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2,902,340

CHEMICAL METHOD OF TREATING FISSIONABLE MATERIAL

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This invention relates to an improvement in the process of preparing a pure fissionable element.

It is known that when uranium is subjected to neutron bombardment there is formed in small quantities a new element having an atomic weight of 239 and atomic number of 93, known as neptunium (symbol Np). This new element by radioactive decay is transformed through a half-life of 2.3 days to a further new element having an atomic weight of 239 and atomic number 94, known as plutonium (symbol Pu). Other isotopes of plutonium may also be formed. In addition certain other elements are formed as a result of fission of the uranium 235 nucleus such new elements being referred to as fission fragments or, including radioactive decay products thereof, as fission products. The fission fragments include two general element groups, a "light" fission fragment group such as Br, Kr, Rb, Sr, Y, Zr, Nb, Mo, 43, Ru, and Rh, and a "heavy" fission fragment group such as Sb, Te, I, Xe, Cs, Ba, La, Ce, Pr and Nd. In radioactive decay many of the fission fragments form other short lived products. As a result, the radioactivity of the mass of uranium remains at a high and very dangerous level for some time following high density neutron bombardment. It is particularly desirable to separate the plutonium from the radioactive fission fragments and fission products, thereby removing from the mass subjected to neutron bombardment the radioactive materials and particularly the light elements such as light metals having very short half-lives and consequently high radioactivities.

Following the bombardment of uranium with neutrons to produce new elements as discussed above, the usual procedure is to dissolve the entire mass in an acid solution such as nitric acid. This solution will then contain the uranium, plutonium, and all of the other products of the neutron bombardment including radioactive fission products.

It is generally necessary to use an excess of concentrated nitric acid in order to obtain a practical rate of solution of the uranium. After the neutron irradiated uranium metal has been dissolved, however, it has been found that the presence of an excess of nitric acid interferes with the recovery of plutonium. Thus, if plutonium is removed from solution by adsorption on organic adsorbents, the presence of excess concentrated nitric acid seriously reduces the efficiency of the process and may even destroy the adsorbent.

In addition, the process of dissolving the bombarded uranium in concentrated nitric acid on a commercial scale oxidizes a substantial portion of the plutonium to its higher oxidation state. The most commonly used plutonium recovery method, namely by bismuth phosphate precipitation, does not work efficiently with plutonium in its higher state of oxidation or in the presence of excess nitric acid owing to the solubility of bismuth phosphate therein. Accordingly, it is necessary to both re-

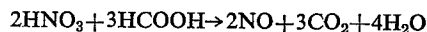
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move the excess nitric acid and reduce the plutonium to its lower valence state.

This excess of acid can be removed by neutralization with various bases but this introduces additional foreign ions into the solution. The deleterious effects of excess nitric acid can also be effectively avoided by lowering the concentration thereof to such an extent that it does not interfere with the recovery processes. Such dilution, however, is undesirable since it increases the total volume of material to be handled to an impractically large degree.

The oxidized plutonium can be reduced by means of a number of specific reducing agents such as ferrous ion, uranous ion, and the like. These reducing agents, however, introduce foreign elements that must themselves be removed before plutonium can be recovered in pure form.

It has now been discovered that the removal of excess nitric acid and the reduction of any oxidized plutonium present may be accomplished while avoiding the above mentioned difficulties. In accordance with the present invention, these objectives are attained by use of formic acid as a reducing agent. Formic acid is a reducing agent that is capable of reducing plutonium in its higher oxidation state to a valence state not greater than 4. In addition, the formic acid destroys excess nitric acid present by reacting with nitric acid probably in accordance with the following equation:



According to this reaction, the nitric acid decomposes to yield nitric oxide, carbon dioxide, and water. The two former impurities, being gases, are readily removable from the aqueous solution. Thus, an important feature of the use of formic acid is the fact that no foreign elements are introduced into the solution by its use.

The use of formic acid to remove the excess nitric acid is effective either when used in 20 percent uranyl nitrate solutions or in hot solutions as they come from the dissolver where the concentration is about 70 percent. The reaction is more rapid in the latter case and the rise in temperature obtained thereby is desirable since complete reaction is insured, and the gases formed are eliminated. An additional advantage in adding formic acid to hot solutions in the dissolving vessel lies in the fact that such a vessel is normally equipped to handle the gases given off which might be objectionable at other points in the process.

When the neutron bombarded uranium is dissolved in nitric acid, usually a sufficient excess of concentrated nitric acid is used so as to give a solution containing about 70 percent uranyl nitrate. In its further treatment, the solution may be diluted to give a lower uranyl nitrate concentration, for example, 40 percent or 20 percent with corresponding decrease in nitric acid concentration.

The action of formic acid varies with the concentration of the solutions treated. With a concentration of 70 percent uranyl nitrate, the reduction proceeds vigorously; with 40 percent solutions, the reduction is rather rapid, and slow with solutions of about 20 percent concentration. The amounts of formic acid required may also vary. With 70 percent solutions of uranyl nitrate, one mole of formic acid is sufficient to remove one mole of nitric acid. In 40 percent solutions, about 1½ moles of formic acid are generally employed for each mole of nitric acid in order to obtain optimum results; however, with equal molar concentrations of formic and nitric acids, it has been observed that at least 80 percent of the plutonium is reduced. In 20 percent uranyl nitrate solutions, one mole of formic acid removes only about one-fifth mole of the nitric acid present in one hour under ordinary conditions of operation. In general, it

may be said that the less concentrated the solution is with respect to uranyl nitrate, the more formic acid required to effect a satisfactory reduction of plutonium.

Other factors affecting the use of formic acid include the size of the reacting vessel, the depth of the solution, the degree of agitation, the temperature at which the reaction is carried out, and the presence or absence of sulfuric acid. The temperature effect is shown by tests where the use of 90° C. gave very rapid action and 75° C. gave moderate speed of reaction. In this connection it should be pointed out that in the recovery of plutonium from solutions of the class contemplated in the present invention by methods involving the utilization of adsorbents, it has been discovered that this object can be best accomplished by maintaining the acidity of said solutions at a value of not more than about 0.5 N.

It has been found that the presence of sulfuric acid or phosphoric acid improves the efficiency of the process, particularly by making it run more rapidly. The theoretical explanation for the improvement owing to sulfuric acid is not definitely known. It has been observed, however, that the presence of sulfuric and phosphoric acid improves the overall yield of plutonium on precipitation.

The following example illustrates the process of the present invention and the relatively wide range of conditions that may be employed in obtaining substantially complete reduction of plutonium:

Example 1

Formic acid was used as a reducing agent for plutonium in solutions of neutron irradiated uranyl nitrate. The experiments were carried out in glass to avoid possible reduction of the product. Starting solutions were prepared using uranyl nitrate hexahydrate made up to a 50 percent solution containing added nitric acid and oxidized plutonium (hexavalent plutonium).

The amount of plutonium present was measured in each case by the number of alpha counts per minute per gram of uranyl nitrate hexahydrate as determined with a Geiger-Müller counter. In this solution, 97.8 percent of the plutonium was in the higher (above 4) oxidation state.

In these tests three conditions were selected: (1) the starting solution contained 50 percent uranyl nitrate and 5.5 percent nitric acid, the ratio of formic acid to nitric acid being 1.5:1; (2) the starting solution contained 50 percent uranyl nitrate and 1.38 percent nitric acid, the ratio of formic acid to nitric acid being 1.5:1; and (3) the starting solution contained 50 percent uranyl nitrate and 5.5 percent nitric acid, the ratio of formic acid to nitric acid being 0.375:1. In all cases the formic acid was added at a constant rate below the surface of the boiling uranyl nitrate solution for a measured period of time. After the formic acid was added, the solutions were then boiled one hour. The results obtained appear in the table below:

Run Number.....	1	2	3
Percent Uranyl Nitrate.....	50	50	50
Plutonium Content in Alpha c./m./g. of Uranyl Nitrate Hexahydrate (97.8% oxidized).....	118.5	118.5	118.5
HNO ₃ Concentration in 50% Uranyl Nitrate Hexahydrate Solution, percent.....	5.52	1.38	5.52
Excess Acidity Based on 20% Uranyl Nitrate Hexahydrate Solution.....	0.4 N	0.1 N	0.4 N
Plutonium in Valent State of 4 or Below Present in Starting Solution, percent.....	4.35	3.75	4.35
Moles HCOOH/mole HNO ₃	1.5	1.5	0.375
Addition Time, hours.....	2	0.5	0.5
Supplementary Boiling, hours.....	1	1	1
Percent Plutonium Reduced.....	99.4	99.8	99.6
Residual Acidity (HNO ₃) Based on 20% Uranyl Nitrate Hexahydrate Solution.....	0.03 N	0.06 N	0.34 N

The first of these solutions, containing the reduced plutonium, was treated to remove plutonium by precipitation of bismuth phosphate as a carrier in accordance with the process described in United States application for Letters Patent of Glenn T. Seaborg et al., Serial No. 478,570, filed March 9, 1943 now Patent No. 2,799,553.

The solutions obtained from runs 2 and 3 were introduced into adsorption columns filled respectively with columbic oxide and Amberlite IR-1 resin (a formaldehyde-sulphonated phenol condensation product) whereby the plutonium present in said solutions was adsorbed thereon and subsequently removed from the adsorbents by the use of a suitable eluting agent such as, for example, 1.25 N sodium bisulphate.

As pointed out above, it has been found in accordance with the present invention that formic acid may be used for the dual purpose of reducing plutonium in nitric acid solutions and destroying excess nitric acid present. Thus, by one simple operation and without the addition of undesirable foreign elements, the plutonium is reduced to a valent state not greater than 4 in which it may be readily removed by precipitation or adsorption, and the excess nitric acid which might interfere with precipitation and adsorption processes is destroyed.

It will be apparent to those skilled in the art that the process of the present invention is susceptible of numerous modifications without departing from the scope thereof. It is, therefore, to be strictly understood that any such modifications are to be regarded as lying within the scope of the present invention.

What is claimed is:

1. In a process for the recovery of plutonium values from an aqueous nitric acid solution containing hexavalent plutonium ions, the step which comprises treating said solution with formic acid whereby plutonium is reduced to a valence state of not greater than +4 and the free nitric acid is destroyed and eliminated.

2. A process for separating plutonium values from nitric acid-containing solutions of hexavalent plutonium salts, comprising treating said solutions with formic acid at elevated temperatures whereby plutonium is reduced to a valence state of not greater than +4 and the free nitric acid is destroyed and eliminated, and then recovering the plutonium from the solution thus treated.

3. A process for separating plutonium values from nitric acid-containing solutions of hexavalent plutonium salts, comprising treating said solutions with a mixture of formic acid and sulfuric acid at elevated temperature whereby plutonium is reduced to a valence state of not greater than +4 and the free nitric acid is destroyed and eliminated, and then recovering the plutonium from the solution thus treated.

4. A process for separating plutonium values from nitric acid-containing solutions of hexavalent plutonium salts, comprising treating said solutions with a mixture of formic acid and phosphoric acid at elevated temperature whereby plutonium is reduced to a valence state of not greater than +4 and the free nitric acid is destroyed and eliminated, and then recovering the plutonium from the solution thus treated.

5. A process for separating plutonium values from nitric acid-containing solutions of hexavalent plutonium salts, comprising treating said solutions at a temperature of from 75 to 98° C. with formic acid in quantities of from 1 to 1.5 moles of formic acid per one mole of nitric acid, whereby plutonium is reduced to a valence state of not greater than +4 and the free nitric acid is destroyed and eliminated, and then recovering the plutonium from the solution thus treated.

6. In a process for separating plutonium, uranium, and fission products, the steps of treating a nitric acid solution containing salts of hexavalent plutonium, uranium, and of fission product elements with formic acid at an elevated temperature whereby plutonium is reduced to a valence state of not greater than +4 and the free nitric

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acid is destroyed and eliminated, and then recovering the plutonium from the solution thus treated.

7. A process for separating plutonium from nitric acid-containing solutions of hexavalent plutonium salts, comprising treating said solutions with formic acid at an elevated temperature whereby plutonium is reduced to a valence state of not greater than +4 and the free nitric acid is destroyed and eliminated, and then recovering the plutonium from the solution thus treated by adsorbing it with an ion exchange material.

8. A process for separating plutonium from nitric acid-containing solutions of hexavalent plutonium salts, comprising treating said solutions with formic acid at an elevated temperature whereby plutonium is reduced to a valence state of not greater than +4 and the free nitric

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acid is destroyed and eliminated, and then recovering the plutonium from the solution thus treated by precipitating it with a bismuth phosphate precipitate.

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