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2,882,125

VOLATILE FLUORIDE PROCESS FOR SEPARATING PLUTONIUM FROM OTHER MATERIALS

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Our invention relates to the treatment of compositions containing element 94, and more particularly relates to dry reaction and volatilization methods for separating element 94 and foreign products, such as fission products and uranium, from each other.

In this specification and claims the name of the element, unless otherwise indicated, designates generically the element 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 94. Element 94 is also referred to in this specification and claims as plutonium, symbol Pu, since it has become known in the art by such name and symbol. ${}_{94}\text{Pu}^{239}$ or Pu^{239} has reference to the isotope of element 94 which has a mass number of 239. Likewise "element 93" means an element of atomic number 93. Element 93 is also referred to in the specification and claims as neptunium, symbol Np.

One object of this invention is to provide simplified means for obtaining element 94 in more concentrated form than it is present in neutron-irradiated uranium.

Another object of the invention is to provide simplified means for separating useful products from dangerous and harmful products found in neutron-irradiated uranium.

Still another object of the invention is to provide a novel fluorination process for obtaining substantially pure element 94.

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

The fission products referred to in this specification are the large number of elements having lesser atomic numbers than uranium, and these fission products are produced by 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:



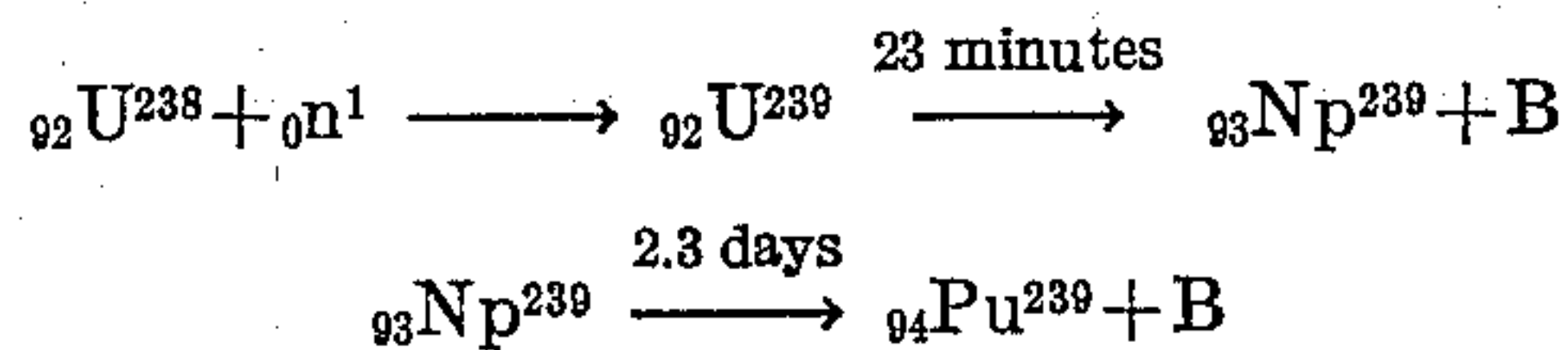
Two groups of elements are thus formed, a light group predominately including elements with atomic numbers from 35 to 44 and a heavy group predominantly including elements with atomic numbers from 51 to 58.

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 for at least one month after their formation. These products are chiefly Sr^{89} ; Y (57-day half life); Zr, Cb and Ru of the atomic numbers from 35 to 44; Te^{127} ; Te^{129} ; I^{131} ; Xe^{133} ; Cs (many-year half life); Ba (12-day half life); La^{140} and Ce of 20-day and 200-day half lives from the group having atomic numbers from 51 to 58 inclusive.

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

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ments present. The transuranic elements are formed by the reaction of neutrons having thermal or resonance energies with U^{238} . This reaction may be exemplified as follows:



The reaction exemplified above is preferably carried out with slow neutrons, i.e. with neutrons having thermal or resonance energies. Since element 94 itself reacts with both slow and fast neutrons, the reaction is terminated after a portion usually less than one percent of the U^{238} has been converted to the 239 isotope.

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 . It is a particular object of this invention to separate element 94 from the fission products of the mixture, since the fission products are toxic and deleteriously affect the utilization of element 94 as a source of power. The uranium may also be removed from the mixture to increase the concentration of element 94 and this, too, may be accomplished by the process of our invention. The concentration of plutonium present may vary quite widely and may be as low as one or several parts per million parts of uranium or may be as much as one percent by weight of the uranium depending upon the degree of bombardment to which the uranium has been subjected. The concentration of fission products in general is about equal to that of the plutonium.

The neptunium present in the mixture decays to plutonium with a half-life of 2.3 days, so that its separation from the plutonium is not so important. However, it is possible to separate the plutonium and neptunium in accordance with the method to be described herein.

The reaction of the uranium with neutrons may be carried out over a period of time such that a large proportion of the element 93 will decay largely to element 94 during the time the reaction is being carried out or else, the neutron-irradiated mass may be stored for several days after the reaction in order to obtain more of element 94, or, the elements 93 and 94 may be removed together and the mixture then stored before use so as to decrease the amount of element 93 and increase the proportion of element 94 in the mixture.

This invention is concerned with the separation of plutonium from uranium and/or fission products by formation of the higher fluorides of uranium and/or plutonium. By reason of the difference in formation and/or volatility of these fluorides we are able to separate plutonium from uranium. Also, because of the difference in volatility of the various other foreign products such as fission products and neptunium as compared to the volatility of plutonium fluorides we can separate these products from the plutonium and thus obtain substantially pure plutonium.

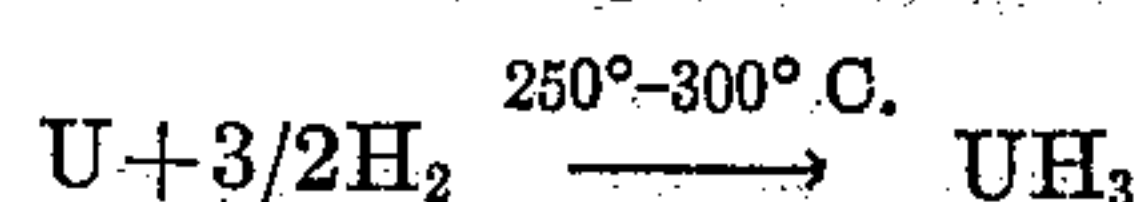
In accordance with the invention neutron-irradiated uranium preferably in metallic state and containing substantial plutonium is converted to the corresponding hydride and thereafter the hydride is converted to the fluoride under conditions such that a separation of the fluoride of the uranium, plutonium and various fission products may be secured.

Thus the hydride may be treated with HF to form uranium tetrafluoride, plutonium tri- or tetrafluoride and fluoride of fission products. This reaction product may be subjected to the action of fluorine, at an elevated temperature below about 315°C . to form and volatilize UF_6 leaving plutonium behind. The plutonium may then

be volatilized as a volatile fluoride which may be PuF_5 and/or PuF_6 by reaction of the residue with fluorine at a temperature of about 500°C .

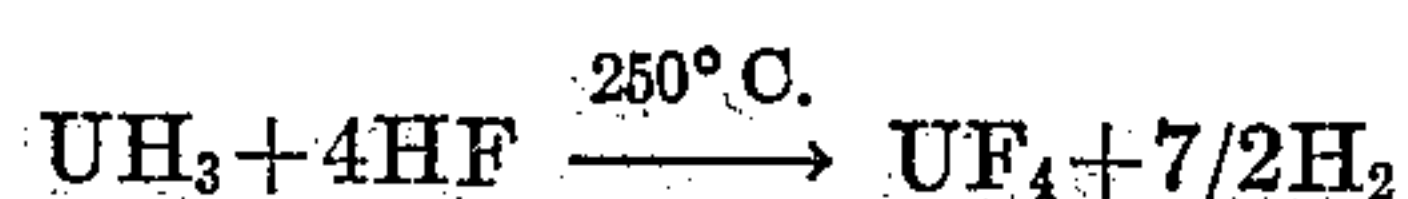
Alternatively the hydrided product may be converted to the tetra- or similar lower fluoride with HF as before and the product subjected to fluorination with elemental fluorine at about 500°C . whereby both uranium and plutonium are volatilized as volatile fluoride. The resulting vapor mixture may be treated to selectively condense the several fluorides, or the entire mixture may be condensed and fractioned to separate the plutonium from other fluorides.

In accordance with a suitable method of performing the invention, neutron-irradiated uranium in metallic state is placed in a reactor chamber, the chamber swept with an inert gas such as nitrogen to remove oxygen and the system evacuated. Hydrogen at any convenient pressure, for example, atmospheric pressure, is introduced into the chamber and the temperature raised to about $225\text{--}450^\circ\text{C}$. The reaction with the hydrogen gas is allowed to proceed until the uranium metal is converted to uranium hydride according to the following reaction:



Specific details of a process for producing the hydride by reaction of hydrogen or a hydrocarbon gas is described and claimed in co-pending applications of Amos S. Newton, Serial No. 546,178, filed July 22, 1944, and granted on August 10, 1948, as U.S. Patent No. 2,446,780, and J. C. Warf, Serial No. 595,181, filed May 22, 1945, and granted on January 2, 1951, as U.S. Patent No. 2,536,616.

Following the hydriding operation the hydride is converted to tetrafluoride. This may be accomplished in accordance with the process described and claimed in an application of Amos S. Newton and Oliver Johnson, Serial No. 578,538, filed February 17, 1945, and matured into Patent No. 2,534,677 on December 19, 1950. In such a process hydrogen fluoride is passed over the uranium hydride at a suitable elevated temperature such as 250°C . for example, although temperatures between 250° and 400°C . may be used thereby converting the uranium hydride to uranium fluoride according to the following reaction:



The excess hydrogen fluoride may be condensed out at the exit of the reaction chamber, and since it is still anhydrous it may be recirculated through the system thus utilizing large excesses of hydrogen fluoride. The hydrogen fluoride treatment just described converts the uranium, plutonium, neptunium and any fission products which are capable of conversion, to their fluorides. During the course of the above-described hydriding and fluorinating operations certain of the fission products which are either volatile in themselves, such as for example Kr, Xe, Br, and I, or which form volatile fluorides, such as for example Cb, Sb, 43 and Ru, are volatilized away and thus removed from the remaining mixture which contains element 94.

The remaining mixture is then treated with fluorine under conditions such as to secure a separation of fluorides. For example, the fluorinated product may be treated to selectively remove uranium as UF_6 leaving plutonium as a residue as described and claimed in an application of Glenn T. Seaborg and Harrison S. Brown, Serial No. 474,063, filed January 30, 1943, and granted on May 6, 1958, as U.S. Patent No. 2,833,617. In such a case the fluorinated product is treated with elemental fluorine at about 140°C . to 315°C . whereby the uranium and neptunium lower fluorides are converted to their higher fluorides and quickly and completely volatilize away from the plutonium and the less volatile fission products. In this case the plutonium remains quantita-

tively behind along with a portion of the fission products, and from the experimental evidence which we have obtained it is believed that it remains behind substantially or entirely in the form of its lower fluoride. The rate of reaction of fluorine with plutonium tetrafluoride is evidently nearly negligible at temperatures at or below 315°C ., so that within a period of several hours no appreciable amount of the higher fluoride is formed at this temperature. In any event, practically no plutonium volatilizes over with the uranium and neptunium.

After removal of the uranium and neptunium together with some portion of the fission products, the fluorination is then continued at a temperature above about 315°C . whereupon the conversion of the plutonium lower fluoride to its higher fluoride becomes appreciable and the plutonium higher fluoride volatilizes. It is generally preferred to increase the temperature, while carrying on this fluorination, to about 500°C ., for at this temperature all of the plutonium distills from the residue. The residue consists mainly of the fluorides of Rb, Sr, Ba, La, Ce and Cs while the distillate consists substantially of pure plutonium higher fluoride.

The following is an example of a method of separation which illustrates this invention, it being understood that this example is given only for purposes of illustration and that it is not intended to limit the invention to the details given in the experiment.

A quantity of massive uranium metal was irradiated with neutrons to obtain uranium metal which contained elements 93 and 94 and fission products all in small concentrations while the major portion of the uranium remained unconverted. The neutron-irradiated uranium was then placed in a reaction chamber, the chamber was evacuated, and the temperature of the neutron-irradiated uranium was raised to approximately 250°C . Gaseous hydrogen at atmospheric pressure was admitted to the reaction chamber in a continuous stream for about two hours at the end of which time the uranium metal was disintegrated and conversion to finely divided uranium hydride was substantially complete.

After the hydride was formed, hydrogen fluoride was passed through the reaction chamber while the temperature was maintained at 250°C . Two to three hours were required for the formation of UF_4 . The course of this reaction was followed by measuring the volume of H_2 evolved. The reaction was apparently over in two hours, but the current of hydrogen fluoride was allowed to run for three hours to assure complete reaction. The excess hydrogen fluoride was condensed out at the exit of the reaction chamber, and, since it was still anhydrous, it was recirculated through the system. During the course of this hydrogen fluoride treatment the uranium, plutonium, neptunium and any fission products capable of conversion were converted to their fluorides. During the course of the above treatments volatile fission products as such or in the form of their fluorides, such as Kr, Xe, Br, I, Cb, Zr, Sb, 43 and Ru, were volatilized away and thus removed from the remaining mixture which contained element 94.

The remaining mixture was then subjected to the action of elemental fluorine at a temperature of about 300°C . for half an hour whereby the uranium and neptunium lower fluorides were converted to their higher fluorides and quickly and completely volatilized away from the plutonium and the less volatile fission products. It was also found that the fission product Mo was volatilized away as a fluoride at this time. In all cases the element 93 volatilized with the uranium. The plutonium remained substantially quantitatively behind along with a portion of the fission products.

The fluorination with elemental fluorine was then continued while the temperature was raised to 500°C . in order to distill the plutonium from the residue. It was found that all of the plutonium was distilled over at 500°C . probably as plutonium higher fluoride.

In accordance with a further modification the neutron-irradiated uranium, after treating with hydrogen to form hydride and fluorination to form lower fluoride, may be treated to vaporize uranium and plutonium together. For example, the fluorinated mass containing uranium, plutonium, etc., may be subjected to fluorine at 500° C. forming and volatilizing off UF₆ and sweeping out plutonium probably as a higher fluoride. The resulting vapor may then be condensed under a pressure of 40 pounds per square inch at 75° C. to collect UF₆ in liquid state. This liquid may then be separated into its component fluorides by distilling low-boiling fluorides (Mo and Te) in a column at total reflux. Thereafter UF₆ may be removed by distillation at a low reflux ratio, and the plutonium may then be recovered in the remaining residue.

The term "plutonium lower fluoride" designates a fluoride of element 94 in which element 94 has a valence or oxidation number not greater than +4. Plutonium trifluoride (PuF₃) and plutonium tetrafluoride (PuF₄) are plutonium lower fluorides. The best evidence available shows that the plutonium lower fluoride produced by the process described above is the compound plutonium tetrafluoride (PuF₄). The term "plutonium higher fluoride" designates a fluoride of element 94 in which element 94 has a valence or oxidation number greater than +4. The higher fluoride produced by the process described above is a volatile plutonium fluoride having a valence greater than +4. Plutonium pentafluoride (PuF₅) and plutonium hexafluoride (PuF₆) are plutonium higher fluorides which are produced.

While there have been described certain embodiments of our invention, it is to be understood that it is capable of many modifications. Various changes and modifications may therefore be made without departing from the spirit of our invention or the scope of the appended claims.

Having thus described our invention what we claim and desire to secure by Letters Patent is:

1. A process of separating plutonium values from a metal mixture containing at least one of the values selected from the group consisting of uranium values, neptunium values and fission product values, comprising contacting said metal mixture with hydrogen gas at a temperature of between 225 and 450° C. under the exclusion of air, whereby uranium hydride is formed; contacting the mixture with hydrogen fluoride gas at a temperature of between 250 and 400° C. whereby uranium tetrafluoride, a lower fluoride of plutonium having a maximum valence of +4, neptunium lower fluoride and fission product fluorides are formed and some fission

products and fission product fluorides are volatilized; heating said mixture to 500° C. and contacting it with fluorine gas whereby uranium hexafluoride, neptunium higher fluoride and plutonium higher fluoride are formed and volatilized away from fission product fluorides; and separating said plutonium higher fluoride from the neptunium and uranium fluorides.

2. The process of claim 1 wherein the plutonium higher fluoride, uranium hexafluoride and neptunium higher fluoride are condensed and the plutonium higher fluoride is then isolated by distilling off the neptunium and uranium fluorides.

3. The process of claim 1 wherein hydriding is carried out under vacuum and the hydrogen fluoride is dry hydrogen fluoride.

4. The process of claim 1 wherein fluorination with fluorine is carried out in two steps, said first step being restricted to a temperature of between 140 and 315° C., whereby uranium hexafluoride and neptunium higher fluoride are formed and volatilized, and said second fluorination step being carried out at about 500° C., whereby plutonium higher fluoride is formed from the plutonium lower fluoride and volatilized.

5. The process of claim 4 wherein hydriding is carried out at a temperature of about 250° C. and atmospheric pressure, reacting with hydrogen fluoride is effected at 250° C., and said first fluorine-reaction step is carried out at about 300° C.

6. A process of producing plutonium higher fluoride of a high degree of purity comprising bombarding uranium metal with neutrons whereby a mixture of uranium, plutonium, neptunium and fission products is obtained; reacting said mixture with hydrogen gas at a temperature of between 225 and 450° C. under the exclusion of air, whereby uranium hydride is formed; contacting the mixture with hydrogen fluoride gas at a temperature of between 250 and 400° C. whereby uranium tetrafluoride, a lower fluoride of plutonium having a maximum valence of +4, neptunium lower fluoride and fission product fluorides are formed and some fission products and fission product fluorides are volatilized; heating said mixture to between 140 and 315° C. whereby uranium hexafluoride and neptunium higher fluoride are formed and volatilized; and contacting said mixture with fluorine gas at about 500° C. whereby plutonium higher fluoride is formed and volatilized away from fission product fluorides.

References Cited in the file of this patent

UNITED STATES PATENTS

2,534,677 Newton et al. ----- Dec. 19, 1950