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SEPARATION OF FISSION PRODUCTS BY ADSORPTION FROM ORGANIC SOLVENTS

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This invention relates to a process for separating rare earths from uranium and, particularly, to the separation of the fission product rare earths from neutron-irradiated uranium.

Reference herein to any of the elements is to be understood as denoting the element generically whether in its "elemental" state or in the form of a compound, unless otherwise indicated by the context.

One of the results of neutron-irradiation of uranium in neutronic reactors of the pile type such as are disclosed in copending application Serial No. 568,904 of Fermi and Szilard, filed in the U. S. Patent Office on December 19, 1944, is the formation in the neutron-irradiated uranium of fission products. These fission products are highly radioactive isotopes of the elements from atomic number 31 to atomic number 66. The concentration of these fission products in the neutron-irradiated uranium is very small, rarely exceeding one thousand parts of fission products per million parts of uranium. These fission products are extremely valuable substances since they may be used as radioactive tracers in many fields of research; they may also be used as sources of radioactivity in therapeutic treatment, and there are many other uses for them. It is necessary for all of these uses, however, that they be separated from the uranium. It is also necessary, in order that the neutron-irradiated uranium be made available for use in a neutronic reactor again, that the fission products be separated from said neutron-irradiated uranium. Because of the high radioactivity of neutron-irradiated uranium, due, particularly, to the presence of the radioactive fission products, it is necessary that any method of separation of fission products from neutron-irradiated uranium be capable of being carried out by remote control. Another limitation upon a separation process for the separation of fission products from uranium, imposed by the fact that fission products are present in such small concentrations, is that the process be quite efficient.

An object of this invention is to separate rare earths from uranium.

An additional object of this invention is to provide a simple and efficient method of separating radioactive rare earth fission products from neutron-irradiated uranium.

Still further objects of the present invention will be apparent from the following detailed description of this invention.

The process of this invention comprises, broadly, the formation of an organic solvent solution containing uranium and a rare earth and the contacting of this solution with a siliceous adsorbent whereby the rare earth is selectively adsorbed from the solution, leaving the uranium in solution.

The process of this invention is particularly adapted to the separation of rare earth fission products from neutron-irradiated u ranium. The process is efficient, giving separations of better than 99% of rare earth fission products in a single cycle. Furthermore, it may be conveniently used as a cyclic operation, incorporating as many cycles

as is necessary to achieve maximum decontamination. The process is suitable for use on a large scale and the process is readily adaptable for remote control operation. Although, as previously mentioned, this process is particularly adaptable to the separation of rare earth fission products from neutron-irradiated uranium, it also may be used for the separation of rare earths from a uranium solution which is nonradioactive.

The preferred embodiment of this invention is concerned with the separation of radioactive fission product rare earths from neutron-irradiated uranium. Neutron-irradiated uranium, following its removal from the pile, is normally dissolved by treating it with concentrated nitric acid. The uranyl nitrate hexahydrate thus formed is then diluted to between about 2% and 20% concentration. The uranium is then often extracted from the aqueous solution by treatment with an organic solvent. There are several types of organic compounds that are satisfactory solvents. These types include ethers, glycol ethers, esters, ketones, alcohols, alkyl phosphates, nitrohydrocarbons, and alkyl sulfides. A common structural property of all of these types of compounds is that they have an atom capable of denoting an electron pair to a coordination bond. The extractive solvent is a liquid substantially immiscible with water and aqueous solutions. If it is a solid at room temperature, the extraction is carried out above its melting point. The following is a list of compounds that are often used as extractants for the separation of uranium from aqueous solutions:

Ethyl ether
Isopropyl ether
Butoxyethoxyethane (ethyl butyl Cellosolve)
Diethyl ether of ethylene glycol (diethyl Cellosolve)
Dibutyl ether of diethylene glycol (dibutyl Carbitol)
Dibutyl ether of tetraethylene glycol
Ethyl acetate
n-Propyl acetate
Butoxyethoxyethyl acetate (butyl Carbitol acetate)
Methyl isobutyl ketone (hexone)
Acetophenone
Mesityl oxide
Cyclohexanone
Tert-amyl alcohol
2-ethyl-1-hexanol
Tributyl phosphate
Trioctyl phosphate
Dioctyl hydrogen phosphate
Octadecyl dihydrogen phosphate
Nitromethane
Ethyl sulfide
n-Propyl sulfide

The extraction of the neutron-irradiated uranium into an organic solvent of an aqueous solution will effect a partial separation of radioactive fission products from the uranium since the uranium is more soluble in the organic solvent than the fission products. In certain instances, however, it is important that a very high degree of separation between the radioactive rare earth fission products and the uranium be obtained, particularly so where the uranium is to be re-used in a neutronic reactor, for example, of the power pile type. Most of the rare earth fission products have a very high thermal neutron capture cross-section, particularly gadolinium, which has a cross-section of approximately thirty thousand barns. Therefore, it is extremely important that uranium, which is to be re-used in a neutronic reactor, be free of all fission products, particularly gadolinium. By the process of this invention, the organic solution containing uranium and rare earth fission products is treated with an adsorbent of the siliceous type. Examples of suitable adsorbents of this type include silica gel, bentonite, and fuller's earth. Fuller's earth, which we have found to be particularly

suitable, is comprised of an active or activable clay containing approximately 50% silicon dioxide, 10% aluminum oxide, 10% magnesium oxide, and small percentages of other oxides, such as ferric oxide, titanium dioxide, calcium oxide, potassium oxide, sodium oxide, phosphorus oxide, sulfur trioxide and carbon dioxide. Should an activable clay be used, it may be advisable to activate the clay prior to use in order to achieve a higher percentage of separation. The adsorbent may be introduced into the organic solution in a batch method. By the preferred method, however, the organic solvent is passed through beds of the adsorbents. The efficiency of the separation will depend to a certain extent upon the amount of adsorbent used in comparison to the amount of rare earths. It has been found that where an ether solution and a fuller's earth adsorbent are used, approximately 100% separation may be obtained by using a sufficient amount of adsorbent, for example, 20 g. of adsorbent per 50 ml. of ether solution of uranyl nitrate and radioactive fission products.

The operation of this invention may be more fully understood by reference to the following description of tests made employing silica gel and fuller's earth as adsorbents, uranyl nitrate, and gadolinium as a representative radioactive rare earth fission product. Various concentrations of uranyl nitrate in an organic solvent were prepared by extracting uranyl nitrate hexahydrate in aqueous solution into a diethyl ether solvent. The concentrations of the solutions ranged from 0.3 to 1.5 M, the latter being essentially saturated. The water layer which separated out and which comes from the water of hydration in the uranyl nitrate hexahydrate was then discarded. Tracer quantities of radioactive gadolinium in the form of gadolinium nitrate was then added to the various ethereal uranyl nitrate solutions. These solutions were shaken vigorously to dissolve the gadolinium nitrate. The extraction process was then carried out by placing 50 ml. of the ethereal uranyl nitrate solution containing the gadolinium into a glass-stoppered graduated cylinder; the quantity of adsorbent desired in the 200 mesh size was then added, and the mixture agitated for a period of from five to ten minutes. The mixture was allowed to stand until the adsorbent had completely settled. A few drops of the clear supernatant liquid was then withdrawn and placed on a small thin platinum foil, and the solution then allowed to evaporate to complete dryness. The foils were weighed both before the addition of the sample and after the complete evaporation of the ether, thus allowing the determination of the weight of the salts in solution. Similar samples had been taken before the addition of the adsorbents. The activity of the salts on the foil was determined by placing the foil in a special holder which was then placed in close contact with a Geiger-Müller counter, thus determining the beta ray activity. The procedure followed the usual radiochemical techniques. The following table gives the results obtained with silica gel and fuller's earth as adsorbents at various concentrations of uranyl nitrate in diethyl ether solution.

From the table it is apparent that the fuller's earth is a more efficient adsorbent for radioactive rare earths than the silica gel and the other adsorbents. It is also readily apparent that nearly complete separation of a rare earth from uranium values may be achieved by a single adsorption cycle where a sufficient amount of adsorbent is used.

Following the separation of the rare earths from uranium by the process of this invention, the rare earths may be recovered from the adsorbent by any of the usual

methods, such as, for example, by desorption with suitable solvents. Aqueous acidic solutions have been found to be particularly suitable desorbents for the rare earths.

Removal of gadolinium from ether solution of uranyl nitrate by adsorbents

Grams adsorbent per 50 ml. solution	Initial molarity of uranyl nitrate	Initial gadolinium beta activity in solution [1]	Final gadolinium beta activity in solution [1]	Activity adsorbed [1]	Percent gadolinium adsorbed
Silica Gel:					
0.0	0.3	66,000			
4.0	0.3	66,000	39,600	26,400	0
8.0	0.3	66,000	33,660	32,340	40
12.0	0.3	66,000	19,800	46,200	49
0.0	1.3	23,000			ca. 70
8.0	1.3	23,000	9,200	13,800	0
12.0	1.3	23,000	8,050	14,950	60
16.0	1.3	23,000	7,130	15,870	65
0.0	1.5	3,000			69
8.0	1.5	3,000	390	2,610	0
12.0	1.5	3,000	180	2,820	87
16.0	1.5	3,000	420	2,560	94
Fuller's Earth:					(86)
0.0	ca. 1.3	23,500			
10.0	ca. 1.3	23,500	2,115	21,385	0
0.0	0.7	10,200			91
5.0	0.7	10,200	816	9,384	0
10.0	0.7	10,200	612	9,588	92
15.0	0.7	10,200	204	9,996	94
20.0	0.7	10,200	102	10,098	98
					99

[1] Counts of beta activity per minute per gram of uranyl nitrate, corrected for UX_1.

The foregoing illustrations and embodiments of this invention are not intended to limit its scope, which is to be limited only by the appended claims.

What is claimed is:

1. A method of separating rare earth values from uranium values, which comprises contacting an organic solution containing dissolved uranium values and rare earth values with a siliceous adsorbent whereby rare earth values are adsorbed, leaving the uranium values in solution.

2. A process of separating a radioactive rare earth fission product from neutron-irradiated uranium, which comprises contacting an organic solution containing neutron-irradiated uranyl nitrate and a radioactive rare earth fission product with a siliceous adsorbent whereby the radioactive fission product is adsorbed thereon, leaving the neutron-irradiated uranium in solution.

3. The process of claim 2 wherein the radioactive rare earth fission product is gadolinium.

4. The process of claim 2 wherein the radioactive rare earth fission product is neodymium.

5. The process of claim 2 wherein the radioactive rare earth fission product is cerium.

6. The process of separating neutron-irradiated uranium values from gadolinium values, which comprises treating a diethyl ether solution of uranyl nitrate containing gadolinium nitrate, with a fuller's earth adsorbent whereby the gadolinium values are adsorbed thereon.

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