Sept. 1, 1959 L. W. NIEDRACH ET AL 2,902,415

PURIFICATION OF URANIUM FUELS

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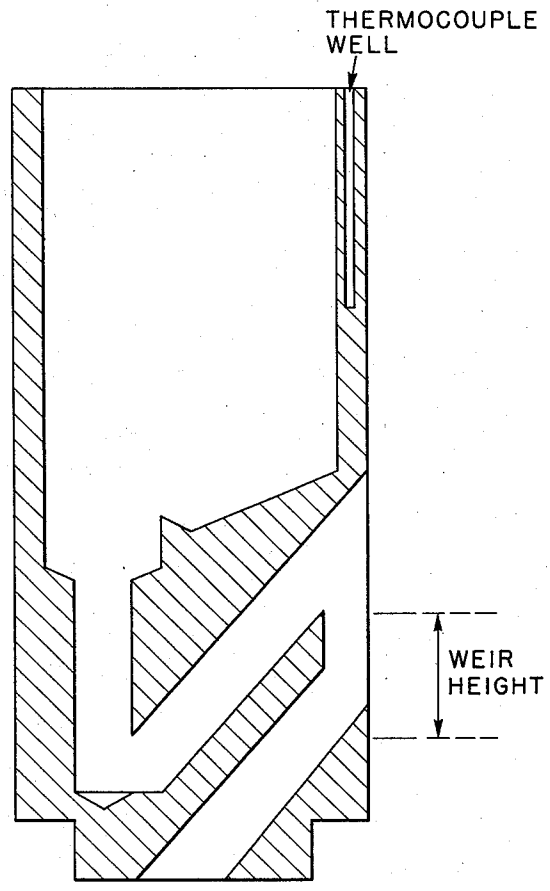


Fig. 1.

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CROSS SECTION OF ELECTROLYSIS CELL WITH PRODUCT COLLECTING WELL

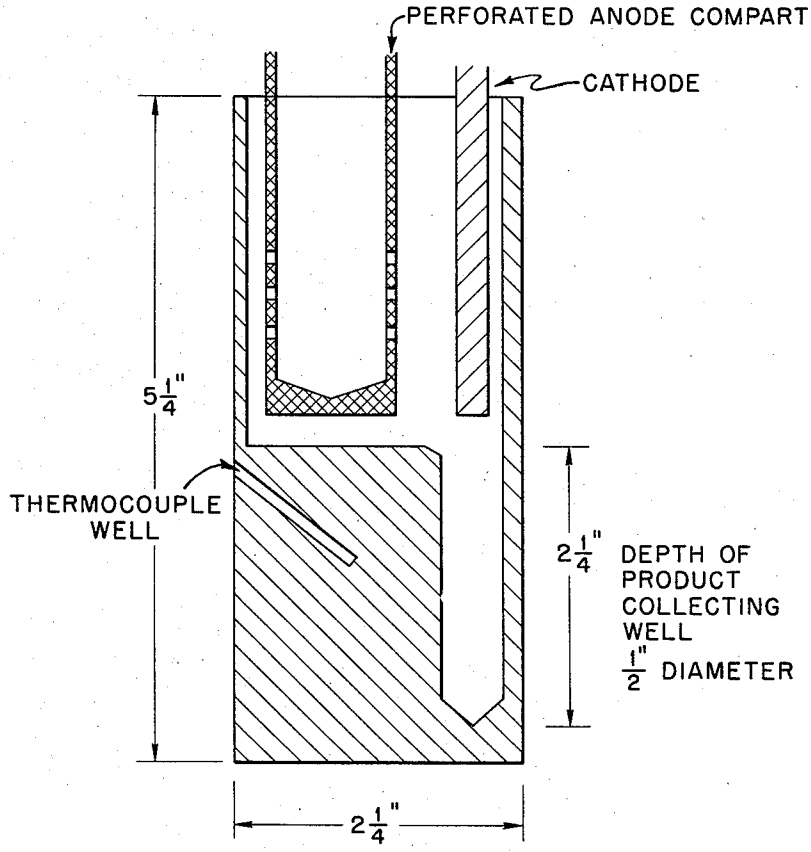


Fig. 2.

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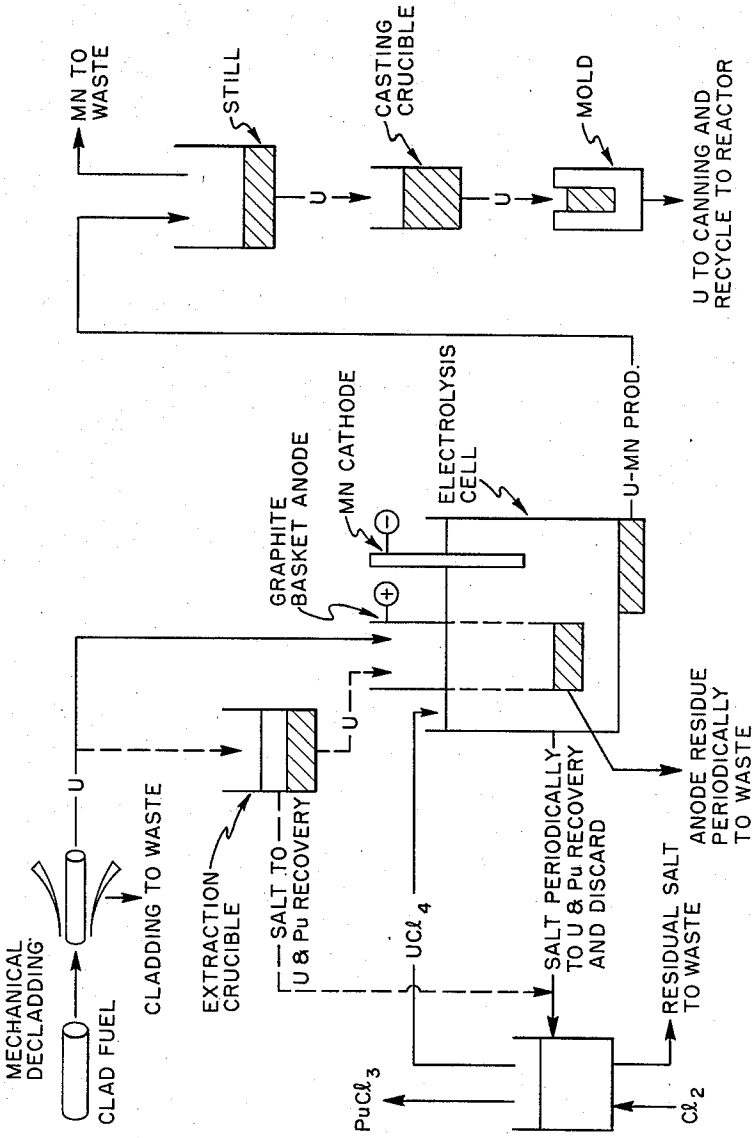


Fig. 3.

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United States Patent Office 2,902,415
Patented Sept. 1, 1959

2,902,415

PURIFICATION OF URANIUM FUELS

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Application October 3, 1956, Serial No. 613,797

3 Claims. (Cl. 204—1.5)

This invention relates to a method of purifying uranium fuel elements used in nuclear power reactors and more particularly to an electrorefining method for decontaminating the uranium from fuel elements in order to remove a large proportion of the fission products therefrom. This electrorefining is carried out using a molten salt electrolyte and by carrying on the electrolysis at such a temperature that a molten uranium containing product is formed at the cathode.

Because of the high melting point of uranium previous work on the electrodeposition of uranium from molten salt baths has resulted in the formation of solid dendritic deposits of uranium at the cathode. These deposits are contaminated with salt from the electrolyte.

This invention has as an object the provision of a method for purifying uranium from fuel elements to remove a large portion of the fission products therefrom which does not require dissolution of the fuel element in an aqueous solution. A further object of the invention is to purify the uranium from fuel elements by a pyrochemical decontamination method which is substantially as effective for removing fission products which are less chemically reactive than uranium as it is for removing fission products which are more chemically reactive than uranium. A still further object is to obtain a molten decontaminated uranium product by an electrorefining process which may be carried on well below the melting point of metallic uranium. Other objects will appear hereinafter.

In the drawings Fig. 1 is a view of one cell used in carrying out the process of this invention, and Fig. 2 is a view of another cell which may be used in place of the cell shown in Fig. 1. Fig. 3 is a flowsheet depicting the preferred embodiment of the invention described in Example 6.

In brief, the electrorefining process of the present invention involves making the uranium to be purified an anode in an electrolytic cell which contains a molten salt electrolyte composed of a mixture of a uranium halide and an alkaline earth metal halide and a cathode composed of a metal such as chromium, manganese, iron, cobalt or nickel which will form an alloy with uranium that melts considerably below the melting point of uranium. Electrolysis is carried out at a temperature high enough so that the uranium deposited on the cathode unites therewith to form a low melting binary alloy of uranium and the cathode metal which drips from the cathode during electrolysis. In its broader aspects this invention contemplates carrying on the electrolysis at a temperature above the melting point of uranium using a cathode made from a material which is not reactive with molten uranium such as graphite, tungsten, or molten uranium itself. This latter high temperature embodiment of the present invention is not to be considered a full equivalent of the embodiment in which a low melting binary alloy of uranium drips from the cathode, since the high temperature embodiment can only be carried

on with difficulty with presently available materials of construction for the cell.

If a uranium fuel is being decontaminated by the present invention it is preferable to employ a manganese cathode so that a U—Mn alloy will form from which the manganese can be readily separated by distillation. However, if a uranium-chromium alloy fuel element is being decontaminated, a chromium cathode is used, and instead of separating the chromium from the U—Cr alloy product, the U—Cr alloy product is adjusted with respect to its composition and then recast into a fuel element.

Figure 1 of the drawing shows a weir-type crucible made of graphite in which electrolyses for extended periods of time can be carried out. Use of this type of crucible allows the binary uranium alloy formed with the metal of the cathode to overflow to a collecting vessel as the electrolysis proceeds. Although a reservoir of the binary uranium-cathode metal alloy must be placed behind the weir prior to the addition of the fused salt, continuous electrolysis for long periods results in many throughputs through this alloy reservoir. Because the overflowing product drops to a collecting vessel, product alloy from short intervals of an extended run can be separated and analyzed. In this way, any variation in the alloy composition may be followed. Also, since anode and cathode weight losses can be taken without disturbing the crucible and its contents, the electrolysis can be resumed under a different set of electrolysis conditions while maintaining the same fused-salt and cell variables.

A second type of cell is illustrated in Figure 2. It employs a graphite anode basket and can be operated with a feed consisting of uranium pellets. For runs of short duration the product metal has been collected in a well of small diameter as shown in the diagram; however, the weir arrangement for removing product alloy, as shown in Figure 1, can also be used with such a cell arrangement.

In use the crucible is supported by molybdenum rods inside a chamber which consists of a lower cylinder and an upper cylinder suitably sealed together. The latter is closed on the top by a brass plate suitably sealed thereto. The entry of movable stainless steel electrode-supporting rods through vacuum seals attached to the brass plate permits adjustment of the depth of immersion of the electrodes in the fused-salt bath and allows continuous electrolysis to be maintained. The electrodes are insulated from each other by mounting the vacuum seals in insulator plugs, which in turn are attached to the brass plate.

A chromel-alumel thermocouple and the molybdenum supporting rods for the crucible enter the chamber through ball and socket joints on the top cylindrical section. The thermocouple is placed in the graphite crucible wall below the crucible top and definitely below the fused-salt bath surface. A tantalum shield serves as a heat reflector and allows temperatures in excess of 1200° C. to be obtained with a spark-gap converter under usual electrolysis cell conditions.

In all cases the assembled electrolysis apparatus is connected to a vacuum system employing a mercury diffusion pump capable of producing and maintaining a vacuum of one micron. Provision has been made for the addition of purified gases into the system. The electrolyses were run under a pressure of about one atmosphere of helium or argon to prevent excessive volatilization of the salt during operation. A continuous record is kept of the temperature, the cell voltage, and the cathode-crucible voltage during an electrolysis run.

The general operating procedure used during an electrolysis was as follows. The graphite crucible was degassed by heating to 1200° C. under vacuum and then

cooled in a helium atmosphere. This procedure was used to minimize surface contamination of the charged uranium as well as the alloy product. When a weir-type crucible was used, sufficient of the binary uranium cathode metal alloy was added to the degassed crucible to fill the weir passages and to overflow a small quantity of alloy. The melting of the alloy was carried out at low pressure, preferably at less than ten microns. The salt phase, which has been premelted under a hydrogen or helium atmosphere, was then added to the crucible. The crucible, electrodes, and other parts of the cell were then assembled, placed in a vacuum system, and heated. Heating of the electrolysis cell to about 500° C. was carried out at 25 microns or less pressure. Approximately one atmosphere of helium was then introduced into the system before the cell was heated to the operating temperature. When the electrolysis temperature was reached, the electrodes were lowered into the salt, and when the temperature had become stabilized the electrolysis was started and maintained at a constant amperage for a desired length of time. During a run the electrodes were lowered into the fused-salt bath as the voltage record indicated the need.

When the electrolysis run was completed and the circuit was opened, the electrodes were removed from the salt bath and the heating was stopped. The system was not opened until the temperature of the cell had fallen to 50° C. Opening of the system at higher temperatures would have resulted in oxidation of the alloy product which quickly would have prevented free flow of the product alloy from the weir opening.

The temperature during electrolysis has been varied from 850° C. to 1075° C. in various runs in which nickel cathodes were used. Within this temperature range it has been found that temperature has a negligible effect on cell efficiency. The range of temperature is, however, limited by salt volatilization at high temperatures and dendrite formation at low temperatures. An operating temperature as high as 1100° C. is possible with chloride containing baths, and dendrites have been observed at 850° C. Operating temperatures of 900° C. to 1050° C. are preferred.

It is recommended that low current densities be maintained at the anode in order to maintain good efficiencies. Current densities of between 0.1 and 0.3 ampere per square centimeter are recommended.

The composition of the salt bath seems to have a minor effect upon the cell efficiency. Salt baths consisting of a mixture of uranium halide and an alkaline earth metal halide and having the following compositions by weight have been successfully employed in carrying out applicants' invention: 66% UCl_3 and 34% BaF_2; 50% UF_4 and 50% BaF_2; 34% UF_4 and 66% $BaCl_2$; 38% UCl_3 and 62% BaF_2; 38% UCl_3 and 62% $CaCl_2$; and 76% UCl_3 and 24% $CaCl_2$. The uranium salt content of the salt bath should be kept above 30% if it is desired to avoid substantial contamination of the alloy dripping from the cathode with alkaline earth metal. In general, the salt bath should consist of an alkaline earth chloride or fluoride containing 30% or more by weight of a trivalent or tetravalent uranium fluoride or chloride such as UF_4 or UCl_3.

The following examples illustrate but do not limit the invention. In carrying out these examples use was made of the apparatus described above and the general operating procedure set forth above was observed.

Example 1

Into the anode compartment of the cell shown in Fig. 2, there was placed an anode charge consisting of a mixture of nine parts of unirradiated uranium with one part of irradiated uranium that had been cooled for nearly 3 years. The anode material of this run had an average level of approximately 1×10^7 counts per minute per gram of uranium in beta activity and 1×10^6 counts per minute per gram of uranium in gamma activity. This gave enough activity that the decontamination through the cell could be followed on the basis of the radioactivity. The molten salt used as electrolyte in this run consisted of 62% by weight of $CaCl_2$ and 38% by weight of UCl_3. A nickel rod was employed as a cathode. During electrolysis the temperature was maintained at about 900° C. A current of 10 amperes was used, and the run was terminated at the end of 55 ampere hours. The anode efficiency was 78%, and the U—Ni alloy obtained as a result of electrolysis contained 92% of U. On comparing the anode charge with the U—Ni alloy product it was found that considerable purification from fission products had been obtained. The cesium decontamination factor attained a value of 260, and the ruthenium decontamination factor was 250. The decontamination factor for the rare earths was 170. The strontium-yttrium decontamination factor was 80, and the zirconium-niobium decontamination factor was 80. It may therefore be appreciated that the electrorefining described in this example was a very effective decontamination technique.

Example 2

Into the anode compartment of the cell shown in Fig. 2, there was placed an anode charge consisting of a uranium base alloy containing 1% of ruthenium, 1% of molybdenum, and 1% of zirconium. The molten salt electrolyte used in this run consisted of 62% by weight of $CaCl_2$ and 38% by weight of UCl_3. The cathode was a nickel rod. During electrolysis the temperature was maintained at about 900° C. A current of 10 amperes was used, and the run was terminated at the end of 49 ampere hours. The anode efficiency was 58%, and the U—Ni alloy obtained by electrolysis contained 91% of U. On comparing the anode charge with the U—Ni alloy product it was found that the concentration of molybdenum in the anode charge was 500 times its concentration in the U—Ni alloy. Furthermore, the U—Ni alloy was decontaminated with respect to ruthenium by a factor of 400 and with respect to zirconium by a factor of 200.

Example 3

Into the anode compartment of the cell shown in Fig. 2, there was placed a charge consisting of ½ inch diameter rods of a uranium base alloy containing 0.92% of ruthenium, 1.01% of palladium, 0.97% of molybdenum, 0.94% of zirconium, and 0.32% of cerium. The molten salt electrolyte used in this run consisted of 62% by weight of $CaCl_2$ and 38% by weight of UCl_3. The cathode was a nickel rod. During electrolysis the temperature was kept at 900–950° C. A current of 7 amperes was used, and the voltage varied from ½ to 1½ volts. The run was terminated at the end of 20 hours after an anode weight loss of 167 grams and a cathode weight loss of 40 grams. The anode efficiency was 40%. The U—Ni alloy obtained by electrolysis contained 19.4% of nickel. On comparing the U—Ni alloy product with respect to the composition of the anode, it was found that there had been decontamination with respect to ruthenium by a factor of 150, decontamination with respect to palladium by a factor of 84, decontamination with respect to molybdenum by a factor of 130, and decontamination with respect to zirconium by a factor of 28. The decontamination factor for cerium was not determined. The anode residue retained the original form of the anode rod, and analyzed 2% in U, 12% in Zr, 30% in Mo, 16% in Ru, and 26% in Pd besides containing undetermined amounts of carbon and cerium. This showed that the electrolysis "leached" the uranium from the anode rod leaving a cellular network of the other metals behind.

Example 4

In the run described in this example a cell was used similar to the one shown in Fig. 2 but provided with a weir in its lower part like the cell shown in Fig. 1 so

that product metal could flow to collecting crucibles for sampling. Into the anode compartment of this cell there was placed a charge consisting of ½ inch diameter rods of a uranium base alloy containing 0.092% of ruthenium, 0.098% palladium; 0.093% of molybdenum, 0.088% of zirconium, and 0.01% of cerium. A mixture of $CaCl_2$ (62% by weight) and UCl_3 (38% by weight) served as the electrolyte. A helium blanket at one atmosphere was maintained throughout the run to prevent volatilization of the salt. A nickel rod which was rotated at 160 revolutions per minute to stir the salt bath and thereby improve the operation of the cell served as a cathode. The weir was charged with a U—Ni alloy containing 10.5% by weight of nickel. During electrolysis the temperature was kept at 900–950° C., but occasionally it was necessary to raise the temperature briefly to 1000° C. because of clogging of the weir. The higher temperature reopened the weir and resulted in free flowing of the metal for a number of hours before it was necessary to repeat the operation. A current of 5 amperes was used, and the voltage varied from 0.5 to 1.5 volts. The run was terminated at the end of 75 hours after an anode weight loss of 755.8 grams and a product overflow of 843 grams. The anode efficiency was 68%, and the product overflow was 81%. The U—Ni alloy obtained by electrolysis contained an average of 24% of nickel. The alloy overflowing from the weir was sampled from time to time, and these analyses were compared with the analysis of the anode charge. From these comparisons the following decontamination factors were determined.

Hours after Beginning of Electrolysis	Decontamination Factor			
	Ru	Pd	Mo	Zr
15.3	90	47	16	6
23.0	90	47	16	44
30.0	33	98	6	55
33.9	90	98	9	88
42.0	90	98	31	55
50.0	90	31	47	100
51.8	80	31	31	88
56.0	90	47	23	15
65.0	90	47	93	120
72.0	90	98	93	29

It may be appreciated from the above table that adequate decontamination from these four elements can be secured during an extended electrolysis. Some variations in the data appear to be caused in part by variations in electrode current densities and in part by physical transport of anode sludge.

Example 5

In the run described in this example a cell was used similar to the one shown in Fig. 2 but provided with a weir in its lower part like the cell shown in Fig. 1 so that product metal could flow to collecting crucibles for sampling during the electrolysis. Into the perforated graphite anode basket of the cell there was placed a charge of uranium in the form of rods ½ inch in diameter. These rods had been lightly irradiated in a nuclear reactor for 24 hours. The gross beta radiation from this anode charge was 8.5×10^6 counts per minute per gram of uranium and the gross gamma radiation from this anode charge was 1.7×10^7 counts per minute per gram of uranium. A mixture of $CaCl_2$ (62% by weight) and UCl_3 (38% by weight) served as the electrolyte. A nickel rod was used as the cathode. The weir was charged with a U—Ni alloy containing 13% of Ni. During electrolysis the temperature was kept at 900–950° C., and a helium atmosphere at about 700 mm. was maintained throughout the run to prevent volatilization of the salt. The current was maintained at 5 amperes while the voltage varied from 0.5 to 1.5 volts. The run was terminated at the end of 67.5 hours after there had been an anode weight loss of 669 grams, a cathode weight loss of 167 grams, and a product overflow of 704 grams. The anode efficiency was 67%, and the product recovery was 84%. The nickel content of the product was 20%. The following decontamination factors were found by comparing the analysis of the anode charges with analyses of the alloy samples overflowing from the weir and collected at intervals.

Time—Hours after Start of Run	Decontamination factors						
	Gross Beta	Gross Gamma	Sr–Y	Cs	Rare Earths	Zr–Nb	Ru
13	300	82	-------	200	350	63	74
24	220	41	5,000	200	400	40	24
33	220	44	-------	200	470	40	33
41	220	36	5,000	200	520	26	33
57	110	14	-------	200	470	16	8
67	110	18	10^4	200	500	16	11

It is evident from the above table that very good decontamination was secured from strontium, yttrium, rare earths, and cesium. All of these impurities concentrated in the salt bath.

Example 6

A flowsheet showing the inventors' preferred method for processing clad uranium fuel is shown in Figure 3. The uranium fuel elements first go to a stripping station of a mechanical type, and the cladding is removed and sent to waste. The stripped elements are then charged to the basket-type anode of the electrolysis cell. Charging is through an air lock, since it is necessary to operate the cell itself in an inert atmosphere.

The salt bath for the electrolysis process consists of a uranium salt and a suitable diluent salt. The alkaline earth chlorides and fluorides are most desirable for the purpose. Since present interest is in operating a cell at the lowest temperature compatible with a molten product, the chloride systems are preferable to the higher melting fluorides. In chloride systems the trichloride of uranium is the most stable state. If necessary, however, UF_4 is charged to the bath, and rapid reduction to the trivalent state occurs.

During electrolysis the uranium and active fission products are anodically dissolved, and fission products less reactive chemically than uranium accumulate in the bottom of the basket as an anodic sludge. The uranium migrates through the salt bath and is deposited upon the manganese cathode, while the fission products more reactive than uranium accumulate in the bath. Alloying of the uranium and manganese occurs, and a molten U—Mn alloy drips from the cathode to the bottom of the crucible.

A manganese (or other metal which forms low melting alloys with uranium) cathode is used in the electrolysis cell in order to obtain molten products at temperatures below the melting point of uranium. For an efficient process a molten product is required so that it can be readily removed from the cell by a tapping operation. To avoid the need for temperatures exceeding the melting point of pure uranium (1130° C.) the formation of uranium alloys having a lower melting point than 1130° C. is necessary if molten products are to be produced.

To provide for continuous formation of the alloy in the process, the cathode is constructed of the desired metal which forms a low melting alloy with uranium. Then as the uranium deposits, interdiffusion occurs, and a low melting alloy forms and drips from the electrode to collect in a pool in the bottom of the cell.

If pure, unalloyed uranium is ultimately desired as the product from the process the use of manganese or some other metal more volatile than uranium is important. When such a metal is used as the alloying agent, it is distilled from the product alloy to obtain the uranium in pure form. In this way the alloying agent is used only as a transient intermediate in the process. The product alloy is removed from the cell periodically by

tapping, or continuously by the use of a satisfactory arrangement of weirs. The alloy, which in the case under consideration contains 5 to 10% by weight of manganese, is then transferred to a volatilization crucible and heated to about 1300° C. to remove the manganese. The molten uranium is run to a casting crucible and from there to molds in preparation for recycle.

Periodically the basket anode is removed and discarded to dispose of the accumulated fission products. The salt bath also has to be discarded periodically because of the build-up of the active fission products which have concentrated in it. The uranium is recovered from the discarded bath by adding an oxidizing agent, such as chlorine, to produce the volatile UCl_4. This is distilled from the salt bath, condensed, and recycled to the electrolysis cell. If plutonium is concentrated in the salt, it too is distilled from the melt with the aid of the oxidizing agent. Because of the instability of the oxidation states higher than Pu (III), only a small concentration of the more volatile Pu (IV) chloride exists at any time, and it reverts to the trichloride and chlorine upon condensation. The rate of distillation of plutonium from the salt bath therefore is much lower than that of uranium. Hence the separation of the two is feasible with the uranium being volatilized from the salt before the plutonium.

As an alternative mode of operation, a fused-salt extraction step is used prior to the electrolysis. This step is performed at a temperature above the melting point of uranium. In this way the active metals and plutonium are removed, thereby eliminating a considerable burden from the electrolysis step. The plutonium and any uranium extracted into the salt are then in turn separated from the salt by the oxidation and volatilization procedure already described. After the extraction step the uranium metal still contains the noble metals and perhaps 10% or less of the original active metals. During the ensuing electrolysis the former remains in the anode sludge and the latter accumulates in the bath. Periodically the electrolysis bath still has to be discarded because of the build-up of the active fission products, but the frequency of this step is much less than without the prior salt extraction step. When discarded, the salt is sent through the same uranium recovery equipment as that used for the extractant salt cleanup. The uranium salt is recycled to the electrolysis cell.

Resort may be had to such modifications and variations as fall within the spirit of the invention and the scope of the appended claims.

We claim:

1. An electrorefining process of decontaminating irradiated uranium which comprises making said uranium the anode in an electrolytic cell which is provided with a fused electrolyte consisting of a mixture of a uranium halide and an alkaline earth metal halide and a cathode which is composed of a metal which is capable of combining with uranium to form a uranium rich alloy which has a melting point lower than that of uranium, passing an electric current through said cell, maintaining the cell temperature in the vicinity of the cathode below the melting points of uranium and of the metal of which the cathode is composed but sufficiently high so that the uranium rich alloy formed by combination of the deposited uranium and the metal of the cathode is produced in a molten state and drips from said cathode, and collecting said uranium rich alloy.

2. An electrorefining process of decontaminating irradiated uranium which comprises making said uranium the anode in an electrolytic cell which is provided with a fused electrolyte consisting of a mixture of a uranium halide and an alkaline earth metal halide and a cathode which is composed of a transition metal of the group consisting of chromium, manganese, iron, cobalt, and nickel which is capable of combining with uranium to form a uranium rich alloy which has a melting point lower than that of uranium, passing an electric current through said cell, maintaining the cell temperature in the vicinity of the cathode below the melting point of uranium but sufficiently high so that the uranium rich alloy formed by combination of the deposited uranium and the metal of the cathode is produced in a molten state, and collecting said uranium rich alloy.

3. An electrorefining process of decontaminating irradiated uranium which comprises making said uranium the anode in an electrolytic cell which is provided with a fused electrolyte consisting of a mixture of a uranium halide and an alkaline earth metal halide and a manganese cathode, passing an electric current through said cell, maintaining the cell temperature in the vicinity of the cathode below the melting point of uranium but sufficiently high so that the uranium rich alloy formed by combination of the deposited uranium and the manganese from the cathode is produced in a molten state, collecting said uranium rich U-Mn alloy, and subjecting said U-Mn alloy to distillation to remove the manganese therefrom.

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