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METHOD OF SEPARATING PLUTONIUM FROM CONTAMINANTS

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This invention is concerned with an improved method separating plutonium from contaminating elements normally associated with plutonium in neutron-irradiated uranium, and more particularly is concerned with obtaining the plutonium in a concentrated and purified form.

The word "plutonium," as hereinafter used in the specification and claims refers to the element of atomic number 94 and to the compounds thereof unless the context indicates clearly that plutonium is referred to in its metallic state.

Natural uranium is composed of three isotopes; namely, U^{234}, U^{235}, and U^{238}, the latter being in excess of 99% of the whole. When U^{238} is subjected to the action of slow or thermal neutrons, a fourth isotope, U^{239}, is produced having a half-life of twenty-three minutes and undergoing beta decay to Np^{239}, which in turn decays with a half-life of two and three-tenths days to yield plutonium. In addition to the formation of 94^{239}, there are simultaneously produced other elements of lower atomic weight known as fission fragments. These fission fragments are composed of elements having atomic numbers from about 32 to 64. The elements of this group, as originally produced, are considerably overmassed and undercharged and hence are highly unstable. By emission of beta particles accompanied by gamma radiation, these elements transform themselves into isotopes of these various elements having longer half-lives. The resulting materials are commonly known as fission products.

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

It may be readily seen that plutonium, as produced by the process generally set forth above, is contaminated with considerable quantities of uranium and fission products. In fact, the plutonium constitutes only a very minor portion of the irradiated mass, i. e., less than 1% thereof. In view of such a low concentration of plutonium in the irradiated metal and the highly radioactive character of the fission products present, it becomes apparent that the procedure employed to recover that element must be highly efficient in order to be at all practicable.

There have been devised a number of procedures for the removal and concentration of plutonium from extremely dilute solutions thereof. In general, such methods involve the formation of various insoluble compounds in said dilute solutions capable of carrying plutonium in one of its valence states. The carrier precipitate and plutonium thus obtained are then dissolved and the plutonium converted to another valence state, in which state

it is soluble in the presence of said carrier. The carrier is then re-precipitated from the new solution, thus removing the fission products present in this solution, but leaving the soluble plutonium in solution. Thereafter, the plutonium may be separated from the solution directly as a plutonium compound or the plutonium may be converted to the valence state in which it is insoluble with the aforementioned carrier and removed from the solution with that carrier. This carrier precipitate may again be dissolved and the plutonium purified further, if considered necessary or desirable, by repeating the above cycle. A carrier precipitate, which carries plutonium is usually referred to as a "product" precipitate, while a carrier precipitate which removes elements other than plutonium, leaving the plutonium in the solution, is usually referred to as a "by-product" precipitate.

The precipitation method of separation is usually divided into four steps. The steps are: Extraction, in which the plutonium is separated from the uranium and most of the fission products; Decontamination, in which the plutonium is separated from the remaining fission products; Concentration, in which the ratio of carrier precipitate or containing solution to plutonium is greatly reduced; and Isolation, in which the final plutonium compound is precipitated directly from solution.

One of the most important of the plutonium separation processes based upon precipitation of plutonium compounds is the lanthanum fluoride process. In this process the neutron-irradiated uranium mass after suitable aging is dissolved in nitric acid to form a uranyl nitrate hexahydrate solution. A lanthanum fluoride carrier precipitate is then formed in, and separated from this solution carrying with it plutonium in a valence state less than 5 and fission products which form insoluble fluorides. This precipitate is then redissolved in nitric acid, the plutonium converted to the hexavalent state, and a by-product lanthanum fluoride precipitate carrier formed in, and separated from this solution. This by-product carrier thus removes the fluoride-insoluble fission products from the plutonium-containing solution. The plutonium contained in the supernatant solution is then reduced to the tetravalent state and carried from the solution with a lanthanum fluoride carrier precipitate. This plutonium-containing precipitate is metathesized with an alkali metal carbonate or hydroxide, the resulting mixed lanthanum and plutonium hydroxide dissolved and the plutonium precipitated directly from the solution without a carrier.

While this type of plutonium separation process is highly efficient in the separation of plutonium from contaminants normally associated with plutonium in neutron-irradiated uranium, particularly the radioactive fission products, the process has certain disadvantages and inconveniences. For example, the process requires a number of precipitation steps in order to obtain the plutonium in the pure state. The lanthanum fluoride carrier precipitate is very difficult to dissolve and consequently large amounts of acids and other reagents are required to carry out the process. This consequently results in a large amount of radioactive waste, which, because of its bulk, is very difficult to dispose of. It will be readily apparent that a process for separating plutonium from contaminants which would require a lesser amount of steps than the precipitation process would have great utility.

It is an object of this invention to provide a convenient and efficient method of recovering plutonium from impurities commonly associated therewith in a neutron-irradiated uranium mass.

It is a further object of this invention to provide a method of separating plutonium from such impurities whereby the plutonium will be obtained in a concentrated and purified form.

Additional objects of our invention will be apparent as the present description proceeds.

Broadly, this invention comprises the hydrofluorination at elevated temperatures of a lanthanum fluoride mass containing plutonium and fluoride-insoluble fission products whereby fission products which form relatively volatile fluorides are volatilized away from the lanthanum fluoride plutonium-containing mass. The mass is then treated with anhydrous fluorine at elevated temperatures whereby the plutonium is oxidized and volatilized as its higher fluorides and thus separated from the lanthanum fluoride and other less volatile constituents of the mass.

In accordance with the preferred embodiment of our invention neutron-irradiated uranium is aged for from sixty to ninety days, thereby substantially converting the neptunium present to plutonium and permitting the most active fission products to decay to more stable states. The uranium mass is then dissolved in a suitable inorganic acid, such as for example nitric acid or a mixture of nitric and sulfuric acids. The uranium is normally present in such solution as the uranyl ion and the plutonium as the tetravalent ion. In order to insure, however, that the plutonium is present in a valence state not greater than +5, the solution may be treated with a reducing agent, such as formic acid of sodium nitrite, in the presence of sulfuric acid. The sulfate ion tends to complex the uranyl ion so that the dissolved plutonium is converted substantially completely to a valence state less than +5 without any of the uranyl ion being reduced. The solution is then treated with a lanthanum fluoride precipitate. This treatment may be effected by either introducing the pre-formed lanthanum fluoride precipitate or preferably by forming the lanthanum fluoride precipitate in the solution by introducing a soluble lanthanum compound, such as lanthanum nitrate, and a soluble fluorine compound, such as hydrofluoric acid. This lanthanum fluoride precipitate is then separated from the solution and carries with it the plutonium present and the fission products, which form fluoride-insoluble precipitates. The most important of these fluoride-insoluble fission products are Sr, Y, Ba, and the rare earths. The uranyl ion and a substantial portion of the fission products are fluoride-soluble and so remain in the solution after the separation. Since the uranium is much greater than 99% of the total mass, this results in a great reduction in the amount of foreign products which contaminate the plutonium. The lanthanum fluoride plutonium carrier precipitate, thus obtained, is placed in a suitable fluorination reactor and subjected at elevated temperatures, for example a range of from 500–600° C., to the action of hydrogen fluoride, preferably in the anhydrous state. This step effectively frees the mass from all water vapor and air. The plutonium, which is present as the tetrafluoride, is not volatile at this temperature, but certain of the fission products, which are carried with the fluoride carrier, are volatile at this temperature and these will volatilize away from the mass. This step not only separates from the mass the fluoride-insoluble fission products having fluorides volatile at this temperature but also acts to remove any traces of other soluble fission products, which may have been carried by adsorption in the fluoride precipitation step. These may include As, Se, Br, Sb, Cb, Te, and I. The radioactive inert gases, Kr and Xe, will also be completely removed by this step. Following this hydrofluorination step, the non-volatile mass, which includes the plutonium tetrafluoride, lanthanum fluoride, and the non-volatile fission product fluorides, is treated with fluorine at temperatures of between about 290–525° C. and preferably between about 400–500° C., whereupon the lower plutonium fluoride is converted to the higher volatile fluoride (probably the penta- or hexafluoride). The volatile plutonium fluoride gas is condensed at temperatures below 290° C. and thus effectively separated from the less volatile impurities in the mass, which include the rare earth fluorides. This step thus effectively separates the plutonium not only from the radioactive non-volatile fluorides but also from the lanthanum fluoride which was introduced as a carrier in the first step of the process. The hydrogen fluoride and fluorine used in this process should be free from oxygen and water vapor in order to avoid the complications caused by oxyfluoride formation. The temperature ranges described above apply to the volatilization at atmospheric pressure. They may be appropriately reduced should the volatilization be carried out at less than atmospheric pressure.

Our invention may be further illustrated by the following specific example.

Example

An 8.6 N sulfuric acid solution was prepared containing lanthanum sulfate in a concentration of approximately 430 mg./l. and plutonium in tracer concentration. To this solution was added about 2.1 times its volume of a saturated aqueous solution of sulfur dioxide and the mixture was allowed to stand at room temperature for twenty-five minutes to effect reduction of any hexavalent plutonium. The sulfuric acid concentration of the resulting solution was about 2.8 N and the lanthanum sulfate concentration was about 139 mg./l. About 27% by volume of 48% aqueous hydrofluoric acid was then added to the solution and the resulting lanthanum fluoride precipitate was separated by centrifuging. The solid residue thus obtained, which contained plutonium and fission products, in addition to the lanthanum fluoride, was placed in a nickel tube fluorination reactor of conventional design after which anhydrous hydrofluoric acid was introduced at a rate of approximately 0.5 liter/hr. for a period of two hours at 525° C. At the end of this period all of the Cb, Zr, Ru, and Sb fluorides present had been volatilized away together with the Br. and I. The plutonium was present as plutonium tetrafluoride which was not volatile and so remained as a residue in the reaction chamber together with the lanthanum fluoride carrier precipitate and such fission products as Ba, Sr, Mo, Y, Ce, and Cs. Anhydrous fluorine was next introduced at a rate of about 0.3 liter/hr. at a temperature of between 400–425° C. under which conditions the plutonium tetrafluoride was converted to a volatile higher plutonium fluoride, which was collected in a suitable receiving vessel at a temperature below 290° C. The lanthanum fluoride carrier and the remaining fission products, most of which were in the form of their fluorides, were left as a residue in the reaction chamber. The plutonium recovered in this manner represented approximately 90–95% of that originally present in the lathanum fluoride carrier precipitate.

It will be apparent to those skilled in the art that the method of recovering plutonium as generally set forth above provides a simple and practical procedure for the procurement of high concentrations of plutonium in a single step. Also, it will be further apparent that by the utilization of such a procedure a relatively high degree of purification of plutonium with respect to fission products and other impurities is obtainable.

While this invention has been illustrated by certain restricted applications thereof, it is not desired to be specifically limited thereto, since it is manifest to those skilled in the art, to which the present invention is directed, that it is susceptible to numerous alterations and modifications without departing from the scope thereof. While it is illustrated as a step in a continuous process for the separation of plutonium from neutron-irradiated uranium, the process may also be suitably used for the separation of plutonium from any contaminant, the fluoride of which has a different boiling point than that of a higher fluoride of plutonium. In general, it may be said that any process for the separation of plutonium from contaminants, wherein the plutonium is treated with hydrogen fluoride in the presence of a lanthanum fluoride carrier, followed by formation of a volatile fluoride of

plutonium and subsequent recovery thereof, is to be construed as lying within the scope of our invention.

What is claimed is:

1. The process of recovering plutonium from a solid composition containing plutonium, lanthanum fluoride, and fission products, which comprises contacting said composition with hydrogen fluoride, heating said composition and hydrogen fluoride to a temperature to between about 500 and 600° C., whereby volatile fission product fluorides are removed, contacting the residual fission product fluorides, lanthanum fluoride and plutonium tetrafluoride with fluorine, heating this mixture of fluorine, plutonium tetrafluoride, lanthanum fluoride, and fission product fluorides to a temperature of greater than about 290° C. to form a volatile fluoride of plutonium, which is immediately volatilized, leaving as a residue substantially non-volatile lanthanum fluoride and fission product fluorides, and recovering said volatile fluoride of plutonium.

2. The process of recovering plutonium in concentrated and purified form from a solid composition containing lanthanum fluoride, plutonium, and fission products, which comprises contacting said composition with anhydrous hydrogen fluoride, heating said composition and hydrogen fluoride to a temperature of between about 500 and 600° C., whereby the fission products which form fluorides volatile below this temperature are removed, contacting the residual fission product fluorides, lanthanum fluoride, and plutonium tetrafluoride with anhydrous fluorine, heating this mixture of plutonium tetrafluoride, fission product fluorides, lanthanum fluoride and fluorine to a temperature of between 290 and 525° C. to form a volatile fluoride of plutonium, leaving as a residue the substantially non-volatile fission product fluorides and lanthanum fluoride, and recovering said volatile plutonium fluoride.

3. The process of recovering plutonium from a solid composition containing tetravalent plutonium, lanthanum fluoride, and fluoride-insoluble fission products, which comprises contacting said composition with anhydrous hydrogen fluoride, heating said composition with hydrogen fluoride to a temperature between about 500 and 600° C., whereby volatile fission product fluorides are removed, contacting the residual fission product fluorides, lanthanum fluoride, and plutonium fluoride with anhydrous fluorine, heating this mixture of plutonium tetrafluoride, lanthanum fluoride, fission product fluorides, and fluorine to a temperature of between 400 and 500° C., whereby a volatile plutonium fluoride is formed and volatilized from the mass, and condensing said volatile plutonium fluoride.

4. A process of recovering plutonium in a concentrated and purified form, which comprises removing plutonium from an acid solution containing uranium in the hexavalent state, fission products, and plutonium in the tetravalent state by treating said solution with a lanthanum fluoride precipitate, removing said precipitate which contains plutonium and fission products, subjecting said precipitate to the action of hydrogen fluoride, heating the mixture of said precipitate and hydrogen fluoride to a temperature of between about 500 and 600° C., whereby the volatile fission product fluorides are removed, contacting the residual fission product fluorides, lanthanum fluoride, and plutonium fluoride with anhydrous fluorine,

heating this mixture of plutonium tetrafluoride, fission product fluorides, lanthanum fluoride, and fluorine to a temperature of between about 290 and 500° C. to form a volatile form of plutonium, leaving as a residue the substantially non-volatile lanthanum fluoride and fission product fluorides, and recovering said volatile plutonium fluoride.

5. A process of recovering plutonium from a solid composition containing lanthanum fluoride, tetravalent plutonium fluoride, and fission products, which comprises subjecting said composition to the action of anhydrous hydrogen fluoride at a temperature of between 500 and 600° C., whereby the fission product fluorides, volatile at that temperature, are volatilized away from the mass, subjecting the residue thus obtained to the action of anhydrous fluorine at a temperature above about 290° C. to form a volatile form of plutonium, leaving as a residue the non-volatile lanthanum fluoride and fission product fluorides, and recovering said volatile plutonium fluoride.

6. The process of recovering plutonium in concentrated and purified form from a solid composition containing lanthanum fluoride, plutonium, and fission products, which comprises subjecting said composition to the action of anhydrous hydrogen fluoride at a temperature of about 500° C., whereby the fission product fluorides, volatile at that temperature, are removed from said mass, subjecting the residue thus obtained to the action of anhydrous fluorine at a temperature of above about 290° C., whereby the plutonium tetrafluoride is converted to a volatile higher plutonium fluoride and volatilized away from the mass, and recovering said volatile plutonium fluoride.

7. The process of recovering plutonium in concentrated, purified form from a solid composition containing lanthanum fluoride, tetravalent plutonium fluoride, and fission product fluorides, which comprises heating said mass to a temperature of between about 400 and 500° C. in a hydrogen fluoride atmosphere until the fission product fluorides, which are volatile at this temperature, are volatilized from the mass, fluorinating the resultant residue with anhydrous fluorine at a temperature between about 290 and 500° C., whereby the plutonium tetrafluoride is converted to a volatile higher plutonium fluoride, and volatilized from said mass, leaving as a residue the essentially non-volatile lanthanum fluoride and fission product fluorides, and recovering said volatile plutonium fluoride.

8. In a process for the recovery of plutonium in concentrated and purified form from a solid composition containing lanthanum fluoride and plutonium, the steps which comprise contacting said composition with hydrogen fluoride and heating the resultant hydrofluorinated mass at a temperature between 500 and 600° C., then contacting the residual mass with anhydrous fluorine and heating the residual mass and anhydrous fluorine to a temperature between 400 and 500° C., whereby the plutonium tetrafluoride is converted to a volatile higher fluoride and volatilized away from the mass, and recovering the volatile plutonium fluoride.

No references cited.