Nov. 20, 1956 M. D. KAMEN ET AL 2,771,340

IMPROVED URANIUM RECOVERY AND PURIFICATION PROCESSES

Filed June 27, 1944 4 Sheets-Sheet 1

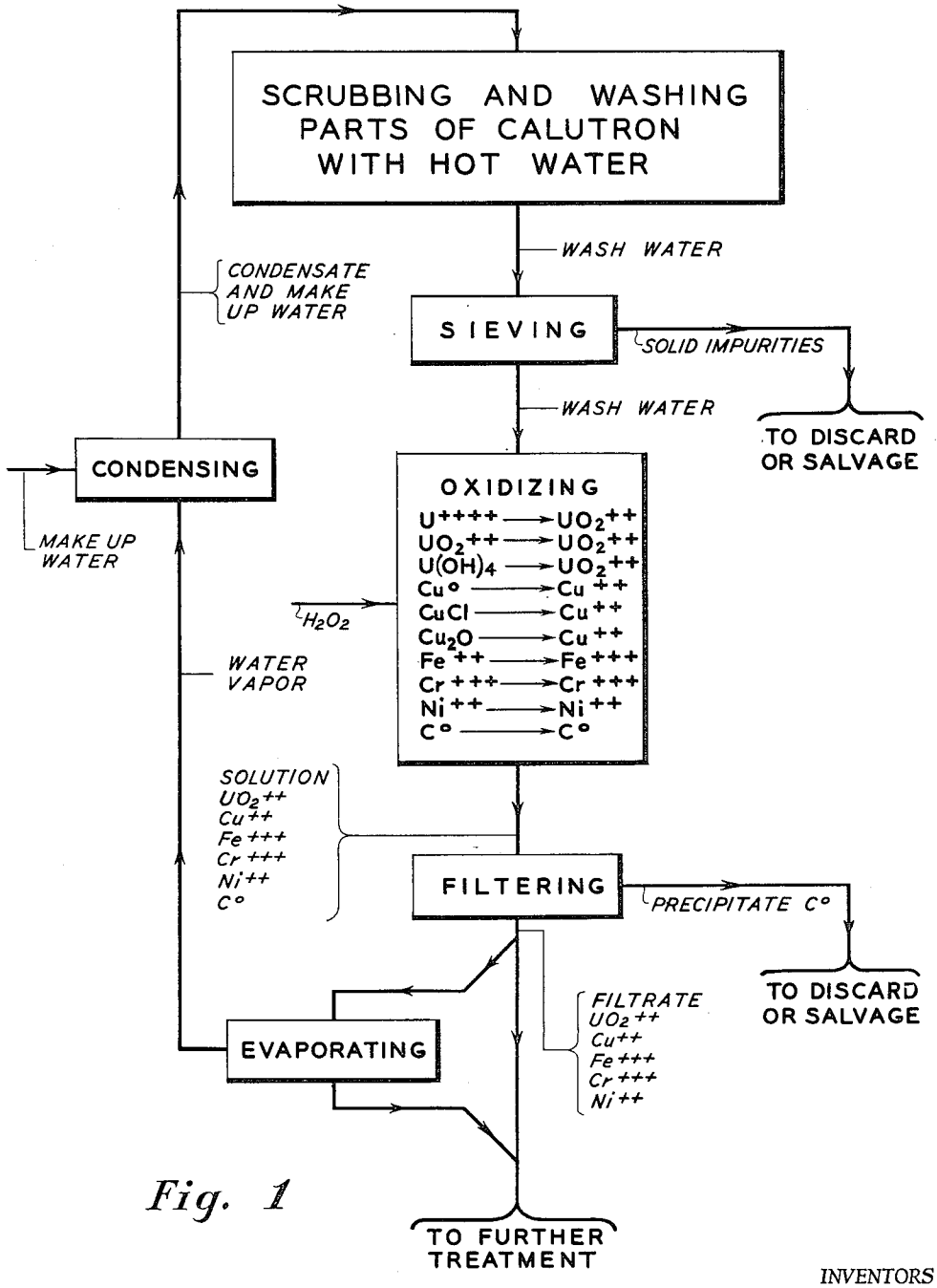


Fig. 1

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IMPROVED URANIUM RECOVERY AND PURIFICATION PROCESSES

Filed June 27, 1944 4 Sheets-Sheet 2

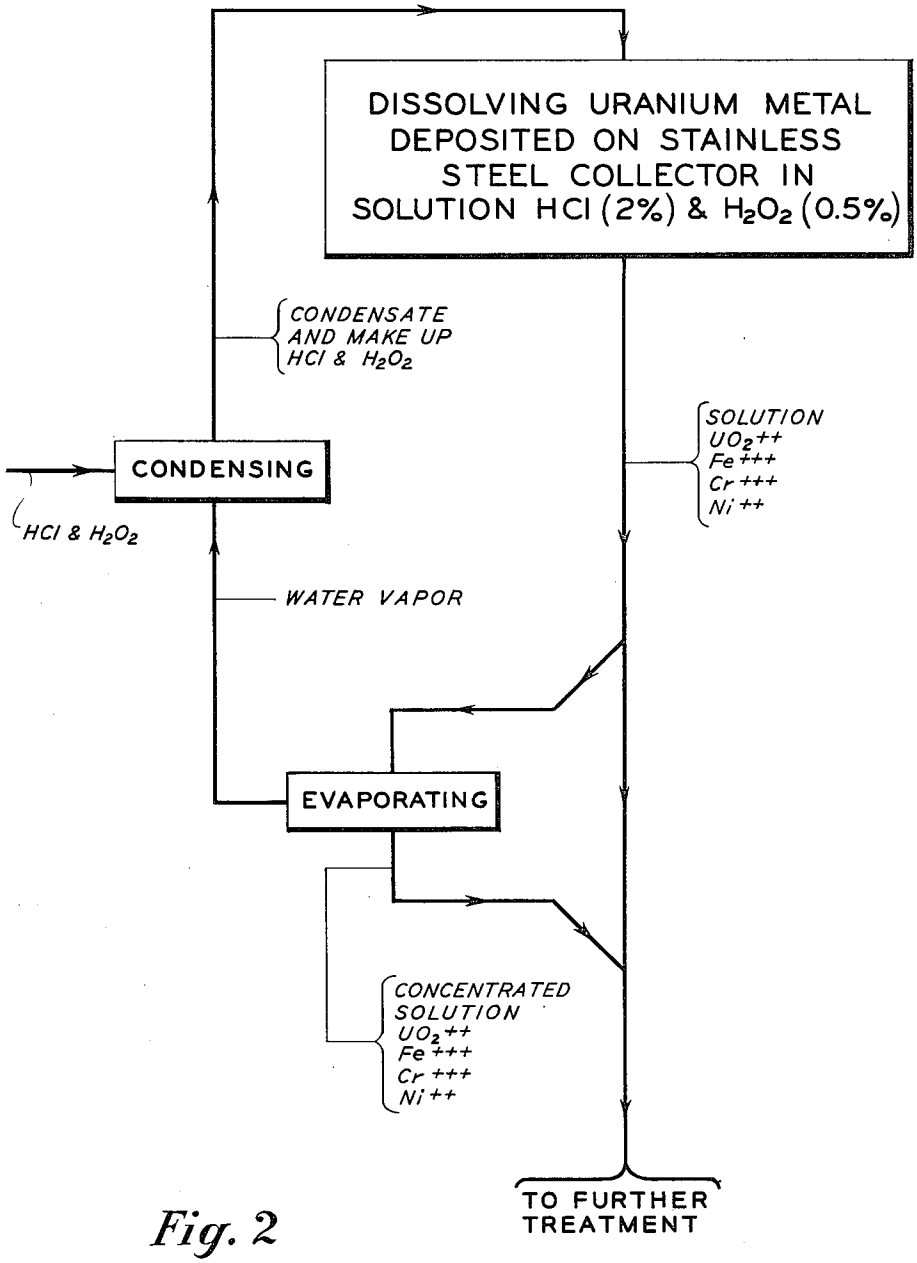


Fig. 2

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IMPROVED URANIUM RECOVERY AND PURIFICATION PROCESSES

Filed June 27, 1944 4 Sheets-Sheet 3

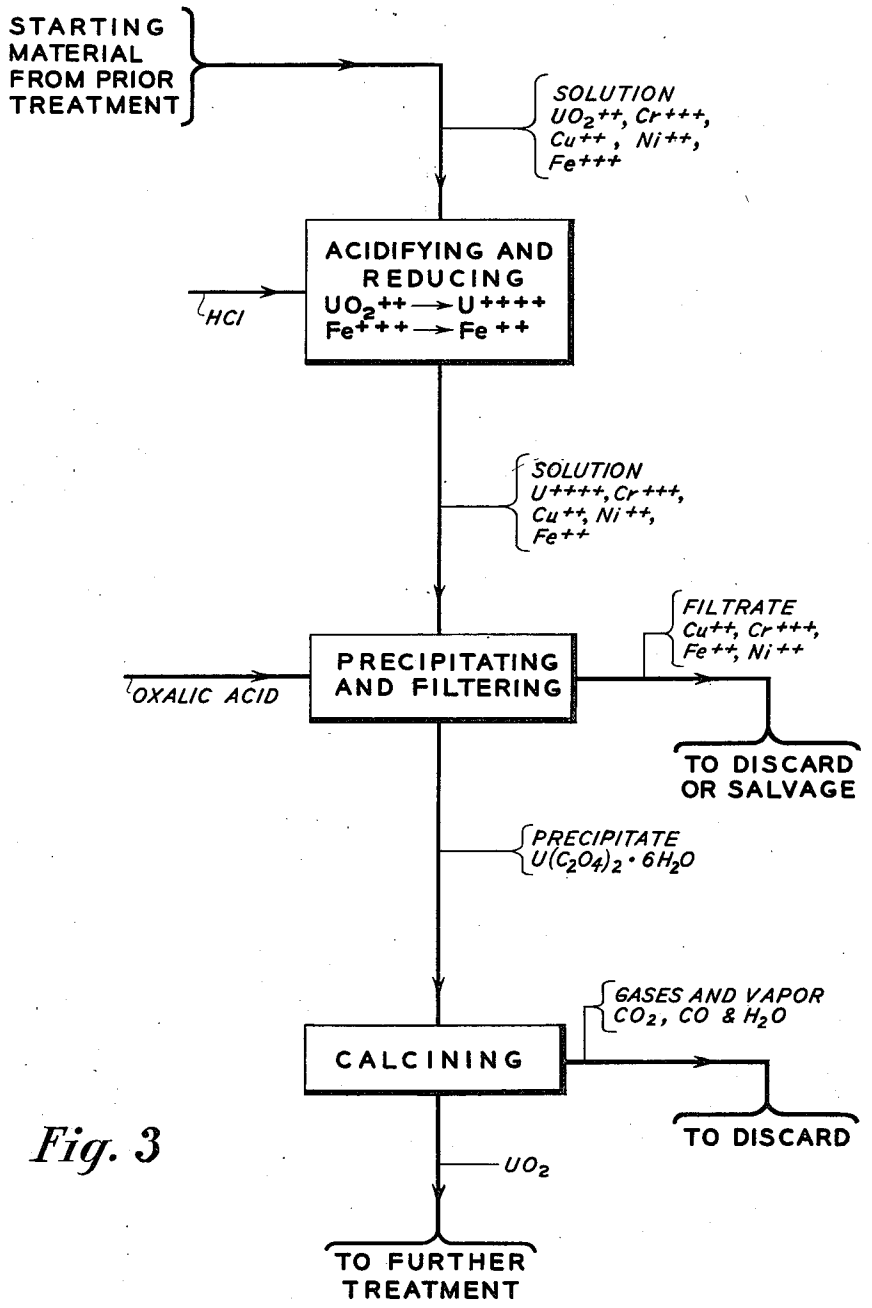


Fig. 3

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IMPROVED URANIUM RECOVERY AND PURIFICATION PROCESSES

Filed June 27, 1944 4 Sheets-Sheet 4

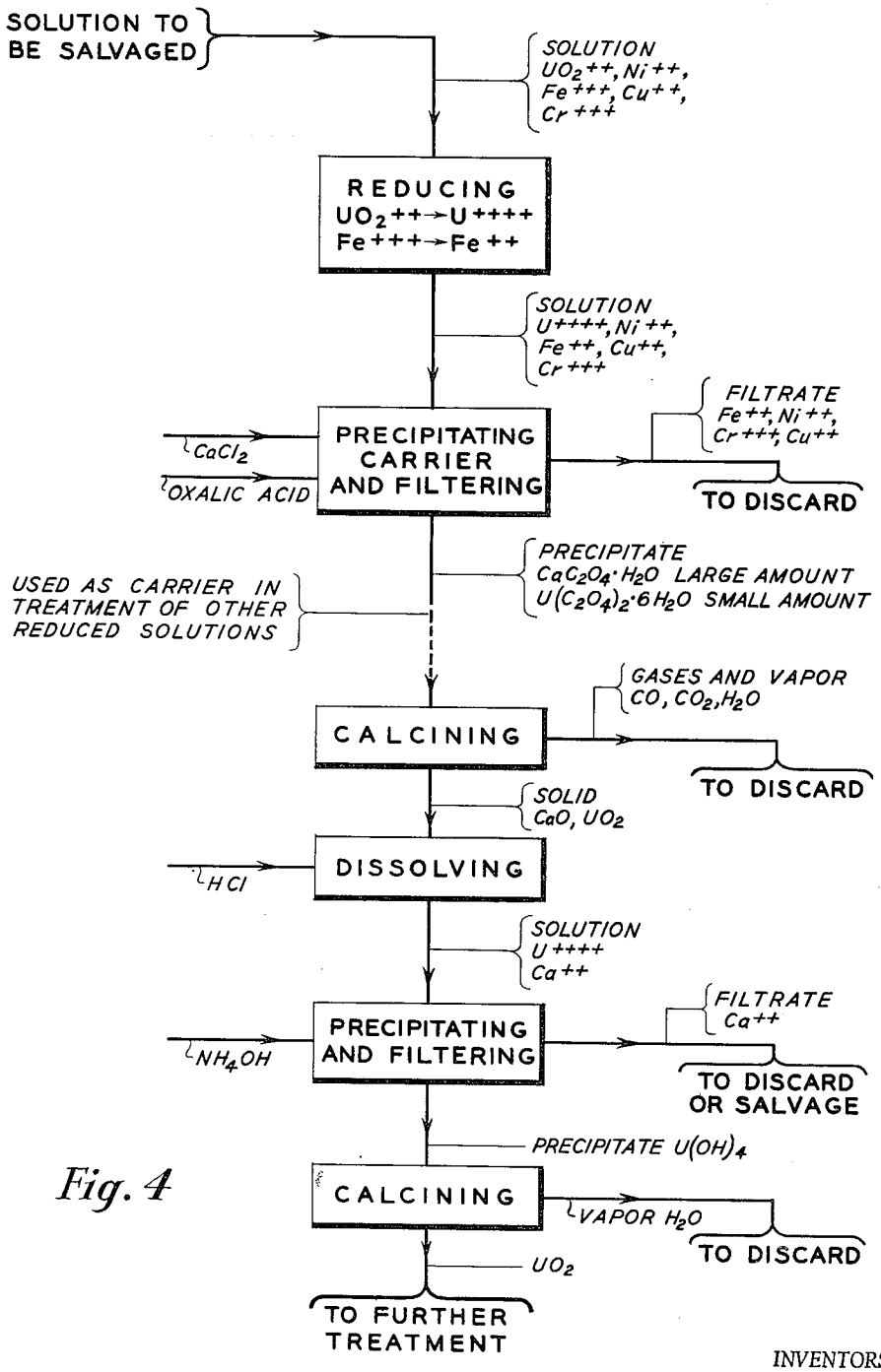


Fig. 4

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United States Patent Office

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IMPROVED URANIUM RECOVERY AND PURIFICATION PROCESSES

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Application June 27, 1944, Serial No. 542,378

10 Claims. (Cl. 23—14.5)

The present invention relates to processes of reclaiming uranium from a calutron 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, now Patent No. 2,758,006, issued August 7, 1956.

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 enriched with U^{235} from the collector of a calutron upon which the enriched 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 precipitated away from metal impurities in the wash solution as uranous oxalate.

A still 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.

The invention both as to its organization and method of operation, together with further objects and advantages thereof, will best be uderstood by reference to the following specification taken in connection with the accompanying drawings, in which Figure 1 illustrates a portion of the flow diagram of the present process, indicating the recovery of the residue of UCl_4 from the parts of the calutron disposed in the source region thereof upon which it is deposited; Fig. 2 illustrates another portion of 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; Fig. 3 illustrates a further portion of the flow diagram of the present process, indicating the purification of the recovered uranium; and Fig. 4 illustrates a still further portion of the flow diagram of the present process, indicating the salvage of a fraction of uranium contained in materials which have been previously subjected to primary uranium recovery treatment.

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, which issued as U. S. Patent 2,709,222 on May 22, 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 several isotopes in order to produce the element enriched with the selected isotope. For example,

the machine is especially useful in producing uranium enriched with U^{235}.

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 de-ionizing and collecting the ions of the selected isotope thus concentrated, thereby to produce a deposit of the element enriched with the selected isotope. Moreover, in such a machine it is not essential that the material initially introduced be a naturally occurring polyisotope, such as naturally occurring uranium. It is feasible to separate any intermixed or intermingled materials capable of producing ions distinguishable from each other by differences in nuclear mass. Since this is true, it is not essential that the initial material mixtures be made up necessarily of the same chemical elements, as various different elements in intermixed form can readily be separated.

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 surfaces 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 uranium enriched with U^{234} and U^{235} will be deposited in the first pocket of said collector while uranium comprising substantially only U^{238} will be deposited in the second pocket thereof. Some metallic uranium of normal isotopic composition will also be deposited on various of the said interior surfaces since certain of the ionized uranium materials have charge-to-mass ratios which cause the material to miss the collector and deposit on said surfaces.

In utilizing calutrons to effect the enrichment of uranium in a selected isotope, e. g., U^{235}, the plant includes relatively large numbers of first-stage calutrons arranged in cascade with a relatively small number of second-stage calutrons. Singly enriched material from the first-stage calutron is recovered from the collector thereof, converted to UCl_4 and used as feedstock in the second-stage machine as disclosed in the aforesaid application of Carter and Kamen. Residual UCl_4 from the second-stage calutron source region and uranium from the second pocket of the second-stage calutron collector is recovered and recycled as likewise disclosed therein. U^{235} is recovered from the first pocket of the second-stage calutron collector and converted to a standard compound of uranium for commercial use, also as described in the aforesaid application. The residue of UCl_4 and metallic uranium from the source regions and other interior surfaces of the first-stage calutron are recovered and recycled in the first-stage calutron. The initial steps of the processes utilized in recovering the various materials noted in the foregoing results in the formation of various impure uranium solutions which are par-

ticularly suited for treatment in the process of the present invention.

Considering now the details of the recovery of the UCl_4 residue from the parts of either a first-stage or a second-stage calutron disposed in the source region thereof, reference is made to the portion of the flow diagram illustrated in Fig. 1. The parts of the calutron disposed in the source region thereof, principally the source-region end of the liner, 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 calutron 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 an oxidizing agent such as 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. Carbon is not oxidized by this treatment. The effect of the oxidation on the various materials contained in the wash solution may be indicated as follows:

$$U^{++++} \rightarrow UO_2^{++}$$
$$UO_2^{++} \rightarrow UO_2^{++}$$
$$U(OH)_4 \rightarrow UO_2^{++}$$
$$Cu^0 \rightarrow Cu^{++}$$
$$CuCl \rightarrow Cu^{++}$$
$$Cu_2O \rightarrow Cu^{++}$$
$$Fe^{++} \rightarrow Fe^{+++}$$
$$Cr^{+++} \rightarrow Cr^{+++}$$
$$Ni^{++} \rightarrow Ni^{++}$$
$$C^0 \rightarrow C^0$$

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 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 reusing 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. The original filtrate mentioned above, or the concentrated filtrate following evaporation, in the event this step is employed, is then stored for further treatment.

It will be understood that the stored water wash derived from the parts of the first-stage calutron disposed in the source region thereof, as explained above, comprises uranium of natural or normal composition with reference to U^{235}; while the stored water wash derived from the parts of the second-stage calutron disposed in the source region thereof, as explained above, comprises uranium which is singly enriched with U^{235}.

Considering now the details of the recovery of the metallic uranium, singly enriched with U^{235}, from the first pocket of the collector of the first-stage calutron, or of the metallic uranium, doubly enriched with U^{235}, from the first pocket of the collector of the second-stage calutron, reference is made to the portion of the flow diagram illustrated in Fig. 2. The inner surfaces of the first pocket of the collector of the calutron are etched with a solvent for the deposited uranium such as an aqueous solution containing HCl (approximately two percent) and H_2O_2 (approximately 0.5%), whereby the deposit of metallic uranium, either singly or doubly enriched with U^{235}, 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 the first pocket of the collector of the calutron which are thus washed with the acid solution 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^{++}. Thus, the acid wash solution employed 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 as described above; otherwise, this step is omitted.

The metallic uranium, impoverished with respect to U^{235}, and deposited in the second pocket of the collector of the first-stage calutron, may be recovered merely by etching the inner surfaces of the second pocket of this collector with a suitable wash acid of the character mentioned above, whereby this deposit of metallic uranium is dissolved. This acid wash is then discarded, as it contains so little U^{235} that further processing thereof is not feasible.

On the other hand, the metallic uranium which has been first enriched with respect to U^{235} and subsequently impoverished with respect to U^{235}, and deposited in the second pocket of the collector of the second-stage calutron, may be recovered by etching the inner surfaces of the second pocket of this collector with a suitable wash acid of the character mentioned above, whereby this 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 the second pocket of the collector of the calutron which are thus etched with the acid solution 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^{++}. The considerations concerning whether the wash acid should be concentrated are the same as those previously noted. In any case, either the original wash acid mentioned above, or the concentrated wash acid following evaporation, in the event this step is employed, is then analyzed in order to determine the U^{235} content thereof. In the event the analysis indicates that the U^{235} content of this wash acid is at least as great as natural or normal uranium, it is stored for further treatment; on the other hand, in the event the analysis indicates that the U^{235} content of this wash acid is less than that of natural or normal uranium, it is discarded, as further processing thereof is not feasible.

To the stored water wash solution derived from the parts of the first-stage calutron disposed in the source region thereof, there is added the stored acid wash solution derived from the second pocket of the collector of the second-stage calutron in order to produce a first composite solution; this first composite solution comprises uranium of substantially natural or normal composition with reference to U^{235}. Also, to the stored water wash solution derived from the parts of the second-stage calutron disposed in the source region thereof, there is added

the stored acid wash solution derived from the first pocket of the collector of the first-stage calutron in order to produce a second composite solution; this second composite solution comprises uranium which is singly enriched with U^{235}. Finally, the stored acid wash solution derived from the first pocket of the collector of the second-stage calutron constitutes a third composite solution; this third composite solution comprises uranium which is doubly enriched with U^{235}.

Considering now the details of the purification of one of the composite solutions described above, comprising the following ions: UO_2^{++}, Cu^{++}, Fe^{+++}, Cr^{+++} and Ni^{++}, reference is made to the portion of the flow diagram illustrated in Fig. 3. Any one of the composite solutions mentioned is already considerably acid, containing Cl^- ion, in view of the derivation thereof as explained above. However, the solution is first acidified, if this is necessary, with HCl, in order to make it about 1N to 3N in hydrogen ion content; and is then reduced in any suitable manner, whereby the uranyl ion, UO_2^{++}, and the ferric ion, Fe^{+++}, are reduced to the uranous ion, U^{++++} and to the ferrous ion, Fe^{++}, respectively.

For example, the solution may be reduced employing ammonium hyposulfite in the manner disclosed in the copending application of Robert Q. Boyer, Serial No. 552,548, filed September 2, 1944. However, it is preferred that the solution be reduced by electrolysis in an electrolytic cell of the character of that disclosed in the copending application of Robert Q. Boyer, Serial No. 532,162, filed April 21, 1944, now Patent No. 2,743,228, issued April 24, 1956. An electrolytic cell of the character mentioned essentially comprises an amalgamated nickel cathode, a graphite anode, and a porous barrier or separating structure disposed between the cathode and the anode, the structure mentioned being formed of alundum. In this electrolytic cell, the barrier or separating structure prevents the chlorine, which is liberated at the anode, from contacting the uranous ion produced at the cathode by the reduction of the uranyl ion and the consequent re-oxidation thereof back to uranyl ion. More particularly, the acidified solution is treated in the electrolytic cell, whereby the uranyl and ferric ions are reduced to uranous and ferrous ions, as previously mentioned. The reduced solution is then treated with an excess of $H_2C_2O_4$, whereby $U(C_2O_4)_2 \cdot 6H_2O$ is precipitated away from the copper, iron, chromium and nickel impurities in the solution. More specifically, the oxalic acid produces uranous oxalate, which is extremely insoluble in the acid solution, and cupric, chromic, ferrous and nickelous oxalates, which are soluble in the acid solution. The precipitation of the uranium as uranous oxalate away from the metal impurities in the solution is most advantageously effected when the acid solution is about 1N to 3N in hydrogen ion, as previously noted.

The solution is then filtered and the uranous oxalate precipitate is washed with a dilute oxalic acid solution in order positively to carry into the filtrate any slight metal impurities occluded. The filtrate containing the Cu^{++}, Fe^{++}, Cr^{+++} and Ni^{++} ions is then discarded or subjected to salvage treatment in order to recover any uranium contained. The $U(C_2O_4)_2 \cdot 6H_2O$ precipitate is then calcined in a non-oxidizing atmosphere, such as nitrogen or hydrogen, at about 500° C. in order to produce UO_2, whereby CO_2 and CO gases and water vapor are 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.

It will be understood that the purification of the first composite solution in the manner described above is productive of a first batch of UO_2 containing uranium of substantially natural or normal composition with reference to U^{235}. Also, the purification of the second composite solution in the manner described above is productive of a second batch of UO_2 containing uranium which is singly enriched with U^{235}. Finally, the purification of the third composite solution in the manner described above is productive of a third batch of UO_2 containing uranium which is doubly enriched with U^{235}. The first and second batches of UO_2 are then converted back to UCl_4 for re-treatment in the first-stage and second-stage calutrons, respectively, while the third batch of UO_2 is available for commercial use.

In order to effect said conversion of UO_2 to UCl_4, a batch of UO_2 is reacted with CCl_4 in the vapor phase at approximately 450° C. in a suitable reaction chamber, in order to produce crude UCl_4, whereby $COCl_2$, CO_2, CO and Cl_2 gases are given off incident to the reaction; all as disclosed in the copending application of James M. Carter, Serial No. 490,293, filed June 10, 1943, which issued as U. S. Patent 2,677,592 on May 4, 1954. The crude UCl_4 thus produced is then sublimed in a suitable molecular still at approximately 600° C. in order to produce a sublimate of UCl_4, whereby residues of UO_2 and $UOCl_2$ are produced incident to the sublimation. The residues of UO_2 and $UOCl_2$ are ultimately converted to UCl_4. The UCl_4 thus produced is of very pure form, and is suitable for re-cycling in the appropriate one of the first-stage or second-stage calutrons, in the manner previously explained. More particularly, the conversion of the first batch of UO_2 is productive of a first batch of UCl_4 containing uranium of substantially natural or normal composition with reference to U^{235}; this first batch of UCl_4 is re-cycled in the first stage calutron. Also, the conversion of the second batch of UO_2 is productive of a second batch of UCl_4 containing uranium singly enriched with U^{235}; this second batch of UCl_4 is re-cycled in the second-stage calutron.

The present process of recovering uranium from wash solutions derived from calutrons is very effective, in view of the fact that it is quite versatile. Thus, not only may uranium be reclaimed from a wash solution containing the impurities mentioned, copper, iron, chromium and nickel, but the wash solution may contain a variety of other impurities, such as manganese and zinc, without adversely affecting the purification. Moreover, the purification can be carried out as explained, without particular reference to the identification of the impurities or the proportions contained in the wash solution; this feature is very advantageous, in view of the fact that both the particular impurities, as well as the related quantities thereof, vary considerably among the different wash solutions derived from the different calutrons.

Also, it will be appreciated that in the present process the various steps of the recovery and purification of the uranium are so correlated that extraneous anions are not introduced in the various solutions, but that the Cl^- anion is encountered throughout, thereby to maintain substantially constant the qualitative anion content in the various solutions. More particularly, the recovery of the residue of UCl_4 from the source regions of the various calutrons by the water wash step is productive of an acid solution containing Cl^- anion; and the recovery of the metallic uranium from the collectors of the various calutrons by the hydrochloric acid-hydrogen peroxide wash step is productive of an acid solution containing Cl^- anion. Also, in the principal purification step prior to electrolytic reduction of the various solutions, the solutions are acidified with hydrochloric acid, thereby maintaining the Cl^- anion in the solutions.

In carrying out the present process it is again noted that in the purification of the second composite solution, comprising the acid wash derived from the first pocket of the collector of the first-stage calutron and the water wash derived from the source region of the second-stage calutron, and in the subsequent conversion of this second composite solution to produce the corresponding second batch of UCl_4, uranium is processed which has been singly enriched with U^{235}. Similarly, in the purification of the third composite solution, comprising the acid wash

derived from the first pocket of the collector of the second-stage calutron, uranium is processed which has been doubly enriched with U^{235}. In view of the fact that the uranium contained in the second and third composite solutions has been either singly or doubly enriched with U^{235}, it is very valuable, and it is essential that none of this uranium be lost. Accordingly, all precipitates and filtrates produced incident to processing the solutions mentioned, which might contain some of this uranium, are subjected to salvage treatment in order positively to reclaim any fractions of the contained uranium.

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. 4. More particularly, in the event the material which is to be subjected to salvage treatment is in solid form, it is first dissolved in HCl, thereby to obtain an acidified 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 first treated with HCl, thereby to obtain an acidified salvage solution. 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, the acidified 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^{++}.

A plurality of salvage solutions of the character mentioned are first prepared in accordance with the composition of the contained uranium fraction with reference to U^{235}. In other words, a first salvage solution is prepared comprising a fraction of uranium which is singly enriched with U^{235}; and a second salvage solution is prepared comprising a fraction of uranium which is doubly enriched with U^{235}; the salvage solutions mentioned being prepared from the materials from the corresponding portions of the prior recovery and purification steps, as previously explained, whereby the solutions are not mixed unless the contained uranium fractions are of substantially the same composition with reference to U^{235}.

The acidified salvage solution containing the ions mentioned is first reduced, whereby the uranyl and ferric ions are reduced to uranous and ferrous ions, respectively. For example, the solution may be electrolytically reduced in the manner previously explained, utilizing the electrolytic cell disclosed in the previously mentioned application of Robert Q. Boyer. Thus, the reduced solution contains the following ions: U^{++++}, Fe^{++}, Cr^{+++}, Ni^{++} and Cu^{++}.

The reduced solution is then divided into a number of portions of appropriate volume for handling purposes, and to a first of these portions there is added a suitable quantity of water-soluble alkaline earth metal salt the oxalate of which is relatively water-insoluble, preferably in solid form. $CaCl_2$ is particularly suitable for this purpose. The first portion is then stirred until the calcium chloride is dissolved, whereupon an excess of $H_2C_2O_4$ is added, whereby $CaC_2O_4 \cdot H_2O$ and $U(C_2O_4)_2 \cdot 6H_2O$ are precipitated away from the metal impurities in the acid solution. The quantity of $CaCl_2$ dissolved in the first portion, as explained above, is such that after precipitation of the calcium oxalate and uranous oxalate by the oxalic acid, the hydrogen ion content of the solution is about 1N to 3N. This arrangement prevents precipitation of the ferrous, chromic, cupric and nickelous oxalates. Also, it will be understood that the calcium oxalate precipitate not only carries the uranous oxalate precipitate which is produced, but it also carries, due to surface action, any small amount of uranous ions which are not precipitated as uranous oxalate. The solution is then filtered and the calcium oxalate and uranous oxalate precipitate is washed with a dilute oxalic acid solution. The calcium oxalate precipitate carrying the uranium is then conserved for further use.

The precipitate obtained in the manner described above is then dissolved in a solution of 3N HCl and any residue is filtered off. The filtrate containing the calcium ions and the uranous ions is then introduced into a second portion of the solution mentioned and an excess of $H_2C_2O_4$ is aded thereto, whereby $CaC_2O_4 \cdot H_2O$ and $U(C_2O_4)_2 \cdot 6H_2O$ are again precipitated away from the metal impurities in the solution. Thus, the calcium oxalate carries the uranous oxalate precipitate which is produced and also any small amount of uranous ions which are not precipitated as uranous oxalate. The solution is then filtered and the calcium oxalate and uranous oxalate precipitate is washed with a dilute oxalic acid solution. The calcium oxalate precipitate carrying the uranium is then conserved for further use.

The above-described cycle, wherein the calcium oxalate precipitate is employed in the treatment of the different portions of the solution, is repeated an appropriate number of times, until this body of calcium oxalate carries an appropriate amount of uranous oxalate; at which time the uranium carried by the calcium oxalate is recovered therefrom.

More particularly, the body of calcium oxalate containing uranous oxalate is calcined in a non-oxidizing atmosphere, such as nitrogen or hydrogen, at about 500° C. in order to produce CaO and UO_2, whereby CO and CO_2 gases and water vapor are given off incident to the calcination.

The calcium oxide and uranium dioxide residue is dissolved in 6N HCl, whereby a solution of uranous and calcium ions is produced. The solution containing the U^{++++} and Ca^{++} ions is then treated with ammonia, either as a gas or in aqueous solution, whereby the uranium is precipitated as $U(OH)_4$ away from the calcium ion in solution. 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_4NO_3, in order to carry any occluded calcium into the filtrate. The filtrate containing the calcium impurity is discarded, and the uranous hydroxide is calcined in a non-oxidizing atmosphere, such as nitrogen or hydrogen, at about 250° C. 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.

It will be understood that when a first salvage solution containing a fraction of uranium which is singly enriched with U^{235} is treated in the manner described above, a first quantity of UO_2 is produced, comprising uranium of a like isotopic composition. Also, when a second salvage solution containing a fraction of uranium which is doubly enriched with U^{235} is treated in the manner described above, a second quantity of UO_2 is produced, comprising uranium of a like isotopic composition. The first and second quantities of UO_2 obtained in the manner explained above may be added to the second and third batches of UO_2 which are produced incident to the primary purification steps, as previously explained. On the other hand, these quantities of UO_2 produced as a result of the salvage operation may be dumped in appropriate ones of the acid and water wash solutions. For example, the first quantity of UO_2 may be dumped in the water wash solution derived from the source region of the second-stage calutron; while the second quantity of UO_2 may be dumped in the acid wash derived from the first pocket of the collector of the second-stage calutron.

In view of the foregoing, it is apparent that there has been provided an improved process of recovering, reclaiming, salvaging, purifying and converting uranium, both in metallic and compound forms, in conjunction

with the calutron method, whereby uranium enriched with U^{235} may be produced on a large scale in commercial quantities.

Also, it will be understood that the present process may be suitably modified so that a compound of uranium other than UCl_4 may be treated either in the first-stage or in the second-stage calutron. For example, the calutron, as well as the conversion steps of the process, may be modified, whereby UCl_6, UBr_4, etc. may be treated in order to produce uranium enriched with U^{235}.

The term "uranium" is employed in the present specification and claims in a generic sense, i. e., as applying to uranium whether in elemental form or in the form of its compounds, unless indicated otherwise 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 parts of a calutron upon which it is deposited, which parts contain metals of the group consisting of iron, chromium, nickel, and copper, which comprises washing said parts with a solvent to obtain a solution containing uranium and said metals as impurities, subjecting the wash solution to treatment in order to separate the uranium from the metal impurities, whereby a small fraction of the uranium remains with the metal impurities, producing a solution of the metal impurities and the fraction of the uranium remaining therewith, reducing the uranium to the uranous state, adding calcium chloride and oxalic acid to the reduced solution to produce a calcium oxalate precipitate under such conditions that the hydrogen ion content of the solution at the completion of the precipitation is in the range of 1N to 3N whereby the uranous uranium is precipitated with and carried by the calcium oxalate away from the impurities in the solution, filtering the calcium oxalate and the carried uranium from the solution leaving the metal impurities in the filtrate, calcining the calcium oxalate and the carried uranium to produce a mixture of calcium oxide and uranium dioxide, dissolving the mixture of calcium oxide and uranium dioxide in an acid, treating the solution with ammonia to precipitate the uranium as uranous hydroxide away from the calcium in the solution, and then separating the uranous hydroxide precipitate from the solution.

2. The process of reclaiming metallic uranium values from deposits formed with a metal surface which surface contains metals of the group consisting of iron, chromium, nickel, and copper, comprising washing said surface with a solution containing approximately 2% of HCl and approximately 0.5% of H_2O_2 to produce an acidic chloride solution containing uranyl ions and the ions of said metals as impurities, adjusting the hydrogen ion content of the solution to the range 1N to 3N, treating said solution to reduce the uranyl ions to the uranous state, then treating said solution with oxalic acid to precipitate uranous oxalate away from the impurities in solution, and separating said uranous oxalate from the solution.

3. The process of reclaiming uranium values present in small quantities in a solid salvage residue containing compounds of the metals of the group consisting of iron, chromium, nickel, and copper comprising producing an acidic chloride solution of said deposits containing uranyl ions and the ions of said metals as impurities, reducing said uranyl ions to the uranous state in the solution, treating said solution with calcium chloride and oxalic acid to form a precipitate of calcium oxalate in the solution under conditions such that the hydrogen ion content of the solution is in the range 1N to 3N at the completion of the precipitation thereby precipitating and carrying said uranous ions from the impurities in the solution, and separating said calcium oxalate precipitate carrying uranium from the solution.

4. The process of reclaiming uranium values from deposits formed on a metal surface which surface contains metals of the group consisting of iron, chromium, nickel, and copper, comprising washing said surface with an aqueous solvent to produce an acidic solution containing uranyl ions and the ions of said metal as impurities, treating said solution to remove the major portion of said uranyl ions leaving a minor portion thereof with said impurities in the solution, reducing said minor portion of uranyl ions to the uranous state in the solution, treating said solution with calcium chloride and oxalic acid to form a precipitate of calcium oxalate under conditions such that the hydrogen ion content of the solution remains within the range of 1N to 3N during the precipitation thereby precipitating and carrying the uranous ions away from the impurities in the solution, filtering said calcium oxalate precipitate from the solution, calcining said calcium oxalate precipitate to produce a mixture of calcium oxide and uranium dioxide, dissolving said mixture in acid to form a solution containing uranous and calcium ions, treating said solution with ammonia to precipitate uranous hydroxide away from the calcium ions, and separating said uranous hydroxide from the solution.

5. The process for recovering metallic uranium isotope 238 values from deposits formed with a metal surface containing metals of the group consisting of iron, chromium, nickel, and copper, comprising washing said surface with an aqueous solution containing about 2% of HCl and about 0.5% of H_2O_2 to produce an acidic chloride solution containing uranyl ions and the ions of said metals as impurities, adjusting the hydrogen ion content of the solution to the range 1N to 3N, treating said solution to reduce the uranyl ions to the uranous state, treating the reduced solution with oxalic acid to precipitate uranous oxalate away from the impurities in the solution, and separating said uranous oxalate from the solution.

6. In a process for recovering uranium values wherein there is produced an acidic aqueous solution containing small amounts of uranous ions and relatively large amounts of impurity ions of the metals of the group consisting of iron, chromium, nickel and copper, the steps comprising producing a calcium oxalate precipitate in said solution under conditions such that the hydrogen ion content of the solution remains within the range 1N to 3N to precipitate and carry uranous values from the solution, and recovering the uranium values from the calcium oxalate precipitate.

7. The process for recovering metallic uranium isotope 235 values from deposits formed with a metal surface containing metals of the group consisting of iron, chromium, nickel and copper, comprising washing said surface with an aqueous solution containing about 2% of HCl and about 0.5% of H_2O_2 to produce an acidic chloride solution containing uranyl ions and the ions of said metals as impurities, adjusting the hydrogen ion content of the solution to the range 1N to 3N, treating said solution to reduce the uranyl ions to the uranous state, treating the reduced solution with oxalic acid to precipitate uranous oxalate away from the impurities in the solution, and separating said uranous oxalate from the solution.

8. The process of reclaiming uranium values from deposits formed on a metal surface which surface contains metals of the group consisting of iron, chromium, nickel, and copper, comprising washing said surface with an aqueous solvent to produce an acidic solution containing uranyl ions and the ions of said metals as impurities, treating said solution to reduce uranyl ions to the uranous state in the solution, acidifying the solution with hydrochloric acid to adjust the hydrogen ion content to the range of 1N to 3N, treating the acidified solution with excess oxalic acid to precipitate the major portion

of the uranium values from the solution, separating the precipitate from the solution, whereby a minor portion of the uranyl ions remain in the solution, reducing said minor portion of uranyl ions to the uranous state in the solution, treating said solution with calcium chloride and oxalic acid to form a precipitate of calcium oxalate under conditions such that the hydrogen ion content of the solution remains within the range of 1N to 3N during the precipitation, thereby precipitating and carrying the uranous ions away from the impurities in the solution, filtering said calcium oxalate precipitate from the solution, calcining said calcium oxalate precipitate to produce a mixture of calcium oxide and uranium dioxide, dissolving said mixture in acid to form a solution containing uranous and calcium ions, treating said solution with ammonia to precipitate uranous hydroxide away from the calcium ions, and separating said uranous hydroxide from the solution.

9. The process of reclaiming uranium values from deposits of a water-soluble uranium compound formed on a metal surface containing metals of the group consisting of iron, chromium, nickel, and copper, comprising washing said surface with an aqueous solvent to produce an acidic chloride solution containing uranyl ions and the ions of said metals as impurities, treating said solution to reduce uranyl ions to the uranous state in the solution, acidifying the solution with hydrochloric acid to adjust the hydrogen ion content to the range of 1N to 3N, treating the acidified solution with excess oxalic acid to

precipitate the major portion of the uranium values from the solution, separating the precipitate from the solution, whereby a minor portion of the uranyl ions remain in the solution, reducing said minor portion of uranyl ions to the uranous state in the solution, treating said solution with calcium chloride and oxalic acid to form a precipitate of calcium oxalate under conditions such that the hydrogen ion content of the solution remains within the range of 1N to 3N during the precipitation, thereby precipitating and carrying the uranous ions away from the impurities in the solution, filtering said calcium oxalate precipitate from the solution, calcining said calcium oxalate precipitate to produce a mixture of calcium oxide and uranium dioxide, dissolving said mixture in acid to form a solution containing uranous and calcium ions, treating said solution with ammonia to precipitate uranous hydroxide away from the calcium ions, and separating said uranous hydroxide from the solution.

10. The process as defined in claim 9 but wherein said water-soluble compound comprises uranium chloride and said aqueous solvent comprises water.

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