

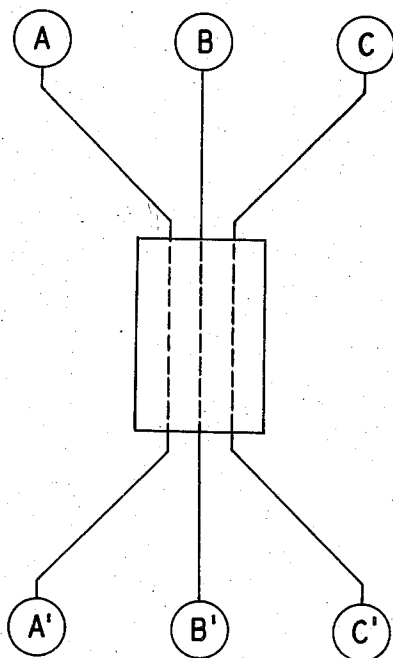
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ZIRCONIUM PHOSPHATE ADSORPTION METHOD

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ZIRCONIUM PHOSPHATE ADSORPTION METHOD

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The invention relates to the separation of various substances present in neutron-irradiated uranium, and more particularly relates to the separation of element 94 from such substances.

It is an object of the invention to provide an improved process of chromatographic adsorption for separating element 94 from one or more substances having relatively different adsorption affinities with respect to a given adsorbent, especially such substances as fission products resulting from the neutron bombardment of uranium. It is a further object of the invention to provide a process of separating element 94 with adsorbents having relatively high specific attraction for element 94 and relatively low specific attraction for other substances present in neutron-irradiated uranium, such as fission products. Further objects will be apparent from the following description and drawing appended thereto.

In the drawing, the sole figure is a schematic representation of one embodiment of the invention.

In the following description, the isotope of element 93 having a mass of 239 is referred to as 93^{239} and the isotope of element 94 having a mass of 239 is referred to as 94^{239} . Element 94 may also be designated as plutonium, symbol Pu. Reference herein to any of the elements is to be understood as denoting the element generically, whether in its free state or in the form of a compound, unless indicated otherwise by the context.

Neutron-irradiated uranium may be prepared by reacting uranium with neutrons from any suitable neutron source but preferably the neutron-irradiated uranium is produced from a chain reaction of neutrons with uranium.

Neutron irradiation of uranium produces 92U^{239} which has a half-life of 23 minutes and by beta decay becomes 93^{239} . This element has a half-life of 2.3 days and by beta decay becomes 94^{239} . Neutron-irradiated uranium contains 93^{239} , 94^{239} and a large number of radioactive fission products produced by reaction of neutrons on fissionable atoms, such as U^{235} which is present in uranium from natural sources. It also contains minor amounts of other products such as UX_1 and UX_2 . Inasmuch as the weight of radioactive fission products is proportional to the amounts of 93^{239} and 94^{239} formed, it is convenient to separate the desired elements when the combined amounts thereof are minute, such as, for example, approximately .02% by weight of the irradiated uranium. By storing the neutron-irradiated uranium for a suitable period of time, the 93^{239} is converted almost entirely to 94^{239} . Because the fission products in general are highly radioactive, it is preferred that these materials be removed.

The fission products consist of a large number of elements which may be classified into two groups; a light group with atomic numbers from 35 to 45; and a heavy group with atomic numbers from 51 to 60. 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 neutron-irradiated reaction mass in substantial quantities at least one month after reaction. These products are chiefly radioactive isotopes of Sr, Y, Zr, Cb,

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and Ru of the group of atomic members from 35–45; and Te, I, Xe, Cs, Ba, La, and Ce from the group of atomic numbers from 51–60 inclusive.

In accordance with the invention, a solution containing a relatively low concentration of plutonium together with other substances, such as fission products, is flowed through a finely divided adsorbent. The process is particularly suitable for neutron-irradiated uranium which has been dissolved in nitric acid and from which most of the uranium and moderate amounts of fission products have been previously removed. The plutonium, when referred to in the following description, is in its reduced or phosphate-insoluble state (plutonium in a valence state of +3 or +4 but not above +4).

Adsorption of the plutonium is facilitated by adsorption from a solution thereof containing mixed mineral acids. Optimum adsorption is obtained using a solution wherein the concentration of HNO_3 (or HCl) is 1 N to 3 N and the concentration of H_3PO_4 is 0.02 N to 0.4 N. Acid concentrations beyond the ranges given decrease adsorption of the plutonium, as does substituting H_2SO_4 for HNO_3 or MCl , although H_2SO_4 may be employed with some degree of success. The plutonium adsorption is decreased by the presence of uranium so that as much of the latter as is possible is preferably removed by any suitable means prior to the plutonium adsorption step. For example, for this purpose the method disclosed in our copending application, Serial No. 551,734, filed August 29, 1944 may be employed.

The adsorbent used is one which has surface properties specifically suitable for the adsorption of the plutonium. It has been found that suitable adsorbents are those of the class whose anions form with plutonium compounds which are insoluble in the solution carrying the plutonium ions. Such adsorbents include zirconium phosphate and barium iodate, as well as adsorbents such as zeolites, that is, for example, sodium aluminum silicate, sodium titanium silicate, and sodium zirconium silicate. Of these, zirconium phosphate in its gelatinous form appears to be most desirable for adsorption of the plutonium when the latter is present with other substances, especially where such substances are fission products resulting from the neutron bombardment of uranium.

To present the largest adsorbing surface area and to aid the flow of solution through the adsorbent, the latter is preferably supported on an inert material. While supporting materials such as silica or powdered glass may be used, finely cut glass wool is especially suitable. To facilitate adherence to the inert material, the zirconium phosphate may be digested with the glass wool one to two hours at above 75°C .

When the zirconium phosphate is prepared by precipitation with H_3PO_4 from a zirconium salt solution, such as a solution containing zirconium nitrate, there is a tendency for a portion of the zirconium phosphate to be present as zirconyl phosphate. To insure against the presence of zirconyl phosphate in the precipitate, it is preferred to digest the precipitate at 90°C . to 100°C . in the presence of nitric acid, such as 2 N to 4 N HNO_3 , for approximately one hour to convert the zirconyl phosphate to zirconium phosphate. While the zirconium phosphate can be converted to zirconium pyrophosphate by drying at elevated temperatures, preferably the zirconium phosphate is used in the ortho-form. The digestion of the initial precipitate to convert it entirely to zirconium ortho phosphate may be done in the presence of the glass wool, thereby causing it to adhere firmly to the support.

It has been found that the amount of zirconium phosphate which will give the most satisfactory adsorptive results is dependent somewhat upon the amount of plutonium in the solution. A suitable proportion has been

found to be approximately 280 parts of zirconium phosphate to one part of plutonium.

In the process of adsorbing the plutonium, the adsorbent is contained in an elongated receptacle or column. The column preferably has a relatively small cross-sectional area in proportion to its length to facilitate the formation of layers in the column. For all practical purposes, where the diameter of the column is approximately 1.2 centimeters, a bed depth of 7 centimeters for the adsorbent is sufficient to cause adsorption of substantially all of the plutonium when present in tracer amounts. Where the bed depth is less than 6.5 centimeters, the adsorption of the plutonium is substantially lowered.

Where a small column, such as a column having a diameter of approximately 1 centimeter is used, the lower portion is preferably packed with the digested zirconium phosphate-glass wool mixture. Sufficient precipitated zirconium phosphate is preferably poured in to form a thin band or layer in the column and the remainder of the column is packed with the mixture. This method of filling a small column increases the proportion of adsorbent to the inert supporting material in the column and thus permits a more concentrated banding effect in small columns. The zirconium phosphate band should not be so thick as to impede the flow of the solution through the column.

Where a large column, such as a column having a diameter of approximately 1 foot in diameter, is to be used, the column may be filled with a slurry of the inert supporting material in a zirconium nitrate solution, nitric acid being added to insure conversion of the zirconyl phosphate to zirconium phosphate, and an excess of phosphoric acid may then be added to precipitate the phosphate. The column is then heated for one hour at 90° C. to 100° C. to convert the precipitate to the ortho-form of zirconium phosphate and to cause the adsorbent to adhere to the inert supporting material. The adsorbent is cooled and washed with water before use.

The adsorption of the plutonium is substantially independent of the flow rate of the solution through the column up to approximately 1.3 milliliters per minute per square centimeter of adsorbent. However, considerably higher flow rates may be used without seriously decreasing the adsorption of plutonium.

As the solution flows through the adsorbent mass, substantially all of the plutonium is adsorbed while large amounts of the other substances, and especially some of the fission products, pass through the adsorbent mass and out of the column with the solution. It is believed that the adsorption of the plutonium and fission products provides a layer effect, i. e., chromatographic adsorption, with the plutonium being preferentially adsorbed and forming a layer in the upper portion of the adsorbent, with such fission products as are adsorbed forming layers below the plutonium (in the case of downward flow of solution through the adsorbent mass). Most of the fission products which are adsorbed are so attracted to the adsorbent as to remain adsorbed during subsequent desorption of the plutonium. The remainder of the adsorbed fission products are loosely held by the adsorbent and can be desorbed.

To remove the adsorbates from the adsorbent, it is necessary to pass wash solutions through the column which, by a continual process of desorption, readsorption, and desorption, move the various adsorbates down the column until the layer of adsorbates originally in the lowest portion of the column passes out with the wash solution and may be collected as a separate fraction. During the elution of the lowest layer the other layers are also moving down the column but at slower rates of travel.

It has been found that certain wash solutions, such as

a solution containing mixed mineral acids, serve better to remove certain of the fission products than the plutonium, while other wash solutions, such as single acids, tend to remove the plutonium but not the fission products. Where plutonium and fission products have been adsorbed, a first wash solution of mixed acids is flowed through the column to remove the fission products. It has been found that a solution 1 N to 3 N in HNO_3 and 0.1 N to 0.4 N in H_3PO_4 is most suitable for this purpose. Practically all of the fission products which are not removed by this wash solution are so strongly adsorbed that they will not be removed when the plutonium is later elutriated off. If desired, the desorbed fission products may be collected as a separate fraction.

To remove the plutonium, wash solutions comprising a single acid are preferred. The higher the concentration of acid in this wash solution the smaller the volume of wash solution needed and the faster the wash solution may be passed through the column. Preferably, the wash solution for desorption of the Pu comprises 7 N HNO_3 . The plutonium may be collected as a separate fraction.

In one embodiment of the invention as diagrammatically represented in the drawing, the solution to be treated comprises the eluant A resulting from a previous adsorption process in which substantially all of the uranium and moderate amounts of fission products were removed from a solution of neutron-irradiated uranium. This eluant or solution A, which is 2 N in HNO_3 and 0.02 N in H_3PO_4 , contains substantially all of the plutonium and moderate amounts of the fission products which were formed during the original neutron bombardment of uranium.

To facilitate the adsorption of the plutonium, the solution to be treated should comprise 1 N to 3 N HNO_3 (or HCl) with 0.02 N to 0.4 N H_3PO_4 . As solution A previously was 2 N in HNO_3 and 0.02 N in H_3PO_4 , it is ready to be flowed through the adsorbent. Of the substances originally formed or present in the neutron-irradiated mass, solution A contains, by weight, 98 percent of the plutonium and fission products having 68 percent of the original beta activity and 57 percent of the original gamma activity. For the sake of brevity, the latter will be referred to hereinafter as "beta activity" and as "gamma activity." The fission products are important from the standpoint of their emission of radioactive rays, primarily because of the harmful effect of such rays. Consequently, the fission products will be considered only with respect to the total amount of beta and gamma activity present at any point of the process. In what follows, the proportions of plutonium, beta activity, and gamma activity will be stated with reference to the total amounts contained in solution A.

As the concentration of plutonium in solution A is approximately 10^{-3} grams per liter of 10 percent neutron-irradiated uranium solution, it is desirable to use 0.00028 pound of zirconium phosphate, in the ortho-form, per pound of solution A, to give the ratio of 280 parts of $\text{Zr}_3(\text{PO}_4)_4$ to one part of plutonium. The zirconium phosphate is digested with finely cut glass wool for one hour at 90° to 100° C. The mixture is packed into a cylindrical glass column 1, preferably 7 centimeters in diameter and 8.5 centimeters in length, until the column is half full. Sufficient zirconium phosphate is then poured into the column to form a thin layer on the mixture. The remainder of the column is filled with the mixture. The bottom of the column is perforated to permit the flow of liquids therethrough while retaining the adsorbent thereon.

Solution A, in the amount of 11.8 liters, is flowed through the column at a rate of 33 milliliters per minute, with all of the solution flowing through in approximately 6 hours. Rate of flow as high as 50 milliliters per minute have been found satisfactory. During the flow of the solution through the column, substantially all of the plu-

onium and moderate amounts of fission products having beta and gamma activity are adsorbed. As solution A passes out of the column, it contains a negligible amount of plutonium, 72 percent of beta activity, and 70 percent of gamma activity to form fraction A'.

To remove as much of the beta and gamma activity as possible before the plutonium desorption step (i. e., to permit the later recovery of Pu in a condition as free as possible from beta and gamma activity), 3.3 liters of wash solution B which is 2 N in HNO_3 and 0.1 N in H_3PO_4 are flowed through the column at a rate of 30 gallons per square foot per hour. Eluant B removes 0.45 percent plutonium, 6.32 percent beta activity and a negligible amount of gamma activity to form fraction B'.

Substantially all of the plutonium is next removed by wash solution C comprising 5.8 liters of 7 N HNO_3 . Fraction C' contains 99.40 percent of the plutonium, and negligible amounts of beta and gamma activity. Moderate amounts of the radioactive fission products remain on the adsorbent.

The various steps as represented in the drawing are summarized in the following table:

Solution A-----	Plutonium and fission products in 11.8 liters of a solution which is 2 N in HNO_3 and 0.02 N in H_3PO_4 .
Solution B-----	3.3 liters of a solution which is 2 N in HNO_3 and 0.1 N in H_3PO_4 .
Solution C-----	5.8 liters of 7 N HNO_3 .
Fraction A'-----	.15% of the plutonium in solution A. 72.00% of the beta activity in solution A. 70.00% of the gamma activity in solution A.
Fraction B'-----	.45% of the plutonium in solution A. 6.32% of the beta activity in solution A. A very small percent gamma activity in solution A.
Fraction C'-----	99.40% of the plutonium in solution A. .07% of the beta activity in solution A. A very small percent gamma activity in solution A.

There is very little mechanical loss of zirconium phosphate if the freshly prepared mass is first washed with a mineral acid to remove any loosely held zirconium phosphate. It is desirable that such acid solution be as highly concentrated as any acid wash which is later used. As zirconium phosphate is extremely insoluble in the various solutions involved herein, only negligible amounts are lost by the action of these various solutions.

After the adsorption-desorption cycle is completed, the adsorbent may be reused without further treatment. For example, the zirconium phosphate adsorbent has been used as many as five times without any decrease in adsorption of the plutonium.

Warm saturated aqueous oxalic acid solution may be used to remove the zirconium phosphate adsorbent from the glass wool in the column. The glass wool may be removed from the column in any convenient manner.

If desired, the plutonium obtained from the fraction C' may be further treated in an adsorption process or otherwise to remove minute amounts of radioactive substances that may be present.

The above detailed description of the invention is given for purposes of illustration and the invention is to be limited only by the scope of the appended claims.

What is claimed is:

1. A method of separating plutonium values from fission product values comprising adsorbing ionic species of plutonium on an adsorbent comprising a substantially insoluble compound of a soluble monomeric anion which forms an insoluble compound with said plutonium ions, desorbing said fission product values with a solution

comprising 2 N HNO_3 and 0.1 N H_3PO_4 , and desorbing said plutonium values with a solution comprising 7N HNO_3 .

2. A method of separating plutonium values from fission product values comprising flowing a 2 N HNO_3 and 0.02 N H_3PO_4 solution containing ionic species of plutonium in a valent state not above 4 and fission product values through a column, said column containing zirconium phosphate in the ortho form supported on finely cut glass wool, desorbing said fission product values by flowing a wash solution comprising 2 N HNO_3 and 0.1 N H_3PO_4 through said column and collecting said fission product values as a substantially separate fraction, and desorbing said plutonium values by flowing a wash solution comprising 7 N HNO_3 through said column and collecting said plutonium values as a substantially separate fraction.

3. A method of separating plutonium values from fission product values which comprises adsorbing ionic species of plutonium and at least a portion of the fission product values from an aqueous solution containing fission product ions and said plutonium ions in a valent state not above 4 with an adsorbent comprising a substantially insoluble compound having a soluble monomeric anion which forms an insoluble compound with said plutonium ions in said valent state, washing a portion of the fission product values from the adsorbent with a dilute acid solution containing 2 mineral acids of a maximum total concentration of 3.4 N and thereafter eluting said plutonium values from the adsorbent with an acid of a concentration of about 7 N solution.

4. A method of separating fission product values from plutonium values present in a maximum valent state of +4 in a mineral acid aqueous solution, which comprises contacting said aqueous solution with a salt the anion of which forms an insoluble compound with said plutonium values whereby said plutonium values and some of said fission product values are adsorbed on said salt, said salt being selected from the group consisting of zirconium orthophosphate and barium iodate; eluting said adsorbed fission product values by contacting said salt with a mixture of nitric and phosphoric acids the total concentration of said acids being between 1.1 and 3.4 N; and then eluting said plutonium values with a mineral acid of a concentration of about 7 N.

5. The process of claim 4 wherein said mineral acid aqueous solution contains hydrochloric acid and phosphoric acid and the mineral acid for eluting the plutonium is nitric acid.

6. The process of claim 4 wherein said mineral acid aqueous solution contains nitric acid and phosphoric acid and the mineral acid for eluting the plutonium is nitric acid.

7. The process of claim 6, wherein the mineral acid aqueous solution to be treated contains nitric acid in a concentration of between 1 and 3 N and phosphoric acid in a concentration of between 0.02 and 0.4 N.

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