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PEROXIDE PROCESS FOR SEPARATION OF RADIOACTIVE MATERIALS

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The invention relates to the treatment of compositions containing element 94, and more particularly relates to the separation of element 94 from fission products and/or uranium by precipitating the element 94 in the form of its peroxide from solutions containing said products while maintaining foreign products in solution. The invention includes the new compound, the peroxide of element 94.

An object of the invention is to provide means for separating dangerous and harmful products from useful products in a neutron irradiated uranium mass.

A further object is to provide a mass containing element 94 which is particularly adapted for use as a source of atomic (nuclear) power.

Another object is to provide a mass containing element 94 which is substantially pure element 94.

Another object is to provide a new compound, the peroxide of element 94.

Other objects and advantages of this invention will become apparent as the following detailed description progresses.

In this specification and claims the name of the element, unless otherwise indicated, designates generically the element either in its free or combined states. The designation element 94 is used throughout this specification and claims to describe the element having an atomic number of 94. Element 94 is also referred to in this specification and will probably become known in the art as plutonium, symbol Pu. $_{94}Pu^{239}$ or Pu^{239} means the isotope of element 94 having a mass number of 239. Likewise element 93 means an element of atomic number of 93. Element 93 is also referred to as neptunium, symbol Np.

The fission products referred to in this specification are the large number of elements of lesser atomic number than uranium produced from the bombardment of uranium with neutrons. The reaction of neutrons with U^{235} results in a breakdown of its heavy nucleus into two fragments which undergo beta particle disintegration into chains of two groups. The reaction of slow neutrons with U^{235} may be exemplified as follows:

$$_{92}U^{235}+{}_{0}n^{1}\rightarrow {}_{36}Kr^{92}+{}_{56}Ba^{141}+3n^{1}+175 \text{ m. e. v.}$$

Two groups of elements are formed, a light group with atomic numbers from 35–44 and a heavy group with atomic numbers from 51–58. The fission products with which we are particularly concerned are those having a half life of more than three days since they remain in the reaction mass in substantial quantities at least one month after reaction. These products are chiefly Sr^{89}, Y (57 day half life), Zr, Cb, and Ru of the group of atomic numbers from 35–44; and Te^{127}, Te^{129}, I^{131}, Xe^{133}, Cs (many years half life), Ba (12 day half life), La^{140}, and Ce of 20 day and 200 day half lives from the group of atomic numbers from 51–58 incl.

In addition to the fission products in the neutron irradiated uranium mass there are also present transuranic

elements resulting from the reaction of neutrons of thermal or resonance energies with U^{238}. This reaction is:

$$_{92}U^{238}+{}_{0}n^{1}\longrightarrow {}_{92}U^{239}\xrightarrow{23\text{ min.}} {}_{93}Np^{239}+\beta^{-}$$

$$_{93}Np^{239}\xrightarrow{2.3\text{ d.}} {}_{94}Pu^{239}+\beta^{-}$$

The reaction is preferably carried out with neutrons of below the fast neutron stage, i. e. with neutrons of resonance or thermal energies. Since element 94 itself reacts with slow or fast neutrons the reaction of the uranium with the neutrons is terminated before all of the 94 is converted to fission products and preferably while a substantial amount of U^{235} remains in the mass.

The neutron irradiated uranium mass therefore contains element 94, element 93, fission products, uranium, and minor amounts of other elements such as UX_1 and UX_2. The foreign products which it is a particular object of this invention to separate from mixture with the 94 are the fission products because these products are toxic and deleteriously affect the utilization of the 94 as a source of power.

The uranium may also be removed to increase the concentration of 94 and this also may be done by the process of our invention.

The neptunium decays to plutonium with a half life of 2.3 days so that its separation from the plutonium is not so important.

The reaction of the uranium with neutrons may be carried out at such a slow rate of introduction of neutrons that a large proportion of the 93 decays to the 94 during the reaction, or the mass may be stored for several days after the reaction to obtain more 94, or the 93 and 94 may be separated together and the mixture stored before use so as to decrease the proportion of 93 and increase the 94.

The methods which we have developed for separating foreign products from mixture with element 94 are, in part, based on our discovery that compounds having peroxide oxygen will precipitate element 94 from solutions at certain ranges of pH, preferably in the presence of certain ions, while fission products, and if desired, uranium, may be maintained in the solution.

We have discovered that element 94 may be precipitated as a peroxide from solutions of such high acidity that no other elements present in solution with the 94 (with the exception of element 93) will be precipitated. However element 94 is ordinarily present in neutron irradiated uranium in very low concentration and in order to make an effective separation of element 94 from uranium and fission products present in such neutron irradiated uranium we precipitate the element 94 from solution of the neutron irradiated uranium as a peroxide in conjunction with a carrier such as thorium peroxide. In order to precipitate the thorium peroxide with the 94 peroxide the pH is maintained above about 2.0 since if the solution is of much greater acidity than this the thorium will not precipitate. After the precipitate of 94 with thorium is obtained the proportion of 94 to thorium may be increased by repeated reprecipitations each time reducing the amount of thorium carrier until a substantial proportion of 94 to thorium is attained. Then the 94 may be separated from the thorium by precipitating it with hydrogen peroxide from a solution of high acidity such as 3 N nitric acid solution at which acidity the thorium peroxide remains in solution.

Element 94 may be readily separated from certain of the elements present in neutron irradiated uranium without any particular regulation of the pH. A large number of the fission products including Ba, Sr, Cs, Cb, Te, Sb, and Mo do not form insoluble peroxides in acid or alkaline solutions so that a separation of such fission

products from 94 may be made by adding a peroxide to any solutions of neutron irradiated uranium.

However some of the most harmful fission products such as Zr, Y, La, and Ce form insoluble peroxides in alkaline, neutral or very slightly acid solutions. In order to remove a substantial proportion of these products the pH of solution should be maintained at a pH of below about 6 and where a carrier such as thorium peroxide is precipitated with the plutonium peroxide the pH is advantageously maintained at between 2 to 6. Preferably also small amounts of non-radioactive compounds of Zr, La, and Ce are added to hold back the precipitation of small amounts of fission products. These substances are referred to in this specification as "hold-back carriers."

If it is desired to prevent the complete precipitation of uranium with the 94 the pH is maintained at a pH of below about 2.5, although by the use of ions which form complexes with uranium such as sulfate, acetate and tartrate we may hold back the uranium precipitation more effectively and at higher pH values. Also by precipitating in alkaline solution, using sodium peroxide or any other alkaline peroxide as a precipitating agent, and preferably with thorium as a carrier, the uranium remains in solution as a peruranate while the thorium precipitates asa peroxide carrying down the 94. The fission products that come down partially or completely are La, Ce, Y, and Zr, while Ba, Sr, Cs, Cb, Te, Ru, Sb, Mo remain in solution. Further separation of 94 from the precipitated fission products can be carried out in several ways, such as an oxidation-reduction procedure and iodate precipitation.

Another variation is to carry out the separation at a pH of from 6–8 in the presence of ammonium acetate. The acetate radical forms a complex ion with uranium preventing its precipitation while the presence of ammonium ion permits the precipitation of thorium with peroxide in neutral solution. The same fission products as above indicated will partially precipitate.

Some results have been obtained in precipitating the peroxide of 93. Its peroxide seems to be more soluble in acid solutions than is 94 peroxide. At pH 4, using uranium peroxide as carrier, approximately ⅓ of the 93 precipitated, while at pH 2.8 a negligibly small amount came down. Thus the peroxide method may also be used for separating element 94 from 93 by maintaining the solution at a pH of between about 2 and 3 when carriers are present.

In precipitating element 94 as its peroxide without uranium it is often desirable to have thorium present as a carrier and precipitate the 94 with the thorium. The 94 may then be separated from the thorium in various ways such as, for example, by dissolving the precipitate in nitric acid, oxidizing the 94 to its fluoride soluble state, and precipitating the thorium with fluoride ion.

Our peroxide separation method may be classified into two main divisions; (1) the uranium precipitation method in which uranium is precipitated with the 94 and acts as a carrier for the 94, and (2) the uranium solution method (also called the thorium precipitation method) in which the uranium remains in solution and the 94 is precipitated by itself or with a carrier such as thorium.

Our experiments on the uranium precipitation method will first be described. We precipitated uranium as the hydrated peroxide from a dilute solution of neutron irradiated uranyl nitrate, the pH of the solutions being 2.5–3.5. The 94 precipitates almost quantitatively (greater than 85%) as plutonous peroxide. In the first experiments precipitation was carried out from very dilute solutions (0.5% to 2.5% uranyl nitrate hexahydrate) using a large excess of H_2O_2. About 15 to 20% of the fission activity of the sample appeared in the uranium peroxide and 94 peroxide precipitate.

In order to reduce the fission activity brought down the uranium peroxide and 94 we carried out some experiments using a hold back carrier, such as lanthanum

nitrate, or other soluble nonradioactive rare earth compounds. We also reprecipitated the uranium peroxide and 94 peroxide. Both operations reduced the amount of fission products in the precipitate containing the 94 and uranium. The addition of a small amount of lanthanum nitrate to the uranyl nitrate and 94 solution before hydrogen peroxide treatment cut down by the factor of 2 the amount of beta activity that precipitated with the uranium and the 94. A reprecipitation of the uranium peroxide and 94 reduced the precipitated fission activity by a factor of 2 to 4.

Further work was carried out to see if the amount of fission activity precipitating with uranium could be reduced by the following modifications: (1) addition of other hold-back carriers than La^{+++}, (2) avoiding large excess of H_2O_2, (3) reprecipitating the uranium peroxide. A ten percent solution of uranyl nitrate containing all of the long-lived fission products was precipitated with a small excess of H_2O_2 (40% excess) adjusting the solution to pH 3. Before addition of peroxide, small amounts of La, Ce and Zr were added as hold-back carriers. The uranium peroxide was centrifuged out and redissolved in a minimum amount of dilute HNO_3. The solution was readajusted to pH=3 with NH_4OH and the uranium peroxide again precipitated, hold-back carriers again being added. The uranium peroxide was dried and a small aliquot taken for beta-activity measurement. Only about 1% of the initial beta emitting fission activity was present in the reprecipitated uranium peroxide.

It was earlier shown that over 85% of the 94 will follow uranium through a reprecipitation. If the pH is allowed to drop too low, 94 will not carry well; while if a base is added too rapidly, local precipitation of uranates will occur carrying much fission activity.

The recovery of 94 from the mass of uranium can be accomplished in various ways. For example the uranium peroxide may be dissolved in alkaline solution through a formation of soluble peroxy-uranates, leaving the insoluble 94 peroxide. An alternate procedure is to dissolve the uranium with HF leaving the 94 behind. (The 94 in the peroxide method is present in its reduced or plutonous state in which it is insoluble in the presence of fluoride ion.)

Our experiments on the uranium solution method, sometimes called the thorium precipitation method since thorium is generally used as a carrier, will next be described. It is to be remembered in connection with these experiments that they were carried out with small proportions of 94 and that with larger amounts the thorium may be omitted entirely, although in general it is used for the first precipitation and then decreased in amount and finally omitted in the reprecipitations.

The theory behind this method is that thorium acts more like reduced 94 than does uranyl uranium and therefore thorium peroxide crystals have a better chance of being isomorphous with 94 peroxide. As a result, thorium is a better carrier than is uranium. There are also several more concrete advantages in this method over the precipitation of all of the uranium, and these will be enumerated presently.

In principle, one might expect to add thorium nitrate to a uranyl nitrate solution containing 94 and fission products, add H_2O_2 and under ideal conditions precipitate only 94 with thorium peroxide, leaving all of the uranium and fission products in solution. Experiments to be described below show that under carefully controlled conditions this ideal situation is closely approached. However, in order to illustrate the properties of thorium peroxide, other successful experiments will be described also.

One means of precipitating thorium peroxide in the presence of uranium is to carry out the precipitation in 0.2 to 0.5 N acid solutions. Unless a very great excess of H_2O_2 is added, little uranium precipitates as peroxide under these conditions. Tests were carried out with 94

and fission activity added. It was found that although the fission activity remained almost quantitatively in solution (~99%), the yields of 94 in the precipitates were poor. For example, in 0.2 N acid only ~30% of the 94 appeared in the thorium peroxide precipitate while the corresponding figure was ~20% from a 0.37 N acid solution. In less acid solutions, the precipitation of 94 was more complete. In one experiment carried out in 0.1 N HNO_3, ~60% of the 94 accompanied the thorium and in another solution 0.05 N in acid, the yield was ~80%. The precipitates in the latter cases contained, in addition, an estimated 10 to 20% of the uranium. This uranium peroxide can be readily eliminated in a further step by dissolving it in NaOH in the presence of excess H_2O_2. The fission activity that comes down in the above precipitation procedure (0.05 N acid) is not too serious, namely 1 to 1.5% of the total. No hold-back carriers were used, and the precipitation was carried out from a 2.5% uranyl nitrate hexahydrate solution.

If the precipitation were to be carried out at still higher pH, not only does the bulk of the uranium precipitate, but thorium fails to come down. This behavior of thorium in precipitating from dilute acid solution but not in neutral or slightly acid solutions is well-known. Therefore, it is necessary to carry out the reaction at some borderline acidity such as 0.05 to 0.1 N, in which case a partial precipitation of uranium results. Further experiments showed that the best result that can be expected with certainty is about a 60% removal of 94. Since the conditions to be maintained are rather exacting, it was decided to look for a method in which conditions are less critical.

It was found that thorium will precipitate from neutral or slightly acid solutions in the presence of ammonium ion. The principle of the procedure to be described couples this property with the fact that uranium can be maintained in peroxide solutions through complex ion formation with various anions. Among these negative ions are fluoride, sulfate, acetate and tartrate. The addition of a salt such as NH_4F would thus aid the precipitation of thorium and at the same time prevent the precipitation of uranium. Ammonium acetate worked very well at pH 7, effecting a quantitative yield of 94 (~90%) but at this pH approximately 50% of the fission products came down with the thorium peroxide. This would naturally follow, since zirconium and rare earth peroxides are insoluble in neutral or alkaline solutions. If the pH was brought down to ~3, uranium precipitated apparently due to the presence of free acetic acid and H_2O_2.

The best results obtained in our discoveries were from $(NH_4)_2SO_4$ solution. The most unsatisfactory condition in this procedure is that precipitation must be carried out from very dilute uranyl nitrate solution. It was found that the concentration of uranyl nitrate hexahydrate must be less than 2%, otherwise thorium and part of the 94 would not precipitate. Below this critical concentration the precipitation has been quantitative.

The composition of the solution from which thorium peroxide was precipitated was as follows:

0.5–2.0 M $(NH_4)_2SO_4$
<2% $UO_2(NO_3)_2.6H_2O$
.01–.02% Th^{+4}
.3% H_2O_2

The resulting solution was at pH=2.8. This solution was heated for a few minutes, after which the thorium peroxide precipitated. Analysis showed that ~90% of the 94 could be isolated in this manner, indicating a practically quantitative precipitation. Less than 1% of the uranium came down with the thorium peroxide.

The fission products can be effectively held in solution by the addition of small amounts of hold-back carriers such as Zr, La and Ce. When this is done, less than 1% of the beta emitting fission activity appears in the washed thorium peroxide. If the hold-back carriers are not added, 9 to 12% of the fission β-activity and a larger amount of the γ-activity comes down with the thorium.

Aside from the large volumes of solution that will be necessary to handle uranium on the ton scale, this last procedure appears to be quite satisfactory as a commercial method. One other point to be remembered, however, is that barium might be produced in high enough concentrations through fission to exceed the solubility product of $BaSO_4$. Another way in which fission barium would precipitate is if a sulfate insoluble impurity should be present in any of the reagents added. Should barium sulfate precipitate with the thorium peroxide, the thorium and 94 could be quickly dissolved in acid before appreciable amounts of the 44-hour gamma-emitting lanthanum daughter of barium have grown.

The following is an example of large scale practice of the uranium precipitation process.

133 gallons of stock uranyl nitrate solution (60% $UO_2(NO_3)_2.6H_2O$) containing 94 fission products is run into a 1500-gallon tank and diluted to 1350 gallons. To this solution is added:

10 lbs. lanthanum nitrate
10 lbs. cerium nitrate
10 lbs. zirconium nitrate

H_2O_2 is then added in a sufficient amount to precipitate all of the uranium. However, acid is liberated in the reaction so that ammonium hydroxide must be added at the same time in sufficient quantity to maintain the pH between 2 and 3. The theoretical amount of 30% H_2O_2 necessary to precipitate ⅓ T. of uranium is 300 lbs. or ~115 gal.

The solution is digested for 10–15 minutes at near boiling temperature. The precipitate is allowed to settle for about one hour, after which the supernatant fluid is pumped off. The precipitate is then washed with about 300 gallons of ~1% H_2O_2 and again, after settling, the supernatant liquid is pumped off.

The next step is to reprecipitate the uranium peroxide. This can be done by heating with about 500 gallons of 2 N HNO_3. The pH is then adjusted with sodium hydroxide or ammonium hydroxide to pH 3 and hydrogen peroxide and ammonium again added as in the first precipitation. The precipitate is again digested and allowed to settle and the supernatant fluid pumped off. The supernatant fluid from the first peroxide precipitation contains 80–85% of the fission activity and little else. That from the second precipitation contains 15–20% of the total fission activity.

The precipitated uranium peroxide, containing approximately 1% of the fission activity and all of the 94, can be handled in any of several ways. One method is to add a considerable amount of rare earth, say 25 lbs., mix well with a slurry of the uranium peroxide and treat with HF. This will dissolve the uranium peroxide, leaving a precipitate of rare earth-94 fluoride. Another method is to add excess H_2O_2 and 10–20 lbs. of thorium, mix well as a slurry, and add enough sodium hydroxide to make the solution approximately 1 N. The uranium peroxide will go into solution as a sodium peruranate, leaving Th and 94 peroxides as a precipitate. The solution would then be centrifuged and the thorium and 94 peroxides may then be readily separated. The alkaline uranium solution may be pumped into a tank and brought to neutrality, precipitating uranium peroxide. The uranium peroxide may be advantageously subjected to neutrons to produce more plutonium.

The following is an example of large scale practice of the thorium precipitation process.

The principle behind the process described below is that thorium can be precipitated as the peroxide at about pH 3 in the presence of NH_4, and in addition, uranium can be prevented from precipitation if sulfate ion is present. The 94 precipitates with the thorium peroxide under these conditions.

Starting with a stock solution of uranyl nitrate (30% uranium) containing 94 and fission products 133 gallons is pumped into a 10,000-gallon tank. This is equivalent to ⅓ ton of uranium. The concentrated solution is then diluted to a volume such that the resulting solution is 1% uranium. The final volume is about 8,000 gal. To the 8,000 gallons of solution is added the following:

10–20 lbs. thorium nitrate
5 lbs. lanthanum nitrate
5 lbs. cerium nitrate
5 lbs. zirconium nitrate
4000 lbs. $(NH_4)_2SO_4$

The amount of $(NH_4)_2SO_4$ specified here is such as to make a 0.5 M solution. To this solution is then added about 80–160 gallons of 30% H_2O_2 after which it would be brought to near boiling for a short time, say 10 minutes. This heating process is used to bring the thorium peroxide down quantitatively. The above-mentioned amount of H_2O_2 is probably a minimum figure. It is advisable to add two or three times this amount. The reason for this is that the presence of Zr and rare earths partially prevents the precipitation of Th at the above-specified H_2O_2 concentration, but the addition of more H_2O_2 will bring down the thorium peroxide almost quantitatively.

Under these conditions, we have a large volume of solution with approximately 10–20 lbs. of thorium as peroxide, and perhaps a similar amount of uranium peroxide in suspension. The whole solution is then run through a centrifuge and the thorium and uranium peroxides are removed. This small amount of material contains 1% or less of the total fission activity. This allows almost immediate laboratory scale handling for the further isolation of the 94.

The supernatant liquid from the thorium peroxide precipitation contains practically all of the uranium, all of the fission products and ammonium sulphate. This may then be run into a concrete tank to which is added NH_4OH. This precipitates all of the uranium and about 90% of the fission products. The amount of NH_4OH added could be just enough to precipitate the uranium. This is allowed to settle, the pH of the ammonium sulphate brought back to 3, and this may be recycled into the 10,000-gallon tank where it would add $(NH_4)_2SO_4$ as well as the necessary water for dilution.

While there have been described certain embodiments of this invention it is to be understood that it is capable of many modifications. Changes, therefore, may be made without departing from the spirit and scope of the invention as described in the appended claims in which it is the intention to claim all novelty inherent in the invention as broadly as possible, in view of the prior art.

We claim:

1. The method of separating plutonium in a valence state not greater than +4 from uranium in the uranyl state which comprises precipitating plutonium by means of a peroxide from a solution having a pH not greater than 7 and containing said elements in the presence of an anion selected from the group consisting of sulfate, acetate, and tartrate which forms a complex ion with uranium which prevents its precipitation.

2. In the method of separating plutonium from fission products and uranium in the uranyl state in a solution containing said products and plutonium in a valence state not greater than +4, the step which comprises adding to the solution a soluble thorium compound, ammonium ion, and an anion selected from the group consisting of sulfate, acetate, and tartrate which forms a complex ion with uranium but which does not precipitate rare earth compounds from acid solution.

3. The process of claim 1 wherein the complexing ion is sulfate ion.

4. The process of claim 1 wherein the complexing ion is acetate ion.

5. The process of claim 2 wherein the anion of a type which forms a complex ion with uranium is sulfate anion.

6. The method of separating plutonium from uranium which comprises forming an aqueous acidic solution containing ions of uranium and of plutonium, treating the uranium ions contained in said solution with sulfate ions whereby soluble complex uranium sulfate ions are formed, treating said solution with a soluble thorium compound and a soluble peroxide compound whereby a thorium peroxide plutonium carrier precipitate is formed, and separating said plutonium-containing thorium peroxide precipitate from the solution.

7. The process of separating plutonium in the reduced state from uranium which comprises forming an aqueous solution containing said constituents, wherein the uranium is present as uranyl nitrate hexahydrate in a concentration less than 2% by weight, treating the solution in the presence of ammonium ions and sulfate ions with a soluble thorium compound and hydrogen peroxide while maintaining the acidity of the solution at a pH of between 2 and 3, whereby a thorium peroxide plutonium-containing precipitate is formed, and separating said precipitate from the uranium-containing solution.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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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 3, line 73, after "down" insert -- with --; column 6, line 19, after "containing 94" insert -- and --.

Signed and sealed this 9th day of June 1959.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents