Jan. 1, 1957 M. D. KAMEN 2,776,184

PROCESSES FOR RECOVERING AND PURIFYING URANIUM

Original Filed April 21, 1944 2 Sheets-Sheet 1

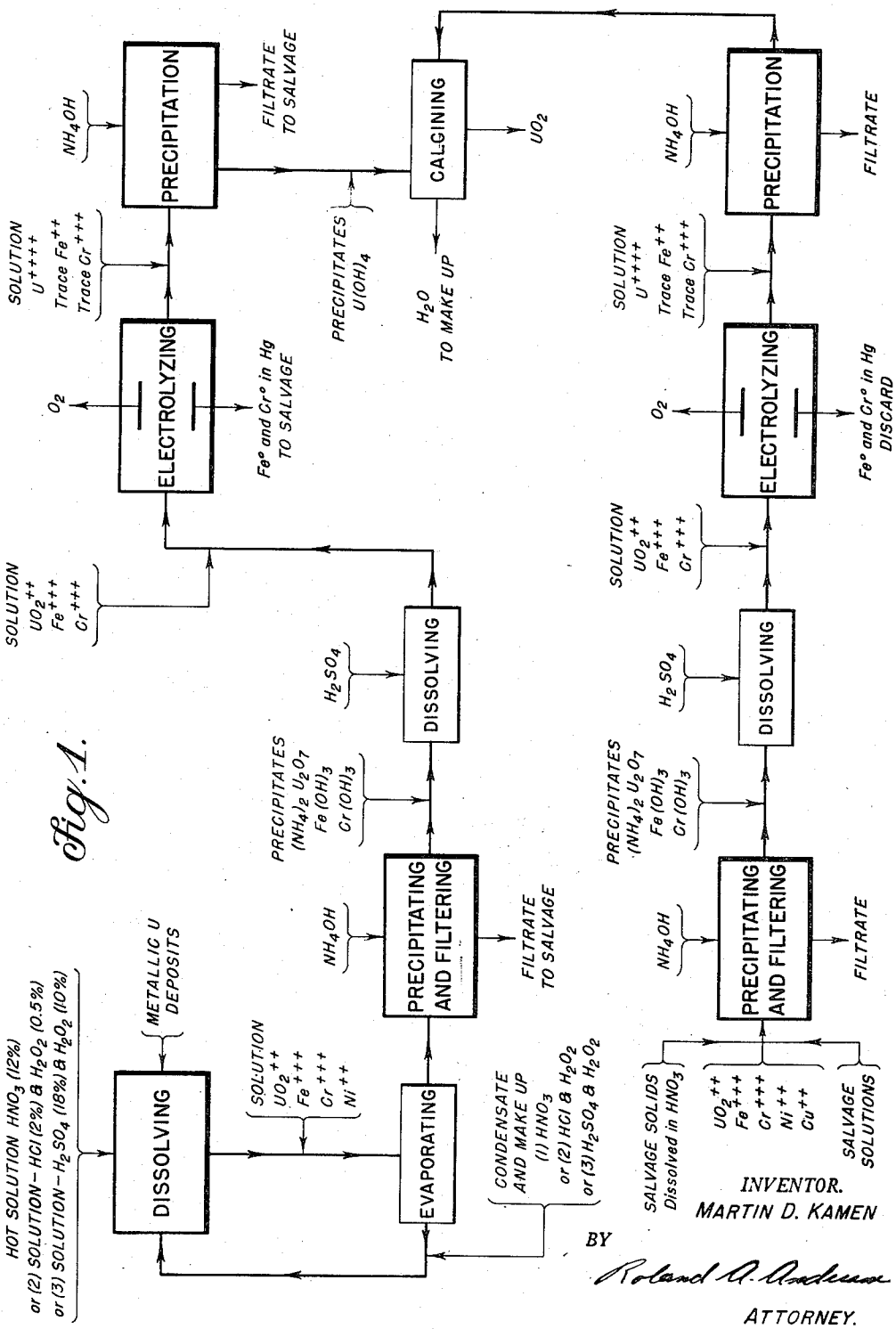


Fig. 1.

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PROCESSES FOR RECOVERING AND PURIFYING URANIUM

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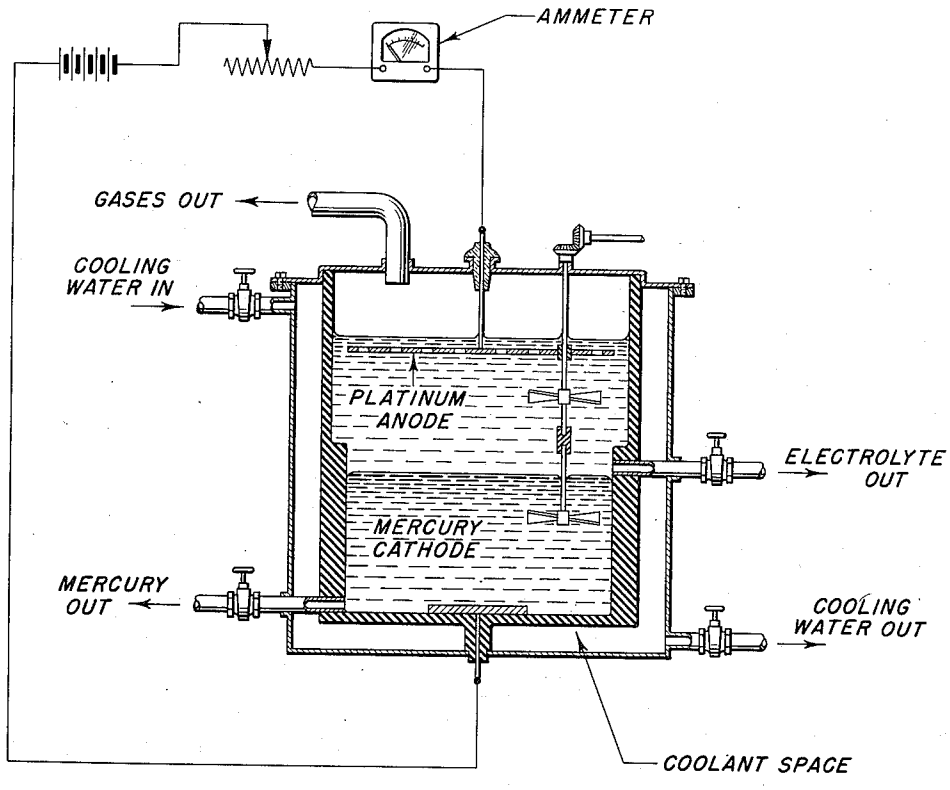


Fig. 2.

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2,776,184

PROCESSES FOR RECOVERING AND PURIFYING URANIUM

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Original application April 21, 1944, Serial No. 532,160. Divided and this application March 9, 1945, Serial No. 581,806

14 Claims. (Cl. 23—14.5)

The present invention relates to the processing of uranium and more particularly to improvements in certain steps of the process disclosed in the copending application of James M. Carter and Martin D. Kamen, Serial No. 532,159, filed April 21, 1944, which issued as Patent No. 2,758,006 on August 7, 1956. The present application is a division of my copending application, Serial No. 532,160, filed April 21, 1944.

It is an object of the invention to provide an improved process of reclaiming uranium from a calutron.

Another object of the invention is to provide an improved process of recovering the residue of a uranium compound which has been subjected to treatment in a calutron from the parts of the calutron disposed in the source region thereof upon which the residue is deposited.

Another object of the invention is to provide an improved process of recovering metallic uranium from the collector of a calutron upon which the metallic uranium is deposited.

A further object of the invention is to provide an improved process of purifying uranium which has been recovered from a calutron.

A further object of the invention is to provide a process of reclaiming uranium from a wash solution derived from a calutron in which the uranium is separated from metal impurities by treatment in an electrolytic cell.

A further object of the invention is to provide a process of reclaiming uranium from a wash solution derived from a calutron in which the wash solution is first reduced by treatment in an electrolytic cell and then the uranium is precipitated away from metal impurities in the wash solution in its lower valence state.

A further object of the invention is to provide an improved process of salvaging fractions of uranium from solutions which have been previously subjected to primary uranium recovery treatment in which the salvage solution is subjected to treatment in an electrolytic cell.

The invention, both as to its organization and method of operation, together with further objects and advantages thereof, will best be understood by reference to the following specification taken in connection with the accompanying drawings, in which Figure 1 illustrates the flow diagram of the present process, indicating the recovery of the metallic uranium from the collector of the calutron upon which it is deposited, and the steps of the subsequent purification of the uranium; and Fig. 2 is a perspective view of an electrolytic cell in which the electrolytic reduction steps of the processes of the present invention may be carried out.

At the outset, it is noted that a "calutron" is a machine of the character of that disclosed in the copending application of Ernest O. Lawrence, Serial No. 557,784, filed October 9, 1944, now Patent No. 2,709,222, granted May 24, 1955, and is employed to separate the constituent isotopes of an element and more particularly to increase the proportion of a selected isotope in an element containing a plurality of isotopes in order to

produce the element enriched with the selected isotope.

Such a calutron essentially comprises means for vaporizing a quantity of material containing an element which is to be enriched with a selected one of its several isotopes; means for subjecting the vapor to ionization, whereby at least a portion of the vapor is ionized causing ions of the several isotopes of the element to be produced; electrical means for segregating the ions from the un-ionized vapor and for accelerating the segregated ions to relatively high velocities; electromagnetic means for deflecting the ions along curved paths, the radii of curvature of the paths of ions being proportional to the square roots of the masses of the ions, whereby the ions are concentrated in accordance with their masses; and means for deionizing and collecting the ions of the selected isotope thus concentrated, thereby to produce a deposit of the element enriched with the selected isotope.

When such a calutron is employed to separate the isotopes of uranium, the un-ionized portion of said material which is vaporized is deposited in the source region of the calutron and upon stainless steel surfaces while the ionized portion is deposited partially on the collector and partially upon various of the vacuum tank and other interior surfaces dependent upon the type of ion which is produced by said ionization and upon the operating characteristics of said calutron. It has been found convenient to employ uranium tetrachloride as the material being vaporized and, accordingly, there will be a deposit of the residue thereof formed in the source region of said calutron while metallic uranium comprising substantially only U^{238} will be deposited in one pocket of the collector of said calutron and metallic uranium enriched with U^{234} and U^{235} will be deposited in the second pocket of said collector.

Considering now the details of the recovery of the metallic uranium from one of the pockets in the collector of the calutron, reference is made to the flow diagram illustrated in Fig. 1. The inner surfaces of said pocket are etched with one of a number of acid solutions, whereby the deposit of metallic uranium is dissolved and various impurities including iron, chromium and nickel are introduced in the acid wash solution, due to the fact that the inner surfaces of said pocket are formed of stainless steel which comprises the materials mentioned. Accordingly, the wash acid contains at least the following ions: UO_2^{++}, Fe^{+++}, Cr^{+++} and Ni^{++}.

A suitable acid wash solution which may be employed for the purpose mentioned comprises an aqueous solution containing HNO_3 (6% to 40% by weight, and preferably approximately 12%). Another suitable acid wash solution comprises an aqueous solution containing HCl (0.5% to 2.5% by weight, and preferably approximately 2%) and H_2O_2 (0.5% to 2.0% by weight, and preferably approximately 0.5%). A further suitable acid wash solution comprises an aqueous solution containing H_2SO_4 (15% to 30% by weight, and preferably approximately 18%) and H_2O_2 (5% to 15% by weight, and preferably approximately 10%). Thus, it will be understood that the first acid wash solution comprises an oxidizing acid, whereas the second and third acid wash solutions contain a separate oxidizing agent in the form of H_2O_2. Hence, the acid wash solution employed in any case produces an oxidizing effect upon both the uranium and the metal impurities which are dissolved therein.

In the event the wash acid is rather dilute in the ions mentioned, it may be concentrated by evaporation; otherwise this step is omitted. In the event the wash acid is concentrated by evaporation, the vapor which is driven off is condensed and to it is added enough make-up HNO_3, or HCl and H_2O_2, or H_2SO_4 and H_2O_2, depending upon the composition of the original wash acid employed, in order to provide a new wash acid which

is again used to wash the pocket of the collector of the calutron, in the manner previously explained. This step, comprising condensing the vapor which is driven off the wash acid incident to concentration by evaporation, is advantageous, in view of the fact that any uranium entrained in the vapor is not lost to the outside.

The original wash acid mentioned above, or the concentrated wash acid following evaporation, in the event this step is employed, is then subjected to ammonia treatment, either with excess NH_4 gas or carbonate-free NH_4OH, whereby $(NH_4)_2U_2O_7$, $Fe(OH)_3$ and $Cr(OH)_3$ are precipitated away from the nickel in the solution in the form of the ammonia complex ion, $Ni(NH_3)_4^{++}$. The solution is then filtered and the precipitate, consisting of ammonium diuranate, ferric hydroxide and chromic hydroxide, is then washed with water containing about one percent NH_4OH and one percent $(NH_4)_2SO_4$ in order to eliminate occluded nickel ammonia complex ion.

Similarly, said residue of UCl_4 deposited on the parts of a calutron is recovered by the following method. The parts mentioned disposed in the source region thereof are scrubbed and washed with hot water, whereby the residue of UCl_4 deposited thereon is dissolved; and various impurities including copper, iron, chromium, nickel and carbon, are introduced in the water wash, due to the fact that the various parts of the caultron which are thus washed with hot water are formed of the materials mentioned. The wash water is then sieved in order to remove any solid impurities which may be picked up, such, for example, as small pieces of metal and carbon. These solid impurities may be either discarded or subjected to salvage treatment in order to recover any occluded uranium. The sieved wash water is then treated with H_2O_2 by adding a slight excess of ten percent H_2O_2 and agitating the solution in order to oxidize the various contained materials. For example, the wash water prior to the step of oxidation may contain suspended $U(OH)_4$ and bits of copper and carbon, dissolved uranium in the $+4$ and $+6$ valence states, as well as dissolved copper, iron, nickel, chromium and possibly other metals in one or more of the positive valence states. Hence, as a result of the oxidation all of the uranium is put in solution as uranyl ion, suspended copper is put in solution as cupric ion, and other dissolved materials are put in their higher stable valence states, if they are not already in such state.

Accordingly, the oxidized wash water contains at least the following: UO_2^{++}, Cu^{++}, Fe^{+++}, Cr^{+++}, Ni^{++} and C^0 (carbon). The oxidized wash water is then filtered in order to remove the C^0, which may be discarded or subjected to salvage treatment in order to recover any occluded uranium.

In the event this filtrate is rather dilute, it may be concentrated by evaporation; otherwise, this step is omitted. In the event the filtrate is concentrated by evaporation, the water vapor which is driven off is condensed and to it is added enough makeup water in order to provide a new wash solution, which is used again to wash the parts of the calutron disposed in the source region thereof, in the manner previously explained. This step, comprising condensing and re-using the water vapor which is driven off the filtrate incident to concentration by evaporation, is advantageous in view of the fact that any uranium entrained in the water vapor is not lost to the outside.

The original filtrate mentioned above, or the concentrated filtrate following evaporation, in the event this step is employed, is then subjected to ammonia treatment, either with excess NH_3 gas or carbonate-free NH_4OH, whereby $(NH_4)_2U_2O_7$, $Fe(OH)_3$ and $Cr(OH)_3$ are precipitated substantially completely away from the copper and nickel which remain in the solution in the form of ammonia complex ions, $Cu(NH_3)_4^{++}$ and $Ni(NH_3)_4^{++}$. The solution is then filtered and the precipitate, consisting of ammonium diuranate, ferric hydroxide and chromic hydroxide, is then washed with water containing about one percent NH_4OH and one percent $(NH_4)_2SO_4$, in order to eliminate occluded copper and nickel ammonia complex ions.

Considering now the details of the purification of the precipitates described above, comprising $(NH_4)_2U_2O_7$, $Fe(OH)_3$ and $Cr(OH_3)_3$, reference is made to the portion of the flow diagram wherein the electrolytic process is indicated. The precipitate is first dissolved in H_2SO_4, whereby the solution contains the following ions: UO_2^{++}, Fe^{+++} and Cr^{+++}. The sulfuric acid concentration of the solution is then adjusted to about 1N by adding water or H_2SO_4 thereto, as required. This solution is then placed in an electrolytic cell such as that shown in Fig. 2, and is employed therein as the electrolyte. Preferably, the electrolytic cell comprises a platinum anode, a mercury cathode, an arrangement for vigorously agitating the electrolyte and the mercury cathode, a water cooling arrangement for the cell, and an arrangement for drawing off and separately collecting, after electrolysis, the electrolyte and the mercury of the cathode.

After the electrolyte has been placed in the electrolytic cell the associated circuit is closed, whereby a voltage of several volts is applied between the anode and the cathode, causing electrolysis to take place at a current density of about 0.1 ampere per cm.^{2} at the anode, the anode and the cathode of the electrolytic cell being of approximately equal areas. When the electrolyte is thus electrolyzed, the contained ions are reduced as indicated below:

$$UO_2^{++} \rightarrow U^{++++}$$
$$Fe^{+++} \rightarrow Fe^{++}$$
$$Fe^{++} \rightarrow Fe^0$$
$$Cr^{+++} \rightarrow Cr^0$$

Thus, after the electrolysis is complete, only the uranous ion, U^{++++}, remains in the electrolyte, and any contained iron and chromium are completely reduced to metallic iron and chromium, which impurities are accumulated in the mercury cathode. Also, it is noted that in the event the electrolyte contains nickel and copper, the nickelous ion, Ni^{++}, and the cupric ion, Cu^{++}, are completely reduced to metallic nickel and copper and accumulated in the mercury cathode in the same manner. Accordingly, as the ferric, ferrous, chromic, nickelous and cupric ions, in the event the two last-mentioned ions appear in the electrolyte, are completely reduced by electrolysis, they are carried into the mercury cathode, whereby the electrolyte is purified to contain only the uranous ion, U^{++++}, after the electrolysis is complete. Also, the electrolytic current effects transfer of H^+ ion to the cathode and SO_4^{--} ion to the anode, whereby some H_2 is liberated at the cathode and O_2 is liberated at the anode in a well-known manner. The U^{++++} ion is not plated out of the electrolyte into the mercury cathode, as it possesses a high over-voltage; whereas the Fe^0, Cr^0, Ni^0 and Cu^0, if present, are plated out of the electrolyte into the mercury cathode, as previously noted.

After the electrolysis has been completed, the mercury used as the cathode in the electrolytic cell is drawn off and subjected to salvage treatment, whereby it may be reconditioned for use. Also, the electrolyte is drawn off and to it NH_4OH is added in order to bring the pH of the solution to a value in the range of about 4.0 to 4.8, preferably approximately 4.4. When the pH of the solution is adjusted to the value mentioned, the uranium is precipitated in the solution as $U(OH)_4$. The solution is then filtered and the uranous hydroxide precipitate is washed with an aqueous solution containing about one percent NH_4OH and one percent $(NH_4)_2SO_4$, in order to eliminate any occluded ferrous and chromic ions. The filtrate containing the ammonium sulfate is then discarded or subjected to salvage treatment in order to recover any uranium contained, while the uranous hydroxide precipitate is calcined in a non-oxidizing atmosphere, such

as nitrogen or hydrogen, at approximately 250° C. in order to produce UO_2, whereby water vapor is given off incident to the calcination. The uranium thus purified, and in the compound form UO_2, is then stored for further treatment or commercial use, as previously noted.

The electrolytic reduction followed by the pH control precipitation of the uranium as uranous hydroxide, as described above, is very advantageous, in view of the fact that the precipitation of uranium as uranous hydroxide may be carried out in the presence of impurities in the form of ferrous and chromic ions. Accordingly, it is not necessary to carry the electrolytic treatment to completion; in other words, the ferric and chromic ions need not be completely reduced to the metallic state Fe^0 and Cr^0 and accumulated in the mercury cathode in the manner explained. In fact, it is sufficient that the electrolysis be carried out in order to reduce the uranyl and ferric ions, UO_2^{++} and Fe^{+++}, to uranous and ferrous ions, U^{++++} and Fe^{++}. In this event the pH control step effects the precipitation of the uranous ion in the solution as uranous hydroxide, leaving the ferrous and chromic ions in the solution. In carrying out the process in the manner indicated, wherein the electrolytic step is employed primarily to reduce the uranyl and ferric ions, the chromic ion, Cr^{+++}, as an impurity must be in rather small amounts, as chromic hydroxide will be precipitated along with the uranous hydroxide in the event the chromic ion concentration of the solution is of the order of a few tenths of one percent. However, this difficulty can be eliminated to a considerable extent by appropriately prolonging the electrolytic treatment so that some of the chromic ion, Cr^{+++}, is completely reduced to the metallic state, Cr^0, and accumulated in the mercury cathode in the manner explained, whereby the solution which is subjected to the pH control step does not contain the chromic ion in an amount greater than that mentioned. Thereafter, when the solution is filtered the ferrous and chromic ions remain with the ammonium sulfate in the filtrate, whereby the uranous hydroxide precipitate is substantially completely free of the ions mentioned after it has been washed in the manner previously noted.

Thus it will be understood that the solution produced by dissolving one of the composite precipitates in sulfuric acid may be treated in the electrolytic cell in order completely to eliminate the iron and chromium impurities, or it may be treated in the electrolytic cell only sufficiently to reduce the ferric ion to ferrous ion,, along with the reduction of the uranyl ion to the uranous ion. In the first case, the pH control precipitation is employed primarily to separate the uranium from the ammonium sulfate; and in the second case, the pH control precipitation is employed to separate the uranium from the iron and chromium impurities, as well as the ammonium sulfate.

Considering now the details of the salvage of small fractions of uranium contained in various materials produced incident to carrying out the process, reference is made to the portion of the flow diagram illustrated in Fig. 1, wherein the electrolytic process is indicated. More particularly, in the event the material which is to be subjected to salvage treatment is in solid form, it is first dissolved in dilute HNO_3, thereby to obtain a salvage solution. On the other hand, in the event the material which is to be subjected to salvage treatment is in liquid form it is ready for further treatment in its present condition. For example, such material might comprise a precipitate of metal impurities carrying a small fraction of solid uranium, or a filtrate containing metal impurities and a small fraction of dissolved uranium. In any case, a salvage solution is first produced, which solution might comprise the following ions of the fraction of uranium and the metal impurities: UO_2^{++}, Fe^{+++}, Cr^{+++}, Ni^{++} and Cu^{++}. The electrolytic process is particularly advantageous when the solution thus produced contains UO_2^{++} ion in very low concentration and Fe^{+++}, Cr^{+++}, Ni^{++} and Cu^{++} ions in fairly high concentrations, the concentrations mentioned being relative. Specifically, this process is recommended when, by weight, the amount of uranium present in the solution is less than one-tenth of that of the iron, chromium, nickel, and copper combined.

The salvage solution is then subjected to ammonia treatment, either with excess NH_3 gas or carbonate-free NH_4OH, whereby $(NH_4)_2U_2O_7$, $Fe(OH)_3$ and $Cr(OH)_3$ are substantially completely precipitated away from the copper and nickel in the solution in the form of ammonia complex ions, $Cu(NH_3)_4^{++}$ and $Ni(NH_3)_4^{++}$. The solution is then filtered and the precipitate consisting of ammonium diuranate, ferric hydroxide and chromic hydroxide is then washed with water containing about one percent NH_4OH and one percent $(NH_4)_2SO_4$, in order to eliminate occluded copper and nickel ammonia complex ions. The filtrate is then discarded and the initially purified precipitate of $(NH_4)_2U_2O_7$, $Fe(OH)_3$ and $Cr(OH)_3$ is dissolved in dilute H_2SO_4, whereby the solution contains the following ions: UO_2^{++}, Fe^{+++} and Cr^{+++}. The sulfuric acid concentration of the solution is then adjusted to about 1N by adding water or H_2SO_4 thereto, as required. This solution is then placed in an electrolytic cell such as that shown in Fig. 2, and is employed therein as the electrolyte. Preferably, the electrolytic cell comprises a platinum anode, a mercury cathode, an arrangement for vigorously agitating the electrolyte and the mercury cathode, a water cooling arrangement for the cell, and an arrangement for drawing off and separately collecting, after electrolysis, the electrolyte and the mercury of the cathode.

After the electrolyte has been placed in the electrolytic cell, the associated circuit is closed, whereby a voltage of several volts is applied between the anode and the cathode, causing electrolysis to take place at a current density of about 0.1 ampere per cm.^{2} at the anode, the anode and the cathode of the electrolytic cell being of approximately equal areas. When the electrolyte is thus electrolyzed, the contained ions are reduced as indicated below:

$$UO_2^{++} \rightarrow U^{++++}$$
$$Fe^{+++} \rightarrow Fe^{++}$$
$$Fe^{++} \rightarrow Fe^0$$
$$Cr^{+++} \rightarrow Cr^0$$

Thus, after the electrolysis is complete, only the uranous ion, U^{++++}, remains in the electrolyte, and any contained iron and chromium are completely reduced to metallic iron and chromium, which impurities are accumulated in the mercury cathode. Also, it is noted that in the event the electrolyte contains nickel and copper, the nickelous ion, Ni^{++}, and the cupric ion, Cu^{++}, are completely reduced to metallic nickel and copper and accumulated in the mercury cathode in the same manner. Accordingly, as the ferric, ferrous, chromic, nickelous and cupric ions, in the event the two last-mentioned ions appear in the electrolyte, are completely reduced by electrolysis, they are carried into the mercury cathode, whereby the electrolyte is purified to contain principally the uranous ion, U^{++++}, after the electrolysis is complete. Also, the electrolytic current effects transfer of H^+ ion to the cathode and SO_4^{--} ion to the anode, whereby some H_2 is liberated at the cathode and O_2 is liberated at the anode in a well-known manner. The U^{++++} ion is not plated out of the electrolyte into the mercury cathode, as it possesses a high over-voltage; whereas the Fe^0, Cr^0 and Ni^0 and Cu^0, if present, are plated out of the electrolyte into the mercury cathode, as previously noted. After the electrolysis has been completed, the mercury used as the cathode in the electrolytic cell is drawn off and subjected to treatment, whereby it may be reconditioned for use. Also the electrolyte containing the U^{++++} ion and a trace of Fe^{++} and Cr^{+++} ions is drawn off and conserved for further treatment.

The term uranium is employed in the present specifica-

tion and claims in a generic sense, i. e., as applying to uranium whether in elemental, combined or ionic form, unless indicated otherwise by the context.

Throughout the foregoing specification, the percentages, ratios, and other relations concerning the various elements and compounds are given with respect to weights, unless otherwise indicated by the context.

While there has been described what is at present considered to be the preferred embodiment of the invention, it will be understood that various modifications may be made therein and it is intended to cover in the appended claims all such modifications as fall within the true spirit and scope of the invention.

What is claimed is:

1. The process of reclaiming uranium values from deposits formed on the parts of a calutron comprising washing said parts with an aqueous solvent and producing an oxidized acidic solution containing UO_2^{++} ions together with impurities including Cu^{++}, Fe^{+++}, Cr^{+++} and Ni^{++} ions, electrolyzing said solution to reduce the UO_2^{++} ions to the uranous state and at least some of said impurities to a lower valent state, treating said electrolyzed solution with ammonia to precipitate uranium hydroxide away from the impurities remaining in the solution, and separating said uranous hydroxide from the solution.

2. The process of recovering uranium values from the residue of a water-soluble compound deposited on the parts of a calutron disposed in the source region thereof comprising washing said parts with water and producing an oxidized acidic solution containing UO_2^{++} ions together with impurities including Cu^{++}, Fe^{+++}, Cr^{+++} and Ni^{++} ions, electrolyzing said solution in an electrolytic cell having a mercury cathode and at an electrolytic current density of about 0.1 amp. per sq. cm. to reduce said UO_2^{++} ions to the uranous state and at least some of said impurity ions to a lower valent state, treating the electrolyzed solution with ammonia to precipitate uranous hydroxide away from impurity ions in said solution, and separting said uranous hydroxide from the solution.

3. The process of recovering uranium values from metallic deposits thereof formed with the stainless steel material of a calutron collector as a result of the impingement of uranium ions thereon during the operation of said calutron comprising treating said deposits with a solvent of the group consisting of sulfuric acid containing hydrogen peroxide, hydrochloric acid containing hydrogen peroxide and nitric acid whereby there is produced a solution containing uranyl ions together with impurities including ferric, chromic and nickelous ions, electrolyzing said solution in an electrolytic cell having a mercury cathode at an electrolytic current density of about 0.1 amp. per sq. cm. to reduce said uranyl ions to uranous ions and at least some of said impurity ions to lower valent states, treating said electrolyzed solution with ammonia to precipitate uranous hydroxide away from said impurity ions, and separating said uranous hydroxide from the solution.

4. The process of reclaiming uranium values from deposits formed on the stainless steel parts of a calutron as a result of the operation thereof comprising washing said parts with an aqueous solvent and producing an oxidized acidic solution containing UO_2^{++} ions together with impurities including Fe^{+++}, Cr^{+++} and Ni^{++} ions, electrolyzing said solution in an electrolytic cell having a mercury cathode at an electrolytic current density of about 0.1 amp. per sq. cm. to reduce said UO_2^{++} ions to the uranous state and to reduce said impurities to the metallic state thereupon to be absorbed and accumulated in said mercury cathode, and recovering the uranium contained as uranous ions in said solution.

5. The process of reclaiming uranium values from deposits formed on the stainless steel parts of a calutron as a result of the processing of a uranium compound therein comprising washing said parts with an aqueous solvent and producing an oxidized acidic solution containing uranyl ions together with impurities including cupric, ferric, chromic and nickelous ions, electrolyzing said solution in an electrolytic cell having a mercury cathode with an electrolytic current density of about 0.1 amp. per sq. cm. to reduce said uranyl ions to the uranous state and to completely reduce said impurities to the metallic state whereupon said impurities are accumulated in said mercury cathode, treating said electrolyzed solution with ammonia to precipitate uranous hydroxide therefrom, and separating said uranous hydroxide from the solution.

6. The process of reclaiming the residual fraction of uranium values remaining with the metal impurities obtained from the treatment of a solution derived by washing the stainless steel parts of a calutron with an aqueous solvent followed by a treatment to separate the major fraction of the uranium therefrom comprising producing a sulfuric acid solution of about 1N concentration and containing said impurities wherein said residual uranium is present as uranyl ions, electrolyzing said solution in an electrolytic cell having a mercury cathode with an electrolytic current density of about 0.1 amp. per sq. cm. to reduce said uranyl ions to the uranous state and to reduce said impurities to lower valent states whereby said impurities are accumulated in said mercury cathode, and recovering uranium contained in the uranous state from said electrolyzed solution.

7. The process of reclaiming uranium values from metallic deposits thereof formed with the stainless steel material of a calutron collector as a result of the impingement of uranium ions thereon during the operation of said calutron comprising treating said deposits with a solvent of the group consisting of sulfuric acid containing hydrogen peroxide, hydrochloric acid containing hydrogen peroxide and nitric acid to produce a solution containing uranyl ions and impurities including ferric, chromic and nickelous ions; electrolyzing said solution to reduce uranyl ions to uranous ions and at least some of said impurity ions to lower valent states in an electrolytic cell having a mercury cathode and at an electrolytic current density of about 0.1 amp. per sq. cm. whereby at least some of said impurities are absorbed and accumulated in said mercury cathode; treating the electrolyzed solution with ammonia to adjust the pH thereof to the range of 4.0 to 4.8 in order to precipitate uranous hydroxide away from the impurities in the solution; and separating said uranous hydroxide from the solution.

8. The process as in claim 7, wherein said uranium values which are reclaimed comprise uranium isotope 238.

9. The process of reclaiming uranium values from metallic deposits thereof formed with the stainless steel material of a calutron collector as a result of the impingement of uranium ions thereon during the operation of said calutron comprising treating said deposits with a solvent selected from the group consisting of sulfuric acid containing hydrogen peroxide, hydrochloric acid containing hydrogen peroxide, and nitric acid to produce a solution containing uranyl ions together with impurities including ferric, chromic and nickelous ions; electrolyzing said solution in an electrolytic cell having a mercury cathode and at an electrolytic current density of about 0.1 amp. per sq. cm. to reduce the uranyl ions to the uranous state and to reduce said impurity ions and to accumulate said impurities in said mercury cathode; precipitating uranous hydroxide from said solution; separating said uranous hydroxide from the solution; and calcining said uranous hydroxide to produce uranium dioxide.

10. The process of reclaiming residual uranium values from a salvage solution which has been subjected to a primary uranium recovery treatment and which contains Fe^{++}, Cr^{+++}, Ni^{++} and Cu^{++} ions, comprising treat-

ing said solution with ammonia to precipitate ammonium diuranate, ferric hydroxide and chromic hydroxide; producing a solution of said precipitate in about 1N sulfuric acid; electrolyzing said solution in an electrolytic cell having a mercury cathode at an electrolytic current density of about 0.1 amp. per sq. cm. to reduce uranyl ions to the uranous state and to reduce ferric and chromic ions to the metallic state whereby iron and chromium are absorbed and accumulated in said mercury cathode; and recovering uranous uranium from said solution.

11. The process of reclaiming uranium values present in small amounts from a precipitate containing iron, chromium, nickel and copper compounds, comprising dissolving said precipitate in dilute nitric acid to produce a solution containing said materials in a quantity greater than about ten-fold that of the uranum; treating said solution to precipitate ammonium diuranate, ferric hydroxide and chromic hydroxide therefrom; producing a solution of said precipitate in about 1N sulfuric acid; electrolyzing said solution in an electrolytic cell having a mercury cathode at an electrolytic current density of about 0.1 amp. per sq. cm. to reduce uranyl ions to uranous and to reduce ferric and chromic ions to the metallic state thereupon to be accumulated in said mercury cathode; treating said electrolyzed solution with ammonia to adjust the pH thereof to the range of about 4.0 to 4.8 in order to precipitate uranous hydroxide therefrom; and separating said uranous hydroxide from the solution.

12. The process as in claim 2, wherein said water-soluble compound comprises uranium tetrachloride.

13. The process of recovering uranium values from the residue of uranium tetrachloride deposited upon the parts of a calutron disposed in the source region thereof comprising washing said parts with water and producing an oxidized acidic solution containing UO_2^{++} ions together with Cu^{++}, Fe^{+++}, Cr^{+++} and Ni^{++} ions, electrolyzing said solution in an electrolytic cell having a mercury cathode at an electrolytic current density of about 0.1 amp. per sq. cm. to reduce said UO_2^{++} ions to the uranous state and to reduce at least some of said Cu^{++}, Fe^{+++}, Cr^{+++} and Ni^{++} ions to lower valent states, treating said electrolyzed solution with ammonia to adjust the pH thereof to the range of about 4.0 to 4.8 and thereby precipitate uranous hydroxide away from the other ions in the solution, separating said uranous hydroxide from the solution, and calcining said uranous hydroxide in a non-oxidizing atmosphere and at about 250° C. to produce uranium dioxide.

14. The process of recovering uranium values from the residue of uranium tetrachloride deposited upon the parts of a calutron disposed in the source region thereof comprising washing said parts with water and producing a solution containing UO_2^{++} ions and impurities including Cu^{++}, Fe^{+++}, Cr^{+++} and Fe^{++} ions, treating said solution with ammonia to precipitate $(NH_4)_2U_2O_7$, $Fe(OH)_3$ and $Cr(OH)_3$ therefrom, producing a solution of said precipitate in sulfuric acid of about 1N concentration, electrolyzing said solution in an electrolytic cell having a mercury cathode and at an electrolytic current density of about 0.1 amp. per sq. cm. to reduce uranyl ions to the uranous state and to completely reduce ferric and chromic ions to the metallic state thereupon to be absorbed and accumulated in said mercury cathode, precipitating uranous hydroxide from said solution by means of ammonia, and separating said uranous hydroxide from the solution.

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