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2,856,262

# ADSORPTION PROCEDURE IN PREPARING $U^{233}$

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

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15 Claims. (Cl. 23—14.5)

The invention relates to the preparation of masses and compositions of the isotope of uranium having a mass number of 233, said isotope being designated as $_{92}U^{233}$ or $U^{233}$. More particularly, this invention concerns a method of which $Pa^{233}$ is segregated by adsorption, eluted and permitted to develop to $U^{233}$ which may be further treated as desired.

In this specification and the claims the name of the element is used to designate the element generically, either in its elemental state or combined in a compound, unless otherwise indicated by the sense in which it is used or by a specific designation such as "metal."

It is known that the bombardment of thorium with fast neutrons of energies above about 2 million electron volts (2 M. E. V.) results in a fission of the thorium.

It is also known that the bombardment of thorium with neutrons having energies of below 1 million electron volts (1 M. E. V.) results in the production of $Pa^{233}$ and ultimately of $U^{233}$ through the prolonged decay of $Pa^{233}$, and further that $U^{233}$ so produced undergoes fission with neutrons of such low energies as below 1 million electron volts (1 M. E. V.) and even with thermal neutrons. The production of $U^{233}$ and/or $Pa^{233}$ is thus complicated by the fact that $Pa^{233}$ and/or $U^{233}$ produced by neutron bombardment may be decomposed by fission under the same bombardment.

In accordance with the present invention I have provided a method of preparing $Pa^{233}$ and $U^{233}$ in substantial amounts and in concentrated form generally as a composition wherein $Pa^{233}+U^{233}$ or the compounds thereof are the preponderant components of the composition and preferably as a composition containing not in excess of about 10 percent by weight of impurities. Further I have discovered that $U^{233}$ may be effectively prepared as a concentrate by separating $Pa^{233}$ from neutron irradiated thorium, preferably by means of adsorption and thereafter permitting the separated $Pa^{233}$ to decay to $U^{233}$. In addition I have found that effective concentrates of these materials may be secured by treatment of neutron irradiated thorium which has been subjected to high intensity irradiation for a time sufficient to produce $Pa^{233}+U^{233}$ in concentrations within a predetermined range.

The reaction of thorium with slow and moderately fast neutrons may be summarized as follows:

$$_{90}Th^{232} + {}_{0}n^{1} \longrightarrow {}_{90}Th^{233} + \text{gamma}$$

$$_{90}Th^{233} \xrightarrow[\text{half life}]{\text{23.5 min.}} {}_{91}Pa^{233} + B- \xrightarrow[\text{half life}]{\text{27.4 days}} {}_{92}U^{233} + B-$$

The fission products which are produced as a result of the fission of $U^{233}$ with slow and moderately fast neutrons appear to be the same as those produced by the fission of $U^{235}$. They consist of a large number of elements which generally fall into a light group with atomic numbers from 35 to 46, inclusive, and a heavy group with atomic numbers from 51 to 60, inclusive, and which undergo beta decay. The fission products



which have a half life of more than three days will remain in the reaction mass in substantial quantities at least one month after the termination of the reaction, and the removal or elimination of these products by my process is particularly advantageous. Among these products are: Sr, Y, Zr, Cb, Ru, Te, I, Xe, Cs, Ba, La, and Ce of a 20 day half life, and Ce of a 200 day half life.

This invention has for one object to provide a method for the preparation and separation of the elements $_{91}Pa^{233}$ and $_{92}U^{233}$ hereinafter referred to as $Pa^{233}$ and $U^{233}$.

Another object is to provide a method of ultimately preparing $U^{233}$ by procedure which involves the initial formation of $Pa^{233}$ and the treatment thereof.

Still another object is to provide a method particularly suitable for the segregation of $Pa^{233}$ from extraneous materials such as those materials present in neutron irradiated thorium.

Still another object is to provide a method for the segregation of $Pa^{233}$ by adsorption.

Still another object of the invention is to provide a method of separating adsorbed $Pa^{233}$ from the adsorption medium.

Another object is to provide a method of adsorption for treating solutions containing $Pa^{233}$ which employs certain resin adsorption materials.

Another object is to provide a method of separating $Pa^{233}$ from relatively crude or raw solutions containing this material by adsorption from the solutions.

Still another object is to provide a method of producing $U^{233}$ wherein $Pa^{233}$ is permitted to develop to $U^{233}$ which $U^{233}$ is later recovered.

Other objects will appear hereinafter.

In accordance with one embodiment of this invention, a mass of thorium is subjected to the action of neutrons, the majority of which have energies below 1 million electron volts, and the reaction of the neutrons with the thorium is terminated prior to the time when the neutrons are absorbed by the $U^{233}$ at the same rate that they are absorbed by the $Th^{232}$.

This limit is approximately when the weight ratio of $U^{233}$ to unreacted $Th^{232}$ is 1 to 100. In other words, the reaction of $Th^{232}$ with neutrons should preferably be terminated prior to the time when the amount of $U^{233}$ is approximately 1 percent of the amount of thorium present in the mass. When the reaction is terminated at or prior to this point there is also no danger during the reaction of a substantial decomposition of the $U^{233}$ taking place by a nuclear self-sustaining chain reaction.

It is generally desirable to terminate the reaction of the neutrons with $Th^{232}$ when the amount of $Pa^{233}+U^{233}$ is much less than 1 percent of the unreacted amount of $Th^{232}$ in order to reduce the amount of fission products and make it possible to isolate the $U^{233}$ by ordinary chemical means without the use of large quantities of special equipment such as refrigerating devices, radiation shields, special radiation resistant materials and the like. In order to reduce such special equipment to a minimum and at the same time have a practical amount of $Pa^{233}$ and $U^{233}$ for isolation by batch process, the reaction is terminated at a weight ratio of $U^{233}+Pa^{233}$ to $Th^{232}$ of not less than about 1 to 1 million and frequently between about 1 to 10,000, and 1 to 1,000.

The reaction of thorium, either in metallic state or as a compound such as an oxide or carbonate of thorium, with neutrons to produce $Pa^{233}$ and $U^{233}$ may be carried out with neutrons from any suitable neutron source. Where the neutron source provides fast neutrons, the fast neutrons are slowed to neutrons having energies of below 1 million electron volts by interposing neutron-

slowing (or moderating) material between the fast neutrons and the thorium. Such neutron slowing materials include carbon-containing, deuterium-containing, or hydrogen-containing materials such as graphite, paraffin, or deuterium oxide. Sufficient neutron slowing material is used so that at least a majority of the neutrons are slowed to energies of below about 1 million electron volts, since at higher energies there is relatively little production of $Pa^{233}$ and considerable fission of the thorium. I may interpose the neutron slowing material between the fast neutrons and the thorium-containing mass, or I may admix neutron slowing material with the thorium. An intimate mixture of thorium with neutron slowing material may be readily obtained by using hydrated thorium compounds such as $Th(OH)_4.xH_2O$. Since the slow neutron absorption cross section of thorium is some ten to forty times larger than that of hydrogen, I may suitably use a ratio as high as about two to four hydrogen atoms per thorium atom without losing any more than about 10 percent of the neutrons as a result of absorption by hydrogen.

While neutrons obtained from any suitable source of high neutron output may be used, it is desirable to subject the thorium to neutrons from a high intensity source in order that suitable concentrations of $Pa^{233}$ and $U^{233}$ may be obtained in a reasonable length of time.

Preferably the thorium is subjected to slow neutrons from a source of neutrons capable of supplying at least $5\times10^{17}$ neutrons per second to the thorium mass and where a relatively high concentration of $U^{233}+Pa^{233}$ is desired should weigh no more than about 20 tons. Preferably this mass should be of such a thickness that at least 50 percent and preferably 75 percent or more of the neutrons supplied are absorbed. Such high neutron intensity may be obtained by subjecting thorium to the action of neutrons obtained by slowing down secondary neutrons obtained from a self-sustaining chain reaction of $U^{233}$, $U^{235}$ or $94^{239}$ with neutrons.

By placing thorium adjacent to a neutron chain reacting mass comprising uranium and/or $94^{239}$ in amount sufficient to establish a self-sustaining neutron chain reaction, the thorium being dispersed in a neutron slowing medium such as carbon or $D_2O$, between $5\times10^{17}$ and $10^{20}$ neutrons per second are supplied to the thorium and at least 50 to 75 percent are absorbed so that a ratio of $U^{233}+Pa^{233}$ to $Th^{232}$ of more than 1 to 1 million may be attained in a reasonable length of time, such as one to three months. In such a case the degree of bombardment desired may be completed before the preponderant amount of $Pa^{233}$ formed has decayed to $U^{233}$.

The method of separation here involved is based upon the initial separation and recovery of $Pa^{233}$, followed by conversion of the $Pa^{233}$ to $U^{233}$ and the subsequent separation of these two elements.

I have found that separation may be accomplished by contacting a solution, in reduced condition, with a suitable adsorbent, such as Amberlite type resin (a phenol-formaldehyde resin containing free sulfonic acid groups), which adsorbs the $Pa^{233}$ after which the $Pa^{233}$ may be washed out (elutriated) from the resin. By reduced condition it is desired to indicate the absence of oxidizing materials in the solution, as oxidizing conditions may adversely affect the adsorbent. My process is broadly illustrated by the following:

A solution is prepared by dissolving a neutron bombarded thorium salt, as thorium carbonate, in nitric acid or other suitable solvent. Such materials contain the $Pa^{233}$ which it is desired to segregate. For example, a solution comprised of thorium nitrate in one normal nitric acid would be satisfactory. This solution would be in the reduced condition as above discussed, and may be subjected to preliminary decontamination by manganese dioxide carrier precipitate treatment in accordance with the detailed procedures described in my companion application, Ser. No. 572,052, filed January 9, 1945. The use of a preliminary decontamination is optional, as the resin. The coarser adsorbents give a more rapid flow factorily on raw or crude solutions.



The thorium nitrate solution containing $Pa^{233}$ is passed through a column containing at least about 1½ ft. of 60 to 200 mesh of suitable adsorbent, such as Amberlite resin. The coarser absorbents give a more rapid flow rate. The preferred adsorbent is a phenol formaldehyde condensation product containing sulphonic acid groups. The method of preparing the resin absorbent which will be referred to hereinafter is described in detail in other copending applications and is not part of the present invention. The $Pa^{233}$ in the thorium nitrate solution is adsorbed on the adsorbent along with a part of the thorium and nitric acid.

A part of the thorium nitrate passes out of the adsorption threatment and may be discarded to waste.

After the adsorption treatment has been completed, the adsorbent is washed with nitric acid or other suitable solvent which removes the thorium materials thereon. Thereafter, the acid or other solvent is washed out with a water wash.

After the adsorbent has been washed substantially free of nitric acid or other solvent, a solution such as a liquid .1 N in $NH_4F$, and/or containing HF, may be employed for washing (the elution) of the absorbed $Pa^{233}$ from the adsorbent. The resultant solution containing $Pa^{233}$ may be treated by the manganese dioxide method for further purifying the $Pa^{233}$, if desired, and allowed to stand for sufficient period until a part of the $Pa^{233}$ disintegrates to $U^{233}$. That is, during a period comprising about two half lives, about three-fourths transformation takes place. Various periods may be employed.

The solution containing $U^{233}$ along with the residual components from the transformation or disintegration may then be ether extracted as described in my companion application, Serial No. 572,052, filed January 9, 1945, to isolate $U^{233}$, or otherwise treated to recover $U^{233}$.

For a further understanding of certain features which have been referred to generally above, certain individual cycles are now considered in further detail.

The solution resulting from dissolving irradiated thorium material in nitric acid may be directly contacted with the adsorption material in accordance with the present invention. That is, the relatively raw or crude $Pa^{233}$ solutions may be immediately subjected to adsorption. Or the raw or crude solutions may be given preliminary treatments by manganese dioxide purification and other steps to eliminate part of the extraneous material prior to adsorption treatment. Likewise, treatments with manganese dioxide may be applied to the eluant containing $Pa^{233}$ removed in the adsorption treatment. In general, $Pa^{233}$ containing solutions may be subjected to manganese dioxide purification or comparable treatment either before or after the contacting of the $Pa^{233}$ containing solution with the adsorption medium.

In the process as generally outlined above, during the first step pertaining to dissolving the thorium materials in nitric acid, it is preferred to separate any precipitate which forms. The formation of precipitate at this point is dependent to some extent upon the initial characteristics of the thorium materials processed. In most plant processes, because of the impurities in the materials either inherently present or introduced during their preparation and fabrication, a precipitate will be present at this point and may require separation.

In the particular modification of my invention under description the thorium material irradiated was in the form of pellets. In forming these pellets a solution of stearic acid in acetone was used as a lubricant on the dies in which the pellets were compressed. Consequently, the pellets contained a thin film of stearic acid. When these pellets were dissolved in nitric acid, a scum due to the stearic acid was left in the solution. In processes where the thorium material has been fabricated by other

methods, of course, such specific type of precipitate may be absent.

In many instances, in dissolving the thorium material which has been irradiated, whether initially processed in pellets or not, a certain amount of flocculent precipitate may result. This precipitate is believed to be silica, presumably present in the ores or other materials from which the thorium was obtained.

Further investigation on methods for the removal of this siliceous precipitate, since its presence may have an adverse effect upon the filtration rates in the event preliminary manganese dioxide purification is applied, have been carried out. It has been found that heating of the nitric acid solutions in which the thorium material is dissolved brings down a substantial part of this siliceous precipitate which in turn can be removed by centrifugation or filtering prior to carrying out manganese dioxide purification.

These siliceous precipitates which are recovered, if it is expected that they contain any $Pa^{233}$, may be dissolved in hydrofluoric acid. The resultant solutions are evaporated down with nitric acid or sulphuric acid, in platinum containers or other fluoride-resistant evaporation equipment, to eliminate the hydrofluoric acid. The resultant nitric acid solution which contains any $Pa^{233}$ may be returned to the initial nitric acid solution from which the siliceous precipitate was separated.

In general, this siliceous precipitate may be largely removed by centrifuging at between 1800 and 3000 R. P. M. As a further safeguard, the centrifuged liquid may be filtered for substantially completely eliminating any siliceous material which has escaped separation by centrifuging.

In a typical run illustrating the aforementioned cycle about 20 aluminum cans containing 4,000 grams of irradiated thorium carbonate were dissolved. For removing the aluminum cans, 12% sodium hydroxide solution was used which dissolved the 380 grams of aluminum of the cans in less than two hours. Thereafter there was added 6.6 liters of 12 N nitric acid with occasional agitation. After about half an hour, heat was applied for about 2½ hours for maintaining the temperature within the range 95–105° C. Approximately 18 liters of water were added, together with further water for adjusting the volume to 24 liters, thereby making the solution one normal in nitric acid.

The siliceous precipitate which formed was separated by centrifuging at approximately 3,000 R. P. M. in an 8 inch stainless steel centrifuge bowl. The solution thus separated was filtered and collected in a receiver and was ready for manganese dioxide precipitation cycles.

In order to provide a more complete understanding of the manganese dioxide procedure for purification, this operation is now described in detail.

The thorium nitrate solution freed of siliceous precipitate is treated with a source of manganese ions such as a 50% manganese nitrate solution. About 47 cc. of such a solution of a specific gravity of 1.54 were added per liter of thorium nitrate solution. The solution was heated to boiling and kept at boiling during the period. About 255 cc. of a 5% potassium permanganate solution was added in three portions of 85 cc. per portion at ten minute intervals.

A manganese dioxide precipitate formed and this was separated by filtration. The precipitate was washed with a one normal nitric acid solution.

The precipitate was redissolved. A nitric acid-hydrogen peroxide solution made up of 37 cc. of 30% hydrogen peroxide and 134 cc. of 12 N nitric acid was the solvent used. Sufficient solvent is used to dissolve the precipitate, preferably avoiding the use of excess.

The peroxide reducing agent was included for the purpose of reducing the manganese dioxide to manganous nitrate. Hydrazine and hydroxylamine or other similar reducing agents may be used in place of the peroxide.



However, for simplified operation and ease in destruction of excess reducing agent, the use of the peroxide is preferred.

After the precipitate has been dissolved by repeated application of the solvent, the resultant solution is heated for about half an hour at 90° C. for removing excess peroxide. The solution is then ready for another manganese dioxide precipitation. The further manganese dioxide precipitations, of which there may be several, are carried out substantially the same as described using several additions of the permanganate. However, since the volumes are gradually being reduced, the quantities of precipitate obtained may be smaller. In general, it has been found that the normality of the solution should be about one normal in nitric acid. The potassium permanganate is added gradually, for example, in three portions at ten minute intervals. The solution is preferably heated near the boiling point for at least a half an hour. A manganese nitrate concentration of 20 grams or less per liter gives some improvement in filterability over higher concentrations. The presence of small amounts of materials such as sodium nitrate and aluminum nitrate, resulting from the dissolving of the aluminum cans, has no harmful effect.

The $Pa^{233}$ containing solutions either purified as above indicated or in the crude condition are brought into contact with an adsorption material.

Such chromatographic adsorption for the separation of substances present in a solution of neutron irradiated thorium may be carried out with a number of adsorbents, including both inorganic adsorbents such as silica gel, diatomaceous earth, or the like and organic adsorbents such as activated carbon, sulphonated carbonaceous material (zeo-carb), but preferably phenol-formaldehyde resins containing free sulphonic acid groups (IR–1 resins) are employed. Particularly advantageous results are obtained in the first portion of the process by the use of ion exchange adsorbents, in which the cation of the adsorbent is exchanged for a similarly charged ion of the substance to be adsorbed. It has been found that the process is particularly effective where the adsorbent used is a relatively inert organic material containing free sulphonic acid groups. Thus, the adsorbent may comprise phenol-formaldehyde resins, lignite, phenoltannic acid resins, or the like, which contain numerous $R—SO_3—R'$ groups, in which R is an organic group and in which R' is hydrogen or a metal ion, although R' is preferably $H^+$ or $Na^+$. A satisfactory adsorbent for use in an adsorption column is a phenol-formaldehyde condensation product containing such sulphonic acid groups. In the adsorption process, the hydrogen of the sulphonic acid group is replaced by a cation of the substance to be adsorbed which thereupon forms a more or less loosely associated molecule with the residue.

As an example of a method by which a sulphonated resin may be prepared, 175 parts of 1-hydroxybenzene-4-sulphonic acid are heated together with 40 parts of a formaldehyde solution of 30% strength for one-half hour to about 105° C. Then, 60 additional parts of formaldehyde are added and the temperature is kept for about ten hours at 90° C. A hard black resin is formed which is stable to water and of conchoidal fracture. This resin is washed with water and ground to a powder. By regeneration with an acid or a solution of common salt, this base-exchanging body regains its original adsorption capacity.

Examples of an adsorption method for separating $Pa^{233}$ from thorium are now described. One gm. Amberlite IR–1 resin was allowed to stand with occasional stirring in contact with 50 ml. of solution containing 300 gm. (irradiated) thorium nitrate per liter and 1 N in $HNO_3$ for one hour. The resin was then separated from the supernatant by centrifugation and the relative activities were determined by following the photoradiation with

an electroscope. About 50% of the $Pa^{233}$ activity had been adsorbed onto the resin.

Further experiments were carried out to obtain the rate of adsorption, with the following results being obtained:

| Time of contact: | Percent $Pa^{233}$ adsorbed |
|---|---|
| 5 min. | 41 |
| 15 min. | 53 |
| Overnight | 45 |

These data indicate that equilibrium is obtained in 5 minutes or less. Since these figures were obtained by holding the samples in question in a standard position near an electroscope, the difference between the 41% and 53% may be due to experimental error.

The elution of adsorbed $Pa^{233}$ was determined as follows:

1.6 gm. Amberlite IR–1 was allowed to stand overnight with 80 ml. of solution 1 N in $HNO^3$ and containing 300 gm. $Th(NO_3)_4.4H^2O$ per liter (this solution resulting from dissolving irradiated carbonate). The Amberlite, which was found to contain about 55% of the initial activity, was washed into a small column and washed with 1 N $HNO_3$, then with 2.5 N $HNO_3$ until it was nearly free of thorium. The nitric acid wash eluted only a small amount of $Pa^{233}$ (not more than 5%). After washing with distilled water, 30 ml. of 0.1 N $NH_4F$ were put through the column, whereby essentially all of the $Pa^{233}$ was eluted.

Other columns were constructed of diameters one and two cm. and about 50 cm. high. One to three liters of the "30%" $Th(NO_3)_4.4H_2O$ (i. e. 300 g. of the salt per liter) were put through these columns after siliceous precipitates had been removed from the solutions by centrifugation followed by filtration. About 70% of the $Pa^{233}$ was adsorbed by the columns under these conditions. After washing the adsorbent in the columns with dilute $HNO_3$ to remove thorium followed by a water wash to remove acid, the $Pa^{233}$ was removed by elution with about 200 ml. 0.1 M $NH_4F$. The $Pa^{233}$ was then removed from the fluoride solution with manganese hydroxide carrier precipitate and dissolved in nitric acid so that it could be subsequently "purified" with $MnO_2$ cycles of the type already described.

The runs indicated that the adsorption method for the extraction of $Pa^{233}$ from thorium solution was satisfactory.

The manganese nitrate solution containing $Pa^{233}$ resulting from the above-described treatments was permitted to stand behind shielding until a substantial portion thereof had decayed to $U^{233}$. Then an ether extraction in the presence of nitrate ions such as may be obtained by making the solution three to four molar in manganese nitrate was applied for removing the $U^{233}$ from extraneous material such as thorium nitrate, manganese nitrate, $Pa^{233}$ and other radioactive substances.

The ether extract containing $U^{233}$ which has been so segregated may then be subjected to any desired treatment for isolating the $U^{233}$ or obtaining derivatives thereof. For example, the $U^{233}$ may be stripped into water or further ether extraction may be applied. Or the $U^{233}$ may be precipitated by the ammonium uranate precipitation method, uranium peroxide precipitation, or precipitation with acridine hydrochloride and thiocyanates. Details relative to the latter method may be found in Mikrochemie, 25, 71 (1938) by A. Langer., page 12. The particular use to which the $U^{233}$ is put or the derivative thereof prepared is not a limitation on the present invention.

In the preceding description the use of nitric acid has been frequently indicated. This is a readily available common acid which is not as corrosive as certain other acids. However sulfuric acid, hydrochloric acid and the like may be used, dependent upon apparatus limitations. Similarly other changes may be made consistent with good industrial practice.



While $NH_4F$ has been described as an eluant and is preferred since this is a nearly neutral reagent, other agents may be used. For example, HF, metallic fluorides and fluosilicates may be used. In the event HF is used, due regard would be had for its etching action on glass and suitable changes would be made in the apparatus for handling such reagents.

It is 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.

I claim:

1. In the process of recovering protoactinium from an adsorbent, the step which comprises washing out the protoactinium with an eluant comprising a flouride.

2. In the process of recovering protoactinium from an absorbent, the step which comprises washing out the protoactinium with an eluant containing $NH_4F$.

3. A process for the recovery of protoactinium from an aqueous inorganic acid solution containing protoactinium cations, which comprises contacting said solution with a cation exchange adsorbent and thereafter eluting adsorbed protoactinium from said adsorbent by means of an eluant comprising an aqueous solution containing fluorine anions.

4. A process for the recovery of protoactinium from an aqueous nitric acid solution containing protoactinium cations, which comprises contacting said solution with a cation exchange phenol-formaldehyde resin containing sulfonic acid groups, and thereafter eluting adsorbed protoactinium from said resin by means of an eluant comprising an aqueous solution of ammonium fluoride.

5. A process for the separation of protoactinium and thorium from an aqueous inorganic acid solution containing protoactinium and thorium cations, which comprises contacting said solution with a cation exchange adsorbent, eluting adsorbed thorium from said adsorbent by means of an eluant comprising an aqueous inorganic acid, to remove residual acid, and thereafter eluting adsorbed protoactinium from said adsorbent by means of an eluant comprising an aqueous solution containing fluorine anions.

6. A process for the separation of protoactinium and thorium from an aqueous nitric acid solution containing protoactinium and thorium cations, which comprises contacting said solution with a cation exchange phenol-formaldehyde resin containing sulfonic acid groups, eluting adsorbed thorium from said resin by means of an eluant comprising aqueous nitric acid, washing said resin with water to remove residual nitric acid, and thereafter eluting adsorbed protoactinium from said resin by means of an eluant comprising an aqueous solution of ammonium fluoride.

7. In a process for the production of a uranium isotope from thorium which contains values of a beta-emitting protoactinium isotope, the improvement steps which comprise separating at least a part of the beta-emitting protoactinium isotope prior to its disintegration by contacting an aqueous nitric acid solution containing thorium values and values of sad protoactinium isotope with an adsorption material which will adsorb protoactinium values, treating the adsorption material with solvents to remove thorium and nitric acid, thereafter treating the adsorption material with an aqueous solution containing fluorine anions to remove the protoactinium values, permitting the solution containing the protoactinium values to decay to values of its daughter uranium isotope, and thereafter recovering at least a part of said uranium isotope.

8. The process for the production of a uranium isotope from a beta-emitting protoactinium isotope, which comprises separating at least a part of said protoactinium isotope prior to its disintegration by contacting an acidic aqueous solution containing values of said protoactinium

isotope with an adsorbent which will adsorb protoactinium values, washing the adsorbent with an acidic aqueous solution, thereafter treating the adsorbent with an aqueous solution containing fluorine anions to remove the values of said protoactinium isotope, permitting the solution containing the values of said protoactinium isotope to decay to its daughter uranium isotope, and thereafter recovering values of said uranium isotope.

9. The process for the production of a uranium isotope from a beta-emitting protoactinium isotope, which comprises subjecting said protoactinium isotope to preliminary purification, separating at least a part of said protoactinium isotope prior to its conversion to its daughter uranium isotope by contacting an aqueous inorganic acid solution containing values of said protoactinium isotope with an adsorbent which will adsorb protoactinium values, washing the adsorbent with an aqueous solution of an inorganic acid, removing values of said protoactinium isotope by elution with an aqueous solution containing fluoride ions, permitting the solution containing values of said protoactinium isotope to convert to values of its daughter uranium isotope, and thereafter recovering said values of said uranium isotope.

10. The process for the production of a uranium isotope from thorium which contains values of a beta-emitting protoactinium isotope, which comprises separating at least a part of said protoactinium isotope prior to its transformation to its daughter uranium isotope by contacting an aqueous nitric acid solution containing values of said protoactinium isotope and thorium values with a cation exchange resin adsorbent, washing the resin with aqueous nitric acid to remove thorium values, thereafter treating the resin with an aqueous solution of ammonium fluoride to remove said protoactinium values, permitting said protoactinium values to convert to values of the daughter uranium isotope, and thereafter recovering values of said uranium isotope.

11. In a process for preparing a uranium isotope from a beta-emitting protoactinium isotope, the step which comprises contacting an aqueous inorganic acid solution containing values of said protoactinium isotope with a cation exchange resin adsorbent which contains a number of $R—SO_3—R'$ groups in which R is an organic group and in which R′ is a replaceable metallic ion.

12. In a process for preparing a uranium isotope from a beta-emitting protactinium isotope, the step which comprises contacting an aqueous nitric acid solution containing values of said protoactinium isotope with a cation exchange phenol-formaldehyde resin.

13. In a process for preparing a uranium isotope from a beta-emitting protoactinium isotope, the step which comprises contacting for a period of contact greater than two minutes an aqueous nitric acid solution containing values of said protoactinium isotope with a cation exchange resin adsorbent which contains a number of $R—SO_3—R'$ groups in which R is an organic group and in which R′ is a replaceable metallic ion.

14. In a process for preparing a uranium isotope from thorium which contains values of a beta-emitting protoactinium isotope, the steps which comprise contacting an aqueous nitric acid solution containing values of said protoactinium isotopes and thorium values with a cation exchange resin adsorbent which contains a number of $R—SO_3—R'$ groups in which R is an organic group and in which R′ is a replaceable metallic ion, washing the adsorbent with an aqueous nitric acid solution to remove thorium values, washing the adsorbent with water to remove residual nitric acid, and thereafter eluting protoactinium values from said adsorbent with an eluant comprising an aqueous solution of ammonium fluoride.

15. A process which comprises subjecting material containing $Th^{232}$ to neutron bombardment to obtain a material containing $Pa^{233}$ values in which the ratio of protoactinium values to thorium is substantially less than one to a million, dissolving the bombarded thorium material containing the said protoactinium values in aqueous nitric acid and subjecting the resulting solution to contact with a cation exchange resin adsorbent.

**References Cited** in the file of this patent

Physical Review, vol. 57, p. 157, "The Nonexistence of Transuranic Elements," by Louis A. Turner.

Chemical Abstracts, vol. 36, 1942, p. 6893, by Hans Schindler.

# UNITED STATES PATENT OFFICE

# CERTIFICATE OF CORRECTION

October 14, 1958

Patent No. 2,856,262

Raymond W. Stoughton

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 7, strike out "and" before "Ce", first occurrence; column 4, lines 2 and 3, strike out ". The coarser adsorbents give a more rapid flow factorily" and insert instead -- adsorption step to be described will function satisfactorily --; line 17, for "threatment" read -- treatment --; line 42, for "solution" read -- solutions --; lines 42 and 43, for "throium" read -- thorium --; column 8, line 61, for "sad" read -- said --.

Signed and sealed this 17th day of February 1959.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

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