oxalate precipitate is formed and plutonium values are carried on said precipitate, and removing said precipitate from the solution.

2. The process of claim 1 in which an oxidizing agent is added to the plutonium-containing oxalate precipitate and the mixture obtained thereby is heated whereby the oxalate anion is decomposed and a plutonium compound is formed of higher solubility in acid than that carried on the oxalate.

3. A process of decontaminating plutonium values from zirconium and niobium values carried on a bismuth phosphate carrier, comprising dissolving said bismuth phosphate carrier in oxalic acid, adding lanthanum nitrate to the solution formed, adding an oxalate-anions-containing substance to the solution at room temperature whereby an oxalate precipitate forms which carries plutonium values, and separating the oxalate precipitate from the zirconium-and niobium-containing aqueous solution.

References Cited in the file of this patent

UNITED STATES PATENTS

2,227,833	Hixon et al.	Jan. 7, 1941
2,316,141	Wainer	Apr. 6, 1943
2,776,185	Werner et al.	Jan. 1, 1957
2,872,286	Finzel	Feb. 3, 1959
2,891,841	Ritter	June 23, 1959

OTHER REFERENCES

Berichte Deu. Chem., vol. 34 (1901), p. 1474 and 5 (complete article 1472–9), Kohlschutter.

Berichte Deu. Chem., vol. 34 (1901), p. 3623,25 and 30 (complete article 3619–35), Kohlschutter.

J. Amer. Chem. Soc., vol. 65 (1943), p. 333 and 4, Marchi et al.

Seaborg: The Chemical and Radioactive Properties of the Heavy Elements, Chemical & Engineering News, vol. 23, pages 2190–2193, Dec. 10, 1945.

Accum: A Practical Essay on Chemical Tests, page 68 (1817). Published by M. Carey & Sons, Philadelphia, Pa.