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FLUORINE PROCESS FOR SEPARATION OF MATERIALS

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

An object of the invention is to provide means for obtaining element 94 in a more concentrated form than it is present in neutron irradiated uranium.

Another 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 power.

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

Another object is to provide a new and useful compound, the higher fluoride 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:

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

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 atomic numbers from 35–44; and Te^{127}, Te^{129}, I^{131}, Xe^{133}, Cs (many year half life), Ba (12 day half life), La^{140}, and Ce of 20 days 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 uranium 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 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, but in accordance with the method to be described herein the separation is effected.

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 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.

This invention is based mainly on the difference in formation and volatility of the higher fluorides of uranium and plutonium. From this difference in formation and volatility we are enabled to separate plutonium from uranium, and from the difference in volatility of various other foreign products such as fission products and neptunium as compared to the volatility of the plutonium fluorides we can separate these products from plutonium and obtain a mass of substantially pure plutonium or a mass of plutonium containing or free from, as is desired, uranium, fission products and neptunium.

In accordance with one embodiment of this invention uranium metal, carbide, oxides, oxyfluorides, oxychlorides, chlorides, or other compounds of uranium capable of reacting with hydrogen fluoride to form uranium tetrafluoride, are irradiated with neutrons to obtain element 93, element 94 and fission products, and the reaction terminated while a substantial proportion of uranium remains unconverted. The mass is then treated with hydrogen fluoride at an elevated temperature of, for example, 500° C. to convert the uranium, plutonium, neptunium to their lower fluorides, and also convert any fission products which are capable of conversion to their fluorides. During this treatment volatile fission products such as Kr, Xe, Br, I, Cb, Zr, Sb, 43, and Ru are volatilized away and thus removed from mixture with element 94.

The remaining mixture is then treated with fluorine at between 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 less volatile fission products. The plutonium remains quantitatively behind with a portion of the fission products, and from experimental evidence which we have obtained it is believed that it remains behind mainly or entirely in the form of its lower fluoride. The rate of reaction of

fluorine with plutonium tetrafluoride is evidently practically negligible so that in a period of less than several hours no appreciable amount of the higher fluoride is formed. Also, the boiling point of the plutonium higher fluoride is higher than that of the uranium higher fluoride so that in any event practically no plutonium volatilizes over with the uranium and neptunium.

The fluorination is then continued at a temperature of above about 315° C. whereupon the conversion of the plutonium lower fluoride to its higher fluoride becomes appreciable and the higher fluoride volatilizes. It is generally preferred to increase the temperature while fluorinating to about 500° C. and at this temperature all of the plutonium distills from the residue. The residue consists mainly of Rb, Sr, Y, Ba, La, Ce, and Cs. The distillate consists of substantially pure plutonium higher fluoride.

It will be understood that where a compound of uranium is irradiated which is not converted to fluoride by treatment with hydrogen fluoride the uranium and other compounds obtained after irradiation may be converted to compounds which are convertible to fluorides. Thus uranium nitrate may be converted to the oxide by heating and the oxide reacted with hydrogen fluoride. Uranium metal, although it may be directly treated with hydrogen fluoride, can be heated with oxygen to form U_3O_8 which may be reduced to UO_2 with hydrogen. This latter compound can then readily be converted to UF_4 by treatment with hydrogen fluoride.

It is not necessary that the treatment with hydrogen fluoride be with anhydrous hydrogen fluoride at elevated temperatures although this is preferable since it too removes volatile fission products in the initial stage of the process. The treatment with hydrogen fluoride may be with aqueous solution of hydrogen fluoride, to obtain UF_4 which is then converted to UF_6 by fluorination.

In accordance with another embodiment of our invention neutron irradiated uranium metal or compound is directly treated with fluorine without going through the hydrofluoride treatment. The procedure is otherwise the same, the higher fluorides of uranium and neptunium being volatilized away from the plutonium lower fluoride at below about 315° C., the temperature being then increased to above 315° C. to about 500° C. and the plutonium lower fluoride converted to the higher fluoride and distilled from the less volatile fission products.

In accordance with another embodiment of our invention we may irradiate uranium tetrafluoride, to obtain a reaction mass which is particularly adapted for direct treatment with fluorine.

We also contemplate the irradiation of uranium hexafluoride to obtain a mixture of uranium hexafluoride and the higher fluorides of plutonium and neptunium, from which a separation may be directly effected by fractional distillation.

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

Several thousand counts/minute of 50-year 94^{238} used as tracer were added to a solution containing 0.25 g. of uranyl nitrate. This was evaporated to dryness and converted to the oxide (U_3O_8) by heating. The U_3O_8 was treated with hydrogen at 500° C., giving UO_2. The UO_2 was in turn hydrofluorinated (treatment with anhydrous HF) at 500° C. and thus converted to anhydrous UF_4. Small samples of this UF_4 were weighed out and fluorinated at various temperatures.

It was found that if the sample was fluorinated at 500° C., both the uranium and the 94 volatilized completely. On the other hand, fluorination at 250° C. completely removed the uranium, but the 94 remained quantitatively behind. These experiments were repeated many times, always with the same results. These experiments indicate that the higher fluoride of element 94 is volatile, but not as volatile as UF_6.

An experiment was performed in which the fluorination took place at 250° C. The small counting disc which had contained the 94 appeared completely empty, as the uranium had disappeared as UF_6. The disc was found to contain all of the 94, however. This disc was fluorinated again at 500° C., and again counted. The 94 had completely volatilized.

We then collected the long-lived 94 (20,000 year 94^{239}) present in a UF_4 sample which had been bombarded with neutrons from 5000 microampere-hours of deuterons on beryllium. A 1-g. sample of this UF_4 was placed in a boat and fluorinated for one hour at about 250–300° C. The fluorination was permitted to go to 98% completion. It was found by chemical analysis that 21 alpha-counts per minute due to the 20,000-year 94^{239} remained behind. (This is about the amount expected to be present in this sample.) Thus it is quite apparent that uranium and 94 can be completely separated by the use of fluorine.

In order to confirm more fully the volatility of the higher fluoride of element 94, about 0.8 gram of U_3O_8, which had been prepared from a strongly active sample of uranyl nitrate bombarded with neutrons was converted to UF_4 by the anhydrous method. This sample was fluorinated at 500° C. and all of the volatile material was collected in a cold trap. All of the 20,000-year 94^{239} present in the original sample was found to have volatilized and condensed in the trap, together with the UF_6 formed.

Thus it has been shown that the higher fluoride of element 94 can be volatilized completely in a fluorine stream at about 500° C. Uranium can be completely separated from element 94, as the very volatile UF_6 will be quantitatively formed at about 250–300° C., leaving the 94 behind. When the temperature is raised to 500° C., the 94 will volatilize quantitatively.

Distribution of long-lived fission products.—It is of importance to know where the various fission product activities will go if one were to use such a procedure. In order to determine this experimentally, a sample * containing all of the long-lived fission products was used. The beta and gamma losses on performing each of the following steps was determined.

(1) $$UO_2(NO_3)_2.6H_2O \xrightarrow{700\,^\circ} U_3O_8$$

(2) $$U_3O_8 + 4H_2 \xrightarrow{600\,^\circ} 3UO_2 + 2H_2O$$

(3) $$UO_2 + 4HF \xrightarrow{600\,^\circ} UF_4 + 2H_2O$$

(4) $$UF_4 + F_2 \xrightarrow{300\,^\circ} UF_6$$

(5) Volatilization of the higher fluoride of 94 at 500° C.

(1) The loss in activity in step (1) was found to be less than 1%, thus indicating that the activity contribution of krypton and xenon is quite small.

(2) A small, but detectable loss in activity of about 1% was found in step (2). This is probably due to the iodine and bromine volatilizing as HI and HBr.

(3) A marked decrease of both beta- and gamma-activity was observed on treatment with anhydrous HF. The gamma-activity loss as measured through 11.5 grams of lead was about 25–30%. In Table 1 the beta-activity loss as a function of absorber through which it was counted is tabulated.

* This sample was produced by the neutrons from 40,000 microampere hours of 14 million electron volt deuterons on beryllium. The bombardment was over a two months period and these experiments were carried out four weeks after its conclusion.

Table 1

Absorber (mg./cm.²)	Loss of activity on treatment with HF at 500° C. (percent)
7.3	38.8
15.0	36.4
40.5	36.2
117.0	36.4

This activity, of course, passes over with the excess HF and the water which is formed as a reaction product. The elements that volatilize are probably Cb, Zr, Sb and possibly 43 and Te.

(4) On fluorinating the UF_4 formed in step (3) at 300° C., the uranium volatilized away completely. However, no detectable amount (<1%) of the beta-activity passed over with it. When element 93 is present it volatilizes in this step (see below).

(5) On raising the temperature to 600° and refluorinating the reaction vessel, no detectable loss of beta-activity was observed. It should be noted that this is the step in which one would volatilize element 94.

The residue contained the balance of the beta-activity (about 60%) and the gamma-activity (about 70%).

About 4 weeks after the above runs were made, another series of experiments was conducted on another portion of this sample. It was found that the fission product mixture behaved as follows:

(1) Ignition to U_3O_8: No loss of activity.

(2) Hydrogenation: No loss of activity.

(3) Hydrofluorination: The amount of volatilization of beta-activity decreased to about 15% of the total. The volatilization of the gamma-activity increased to about 60–70% of the total.

(4) Fluorination at 250° C.: <1% of the beta- and gamma-activity goes with the UF_6.

(5) Flourination at 500° C.: <1% of the beta- and gamma-activity goes with element 94.

The volatility of the higher fluoride of element 93 (neptunium) was also determined and it was found that the neptunium higher fluoride volatilized with the uranium at a temperature below 315° C., so that it was not present in our procedure in the distillation of 94.

The experiments to determine this are given below: About 10,000 beta-counts per minute of 2.3-day 93^{239} tracer were added to a solution containing 100 mg. of uranyl nitrate. This was ignited to U_3O_8 and then converted to UO_2 by hydrogenation. Small samples of this were weighed into small copper discs and converted to UF_4 by hydrofluorination (treatment with anhydrous HF). No loss of 93 was observed in this step. The UF_4 samples were then fluorinated at 300° C. for half an hour. In all cases, the 93 volatilized with the uranium. This indicates that the higher fluoride of element 93 is more volatile than that of element 94. Its behavior thus more closely resembles that of uranium.

As a check, about 10–15 mg. of the UF_4 containing 93 tracer was fluorinated, and the volatile products were collected in a trap maintained at Dry-Ice temperature. The trap was analyzed for element 93 and it was found that all of the 93 that had volatilized had collected in the trap.

The lower limits of temperature for volatilizing uranium and element 94 were determined from the following experiments:

Several samples of UF_4 containing 94^{238} tracer incorporated by the "anhydrous" method were fluorinated at various temperatures for an arbitrary interval of 30 minutes and the percent of element 94 volatilized at a given temperature was measured. For the samples used (about 8 mg.) the onset of volatility was about 320° C. and volatilization was found to be complete at 520° C. In all cases, of course, the uranium disappeared completely.

The experiments were repeated for UF_4 without 94^{238} tracer and it was found that the onset of volatilization of UF_6 was about at 150° C. Volatilization was complete at 270° C. Temperatures were measured with a Chromel-Alumel thermocouple. Curves were made showing the volatilization of uranium and element 94 as a function of temperature. It was found that one has a 35-degree range of temperature from the point of complete volatilization of uranium and the onset of volatilization of element 94. A wider range may be obtained if the duration of fluorination were increased.

The stability and ease of formation of the volatile fluoride of element 94 was determined. A UF_4 sample containing element 94 was treated with fluorine for half an hour at 300° C., thus removing all uranium and leaving the 94 behind. The 94 sample was then heated in an inert atmosphere of hydrogen fluoride for half an hour at 600° C. No 94 volatilized off, thus showing that either (1) the higher fluoride is not formed at temperatures below 320° C., or (2) that the higher fluoride of element 94 decomposes if heated in an atmosphere other than fluorine.

Table 2 shows a summary of a suitable process for the extraction of element 94 from a large amount of UO_2 and fission products and the distribution of the fission products at periods of approximately one month and two months after irradiation has stopped.

Table 2

Step	Process	Result		Elements volatilized
		1 month old sample	2 months old sample	
1	Treatment with anhydrous HF at red heat.	Conversion of UO_2 to UF_4 and volatilization of elements carrying 35-40% of the beta-activity and 25-30% of the gamma-activity.	Conversion of UO_2 to UF_4. Volatilization of elements carrying about 15-20% of the beta-activity and 60-70% of the gamma-activity.	Kr, Xe, Br, I, Cb, Zr, Sb, 43, Ru.
2	Treatment with fluorine at 250-300° C.	Volatilization of UF_6 free from fission contamination (<1%).	Same	Mo, U, 93.
3	Treatment with fluorine at about 500° C.	Volatilization of element 94 free from fission contamination (<1%).	Same	94.
		Residue contains approximately 60-65% of beta-activity and 70-75% of gamma-activity.	Residue contains approximately 80-85% of the beta-activity and 30-40% of the gamma-activity.	Residue consists mainly of Rb, Sr, Y, Ba, La, Ce, Cs.

The fission activity will be in two portions, either or both of which can be discarded or utilized: (*a*) In water solution resulting from condensation of the water formed in step (1). (*b*) As the residue resulting from steps (2) and (3).

While there have been described certain embodiments of our 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 in the invention as broadly as possible, in view of the prior art.

We claim:

1. A method of producing substantially pure plutonium fluoride, comprising bombarding a uranium-containing mass selected from the group consisting of uranium metal, uranium carbides, uranium oxides, uranium oxyhalides, and uranium chlorides with neutrons whereby a mixture containing uranium values, plutonium values, neptunium values and fission product values is obtained; reacting said mixture with hydrogen fluoride at about 500° C. whereby that part of said fission product values that is volatile at 500° C. is volatilized and a residue is obtained; reacting said residue with fluorine gas at a temperature of between 140° and 315° C. whereby said neptunium values and uranium values are volatilized as fluorides while said plutonium values and fission product values stay in a remainder; and reacting said remainder with fluorine gas at a temperature of between 315° and 600° C. whereby said plutonium values are volatilized in the form of fluoride away from said nonvolatile fission product values.

2. The process of claim 1 wherein said hydrogen fluoride is anhydrous hydrogen fluoride.

3. The process of claim 1 wherein said residue is reacted with fluorine gas at between 250° and 300° C. and said remainder at about 500° C.

4. A method of producing substantially pure plutonium fluoride, comprising bombarding uranium metal with neutrons whereby a mixture containing uranium, plutonium, neptunium and fission products is obtained; heating said mixture in the presence of oxygen whereby U_3O_8 is formed; contacting the mixture with hydrogen at a temperature of between 500° and 600° C. whereby said U_3O_8 is reduced to UO_2; reacting said mixture with hydrogen fluoride at about 500° C. whereby that part of said fission products that is volatile at 500° C. is volatilized and a residue is obtained; reacting said residue with fluorine gas at a temperature of between 140° and 315° C. whereby neptunium values and uranium values are volatilized as fluorides while plutonium values and fission product values stay in a remainder; and reacting said remainder with fluorine gas at a temperature of between 315° and 600° C. whereby said plutonium values are volatilized in the form of fluoride away from said nonvolatile fission product values.

5. A method of producing substantially pure plutonium fluoride, comprising bombarding a mass containing uranium values with neutrons whereby a mixture containing uranium values, plutonium values, neptunium values and fission product values is obtained; reacting said mixture with fluorine at a temperature of between 140° and 315° C. whereby said neptunium values and uranium values are volatilized as fluorides while said plutonium values and fission product values stay in a remainder; and reacting said remainder with fluorine gas at a temperature of between 315° and 600° C. whereby said plutonium values are volatilized in the form of fluoride away from fission product values.

6. A method of producing substantially pure plutonium fluoride, comprising bombarding uranium tetrafluoride with neutrons whereby a mixture containing uranium tetrafluoride, neptunium fluoride, plutonium fluoride and fission product fluorides is obtained; reacting said mixture with fluorine gas at a temperature of between 140° and 315° C. whereby said neptunium values and uranium values are volatilized as fluorides while said plutonium values and fission product values stay in a remainder; and reacting said remainder with fluorine gas at a temperature of between 315° and 600° C. whereby said plutonium values are volatilized in the form of fluoride away from fission product values.

7. A process of producing substantially pure plutonium fluoride, comprising bombarding uranium hexafluoride with neutrons whereby a mixture containing uranium hexafluoride, plutonium fluoride, neptunium fluoride and fission product fluorides is obtained, heating said mixture to from 140° to 315° C. wehreby uranium fluoride and neptunium fluoride are volatilized, and heating a residue to a temperature of between 315° and 500° C. whereby plutonium fluoride is volatilized.

8. A method of isolating plutonium in the form of substantially pure plutonium fluoride from a neutron-irradiated mass containing plutonium values, fission product values and values selected from the group consisting of uranium values and a mixture of uranium values and neptunium values, comprising reacting said values with fluorine gas at from 140° to 315° C. whereby neptunium values and uranium values are volatilized as fluorides while said plutonium and fission product values stay in a remainder, and reacting said remainder with fluorine gas at a temperature of between 315° C. and 600° C. whereby said plutonium values are volatilized in the form of fluoride away from fission product values.

9. A method of separating plutonium values from uranium values contained in a mixture comprising reacting said mixture with fluorine gas at a temperature of between 140° and 315° C. whereby said uranium values are volatilized in the form of fluoride away from said plutonium values.

10. A method of separating plutonium values from uranium values and fission product values contained in a mixture, comprising contacting said mixture with hydrogen fluoride at about 500° C. whereby that part of said fission product values that are volatile at 500° C. is volatilized and a residue is obtained; reacting said residue with fluorine gas at a temperature of between 140° and 315° C. whereby said uranium values are volatilized as fluorides while said plutonium values and fission product values stay in a remainder; and reacting said remainder with fluorine gas at a temperature of between 315° and 600° C. whereby said plutonium values are volatilized in the form of fluoride away from said nonvolatile fission product values.

11. A process of separating plutonium values from a mixture of uranium hexafluoride and plutonium tetrafluoride, comprising heating said mixture to a temperature of from 150° to 270° C. whereby said uranium hexafluoride is volatilized away from said plutonium tetrafluoride.

12. A process of separating plutonium values from fission product values that are nonvolatile at a temperature up to 500° C., comprising the step of reacting said values with fluorine gas at from 315° to 500° C. whereby said plutonium values are volatilized as fluoride away from said fission product values.

13. A process of separating plutonium values from a mixture containing said values together with neptunium values comprising reacting said mixture with fluorine gas at a temperature of between 140° and 315° C. whereby said neptunium values are volatilized as fluoride away from said plutonium values.

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