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PROCESS FOR SEPARATING URANIUM FISSION PRODUCTS

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FIG. 1.

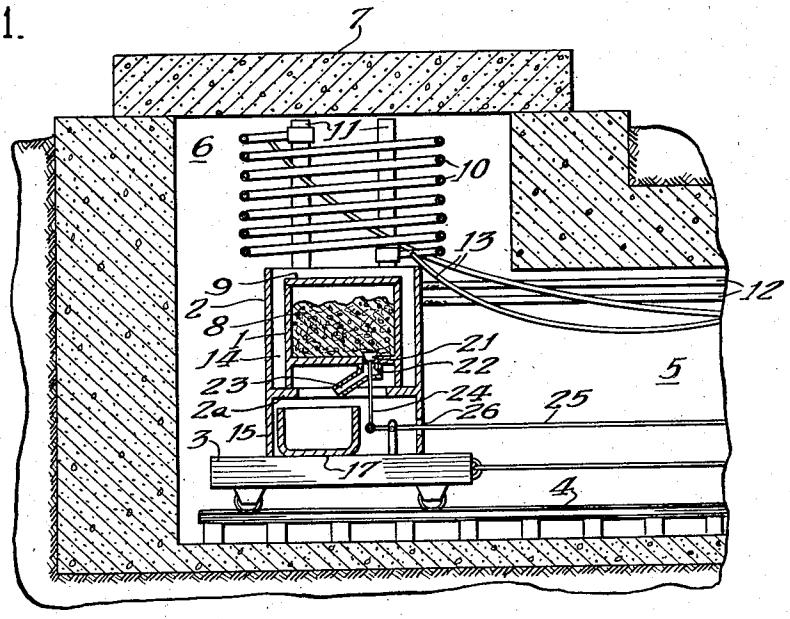
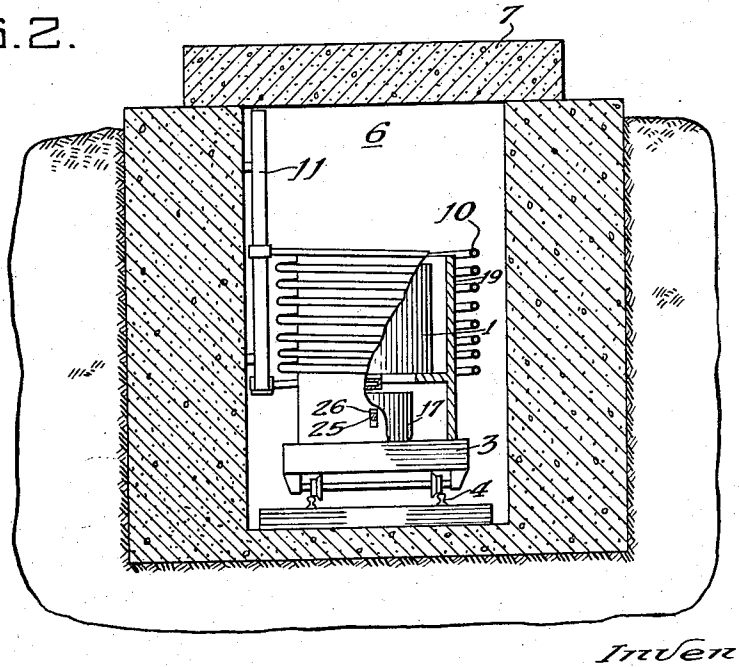


FIG. 2.



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PROCESS FOR SEPARATING URANIUM FISSION PRODUCTS

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12 Claims. (Cl. 75—84.1)

Our invention relates to the purification of neutron irradiated uranium metal and more particularly to the removal of highly radioactive substances from neutron irradiated uranium.

The term "element 94" is used throughout this specification to designate the element having atomic number 94. The designation 94^{239} refers to the isotope of element 94 having a mass number of 239. Element 94 is also referred to in this specification, and probably will become known in the art, as plutonium, symbol Pu. Likewise, element 93 means the element having atomic number 93, which is also referred to as neptunium, symbol Np. 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 otherwise indicated by the context.

Natural uranium comprises largely isotope U^{238}, together with about $1/139$ as much U^{235} and a very much smaller amount of U^{234}. When this or other mixture of the isotopes U^{235} and U^{238}, either as metallic uranium or as a uranium compound, is subjected to bombardment by neutrons or undergoes a self-sustaining neutronic chain reaction, a number of nuclear reactions take place. Isotope U^{238} captures neutrons to form U^{239}, which undergoes beta decay to form transuranic elements:

$$U^{238} + {}_0n^1 \longrightarrow U^{239} \xrightarrow{23\ \text{min.}\ (B^-)} 93^{239} \xrightarrow{2.3\ \text{Days}\ (B^-)} 94^{239}$$

Isotope U^{235} undergoes fission, i. e., a breakdown of its heavy nucleus into lighter fragments which are generally very unstable and highly radioactive. Such fragments usually undergo beta-particle disintegration in successive steps, leading ultimately to stable isotopes of higher nuclear charge than the original fragments. The fission of U^{235} is predominantly binary, and may be exemplified by the following type of equation:

$$U^{235} + {}_0n^1 \rightarrow Kr^{92} + Ba^{141} + x_0n^1 + 175\ \text{m. e. v.}$$

where x is a small number greater than unity.

Substantially all of the fission fragments have mass numbers wtihin the range 77–158, although small quantities of isotopes of lower and higher mass numbers may result from unbalanced binary fissions, ternary fissions, or other reactions of infrequent occurrence. A very large majority of the fission fragments comprises a light group of mass numbers 84–106 and a heavy group of mass numbers 128–150.

The various fission fragments and decay products of the initial fission fragments are referred to herein as fission products. These fission products predominantly fall within a range of atomic numbers from about 32 to about 64. The fission products from the light group of fragments referred to above have atomic numbers ranging from about 35 to about 46; and the fission products from the heavy group of fragments have atomic numbers ranging from about 51 to about 60.

The various radioactive fission products have half-lives ranging from a fraction of a second to thousands

of years. The effect of those having very short-lives may be practically 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 may 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, and Ru of the light group and Te, I, Cs, Ba, La, Ce and Pr of the heavy group.

The total amount of 93^{239} and 94^{239} produced from U^{238} in natural uranium by neutron bombardment is a function of neutron density and of the time of bombardment. Since 94^{239} is fissionable under the conditions for fission of U^{235}, the net yield of 94^{239} per unit of time will decrease as the ratio of U^{235} content to 94^{239} content of the mass decreases. For this reason, a neutronic reaction for 94^{239} production is suitably terminated when only a fraction of the U^{235} has been converted to fission products. The reaction mass at this point contains a large amount of U^{238}, a much smaller amount of U^{235}, still smaller amounts of 93^{239}, 94^{239} and fission products, and traces of other products such as UX_1 and UX_2. By aging such a mass for a suitable period of time, the 93^{239} may be substantially completely converted to 94^{239} or at least until the 94 content exceeds the 93 content of the irradiated product, with simultaneous conversion of at least a portion of the short-lived radioactive fission products to longer-lived or stable isotopes.

The plutonium content of the aged reaction mass will usually be considerably less than 1 percent of the weight of the unreacted uranium, and may even be less than one part by weight per million parts by weight of uranium. The concentration of fission products will be of the same order of magnitude.

The problem of securing a satisfactory removal of the fission products from the uranium and thereby reducing the radio-activity thereof is difficult particularly because of the low concentrations of the fission products which are present.

In accordance with the present invention it has been found that fission products may be removed and the radioactivity of the uranium reduced to a substantial degree from neutron irradiated uranium by heating neutron irradiated uranium in metallic state to a temperature above 1000° C., preferably fusing the metal and removing the fission products or a portion thereof. In general the fission products are transferred to a different phase and are removed in the form of such a phase. For example numerous products such as radioactive barium, strontium, cesium, rubidium, iodine etc. may be vaporized from uranium metal at least to an appreciable degree. Moreover if the uranium is maintained in molten state at the proper time gaseous decay products of the fission fragments such as rare gases including radioactive xenon will be released.

In addition removal of certain of the fission products may be facilitated by introducing agents into the melt which convert the fission product to a more volatile composition which can vaporize from the melt or to a composition of higher melting point or other composition point which can separate as a solid scum or molten slag. For example an uranium halide or other halide such as uranium tetrafluoride, tetrabromide or calcium fluoride or carbon tetrachloride or elemental halogen such as iodine, may be added to extract certain of the radioactive isotopes by permitting stratification of the added halide or converting the isotope itself to a volatile or more easily removable halide and permitting vapori-

zation or separation thereof. Where the fission products are removed by aid of a slag forming agent such as UF_4 or alkali metal or alkaline earth metal halides, the slag serves to extract the fission product from the uranium. Proper precautions are generally observed to secure sufficient contact between the slagging component and the uranium as will be understood in the art.

In accordance with a further modification the uranium may be melted with carbon, preferably below 1650° C. where the amount of uranium carbide formation is low, and in such a case certain of the fission products are removed probably by formation of high melting point carbides which separate as a scum or slag or are absorbed or adsorbed by the carbon. Thus cerium, lanthanum, yttrium and zirconium may be effectively removed when the uranium is melted in contact with carbon at a temperature below that at which substantial uranium carbide is formed, preferably below 1650° C. This process usually results in formation of a slag comprising the carbides of the impurities and the purified metal may be tapped from beneath the slag and cast.

Numerous other modifications may be resorted to. For example molybdenum and tellurium may be removed to an appreciable degree by adding nonradioactive isotopes of these metals to the uranium and heating the molten mass in contact with limited supply of oxygen sufficient to form oxides of these agents without formation of excessive amounts of uranium oxide. In such a case the molybdenum and tellurium oxides formed are vaporized and removed.

As another example a nonradioactive isotope of a fission product or an isotope of lower activity may be added and removed by vaporization and/or slagging as herein contemplated. Thus nonradioactive, or slightly radioactive iodine, tellurium, barium, cerium or rubidium may be added and vaporized off. In such a case a major portion of the more radioactive isotope of the same element is carried into vapor state and thereby removed thus decreasing the radioactivity. Likewise molybdenum may be added, converted to a carbide and purified uranium removed from the carbide which may appear as a slag or scum on the molten metal or may be picked up by solid carbon surfaces.

The invention may be more fully understood by reference to the following description of certain embodiments thereof and to the accompanying drawings in which:

Fig. 1 is a diagrammatic view in side elevation, partially in section, of an induction coil in combination with a crucible containing irradiated uranium, and other associated apparatus in which the present invention may be performed; and,

Fig. 2 is a diagrammatic cross sectional view of the chamber shown in Fig. 1 and showing the crucible partially in section.

Radioactive impurities in irradiated uranium may be one or more of the following: bromine, krypton, rubidium, strontium, yttrium, zirconium, columbium, molybdenum, gadolinium, ruthenium, rhodium, antimony, tellurium, iodine, xenon, cesium, barium, praseodymium, neodymium.

In Figs. 1 and 2 the apparatus for practicing our invention comprises a graphite crucible **1** supported within a stand **2** on a radial platform **2***a*, the stand **2** being carried by a cart **3**. The space between the crucible **1** and the stand **2** is filled with a suitable insulation **14** such as magnesia, zirconia or other refractory insulating material (not shown). As a shield against gamma ray radiation the cart **3** runs on a track **4** extending through concrete trench **5** into and out of a concrete pit **6** which is covered by a lead cover **7**. The graphite crucible **1** is loaded with a mass of irradiated uranium **8** and covered with a cover **9** while standing in the trench **5**, the cart **3** with a loaded crucible **1** is run into the pit **6** for purification of the irradiated uranium by heating and melting with consequent diffusion of the impurities. An induction coil **10** comprising hollow tubing and movable up and down on bus bars **11** attached to the side of pit **6** is designed to surround the stand **2** and crucible **1** and melt the uranium by induction when the cart **3** is positioned in the pit **6**. The coil **10** slides up to clear the stand **2** and permit the cart **3** to move in and out of the pit **6** for the purpose of loading and unloading the crucible **1**. A current is supplied to the coil **10** and bus bars **11** through leads **12** which are attached to terminals on the bus bars **11**. The leads **12** run from the pit **6** through the trench **5** to a suitable power source. The induction coil **10** is provided with a cooling system comprising flexible rubber tubes **13** connected to the top and bottom of the induction coil **10** to supply a flow of water which runs through the hollow interior of the tubing of coil **10**.

A mold **17** is placed on the cart **3** in a lower compartment **15** beneath the platform **2***a* and is so positioned that the molten uranium from the crucible **1** may be cast into it. The casting of the uranium into the mold **17** is accomplished by raising a plug **21** which seats in an aperture **22** in the bottom of the crucible **1**. The aperture **22** is set off center and has formed on its under or outer side a spout **23**. In casting the uranium or raising the plug **21** the molten uranium flows through the aperture **22** along the spout **23** and into the mold **17**. During the casting operation the plug **21** is raised by means of a rod **24** attached to the plug and pivoted on the end of a lever **25**, the lever **25** extending through an opening **26** in the stand **2** to a point where it may be manipulated without danger to the gamma radiation.

The preferred mode of purifying irradiated uranium will now be explained.

In the performance of the invention the crucible **1** and contents are covered by the cover **9** and the car **3** is then rolled into the pit **6** and positioned beneath the raised induction coil **10** as shown in Fig. 2. The induction coil **10** is then lowered over the stand **2** and crucible **1** into the position shown in Fig. 2 and the current turned on to heat the uranium mass generally to between 1200° C. and 1650° C. fusing the contents of the crucible. Where the crucible is made of graphite and/or where other slag forming ingredients are incorporated a slag of uranium-carbon alloy or other slag is formed, the uranium-carbon alloy slag tending to line the inner surface of the crucible. The metal is maintained in molten state for a substantial period of time usually approximately 2 hours or until a suitable separation of phases has occurred. Thereupon the plug **21** is forced upward by the levers **24** and **25** to allow flow of the melt of purified uranium into the mold **17**. The residue of the slag composed of the flux and the radioactive impurities clings to the wall of the crucible **1** and is thus separated from the purified uranium. The cart **3** is then drawn out of pit **6**, the mold **17** removed for further working of the purified uranium and the crucible **1** is disconnected from the levers **24** and **25** to be set aside for the radioactivity of the fission fragments in the slag to decay. A fresh crucible **1** and mold **17** are placed in the stand **2** on the cart **3** and the process is ready to be repeated.

In this apparatus the parts are inexpensive so that in the case of a breakdown the entire unit may be abandoned until the decay of radioactivity has proceeded to the point where repair can be made. In the same way the parts as they become radioactive may be discarded or set aside to allow for radioactive decay and fresh parts substituted for them. Moreover the arrangement of the apparatus and the procedure of the process permits the entire operation to be conducted by remote control and thereby eliminate many of the dangers from gamma or other radiation.

The metal thus purified is found to be sufficiently free from radiation and heating due to radioactive decay may be more safely handled than the raw irradiated uranium.

Thus the process serves as an initial treatment of the highly radioactive irradiated uranium to reduce the radioactivity to safe or manageable limits. The radioactive impurities may have considerable commercial value as a by-product and by their absorption in the uranium carbide or similar slag they are concentrated in a small volume of material. The radioactive elements are easily handled and stored in this medium and may be removed from the uranium carbide without having to work up the bulk of raw irradiated uranium thus making the recovery easier. The radioactive gases which evaporate from the fused irradiated uranium may be collected on charcoal if it is desired to effect their recovery or prevent their escape. The following examples are illustrative:

Example 1

Samples of neutron irradiated uranium containing several parts per million of fission products were heated in graphite crucibles at temperatures from 600° C. to 1800° C. for a period of about two hours and the amount of removal of the fission products determined by analysis. The following table shows the amount thus removed in percent of the amount of the radioactive isotope initially present.

PERCENT REMOVED

Element	600° C.	1,000° C.	1,200° C.	1,400° C.	1,800° C.
Rare gases	0.04	2.12	88.7	99.4	100
Iodine	0.007	0.98	84.4	98.8	100
Barium	0.0008	0.37	82.8	97.8	100
Strontium		0.25	84.8	99.5	100
Zirconium	0.0036	----------	79.5	95.4	----------
Average	0.013	0.93	84.0	98.2	100
Cerium	0.002	5.3	65.9	75.5	94
Praseodymium					
Lanthanum and Yttrium		3.6	73.8	80.4	----------
Average	0.002	4.5	69.8	78	94

About 70 to 80 percent of the total gamma activity was thus removed. Further removal may be effected by repeating this process.

Example 2

150 grams of neutron irradiated uranium which had received 53,000 microampere hours of neutron bombardment was heated in a graphite crucible to 1400° C. and a mixture of argon and nitrogen bubbled through the melt until one liter of nitrogen had been introduced. The molten metal was drained from the slag and analyzed. Fission products were removed as follows:

Element:	Percent removed
Ba	95
Sr	95
Te	66
Ce	98.7
Zr	71
Rare earths	97

The removal of tellurium, cerium and rare earths was substantially higher than when no nitrogen is used.

Example 3

A weakly bombarded sample of metal was run using 5 grams CaF_2 per 100 grams of metal as a flux for the purpose of determining the effect of such a flux in removing the fission products. The flux was placed in the bottom of the crucible, the uranium placed on top and the mass melted. The molten mass was heated for one hour at 1400° C. in a graphite crucible and a slag layer separated from the metal. The purified metal was tapped from the bottom of the crucible and cast. Upon examination of the cast metal it was found that the total gamma activity of the metal was reduced 74.25% when measured through 0.739 g./cm.^{2} Pb. The activities were divided about equally between the flux and the carbide. The use of the flux appeared to improve the quality of the recast.

Example 4

The process of Example 3 was repeated using UF_4 in lieu CaF_2. After heating for 2 hours the metal was cast and sampled. Then it was remelted to 1400° C. and carbon tetrachloride-argon mixture bubbled through the melt for about 2 hours. The metal was maintained at 1400° C. for 2 more hours in the absence of air and in a graphite crucible. The following table indicates the results:

Element	Remaining Percent Before CCl_4 Treatment but After UF_4 Treatment	Remaining Percent After CCl_4 Treatment
Radioactive Xe	0.006	None found.
Radioactive I	0.0	Do.
Radioactive Ba	<2	Do.
Radioactive Sr	<2	Do.
Radioactive Mo	94	68.
Radioactive Te	69	61.
Radioactive Ce	1.4	0.3.
Radioactive La and Y	1.9	None found.
Radioactive Zr	2.5	Do.
Radioactive 93	90	90.
Radioactive 94	90	90.
Radioactive Ux	12.8	None found.

It will be apparent to those skilled in the art that various modifications may be made without departing from the principles of the invention as disclosed herein and for that reason it is not intended that the invention should be limited other than by the scope of the appended claims.

Having thus described our invention the following is claimed:

What is claimed is:

1. A process for separating radioactive fission products from metallic uranium containing said elements in a mixture, comprising adding a reagent for said elements to said mixture, said reagent being selected from the group consisting of uranium halide, and carbon; melting said mixture while in contact with said reagent; maintaining said contact for a sufficient time for some of the radioactive fission products to react with the reagent; and separating the compounds formed of said elements from the metallic uranium.

2. The process of claim 1 wherein the mixture is held at a temperature of about 1400° C. during reaction.

3. The process of claim 1 wherein the reagent is uranium bromide.

4. The process of claim 1 wherein the reagent is uranium fluoride.

5. The process of claim 4 wherein the melted reaction mixture, after reaction at about 1400° C. for about two hours, is treated with a CCl_4-argon current for about two hours and thereafter a temperature of approximately 1400° C. is maintained in the absence of air for another two hours.

6. The process of claim 1 wherein the reagent is carbon, the reaction temperature approximately 1400° C. and a mixture of nitrogen and argon is bubbled through the molten mass during reaction.

7. The process of claim 1 where the reagent is carbon and the melted mixture remains in contact therewith for a sufficient time to form a carbide of one or more of the radioactive elements in the mixture.

8. The process of claim 1 where the reagent is carbon and the melted mixture remains in contact therewith for about two hours.

9. The process of claim 7 where the temperature is maintained at about 1400° C.

10. The process of claim 7 where a mixture of argon and nitrogen is bubbled through the mixture.

11. The process of claim 8 where the temperature is maintained at about 1400° C.

12. The process of claim 1 where the reagent is a uranium halide.

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