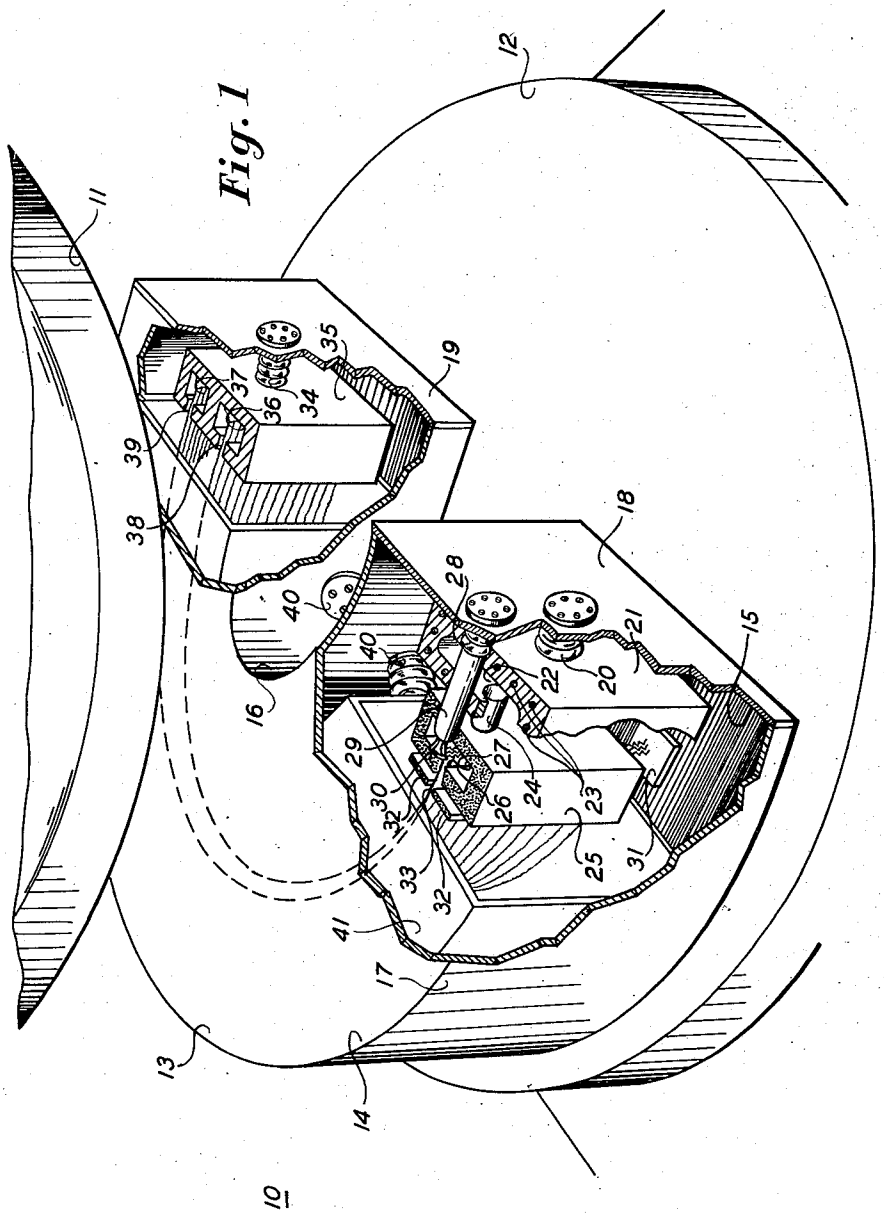
Oct. 7, 1958 J. M. CARTER ET AL 2,855,270

PROCESS OF RECOVERING URANIUM

Filed Oct. 20, 1944 5 Sheets-Sheet 1

Fig. 1



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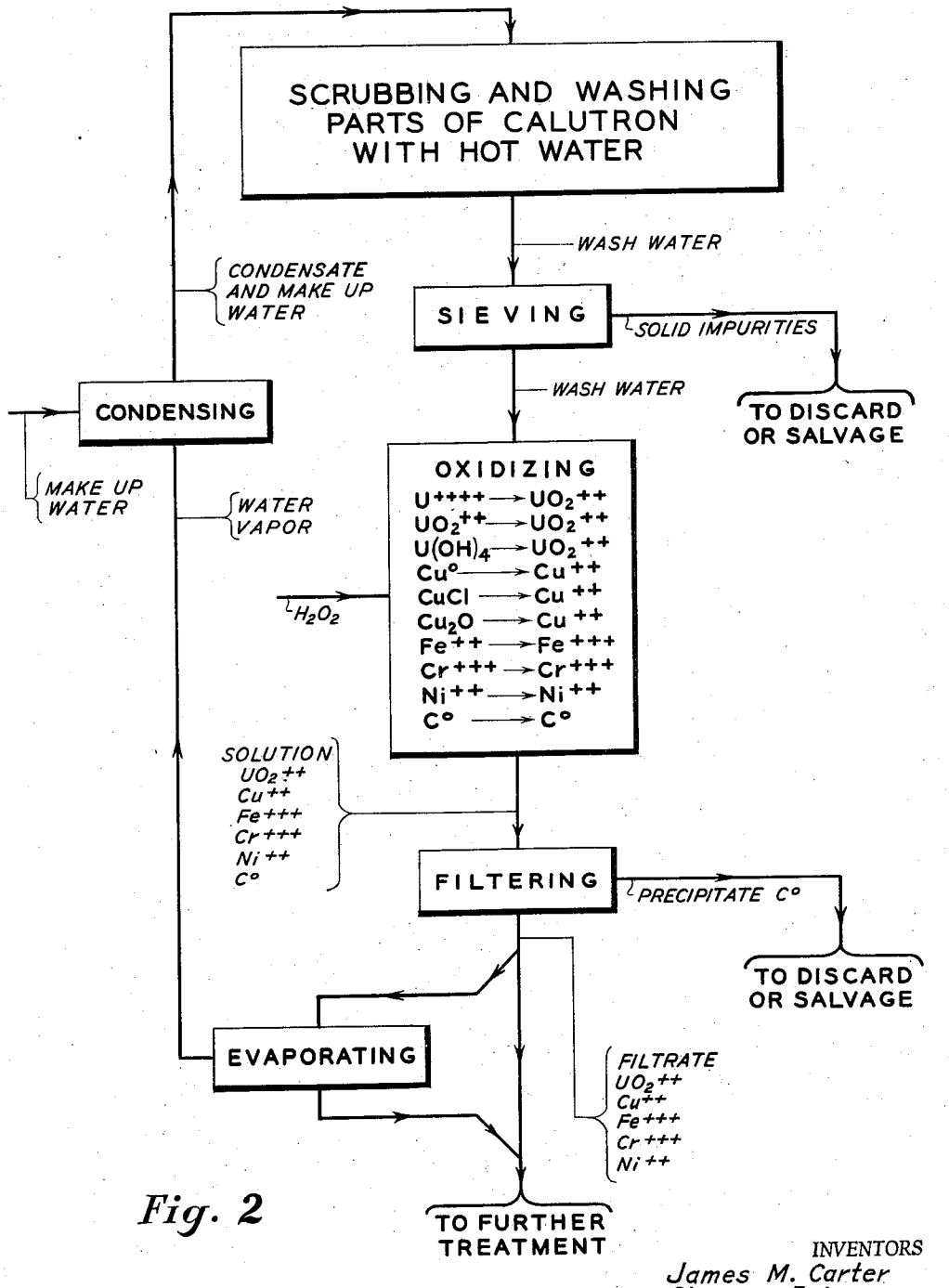


Fig. 2

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Oct. 7, 1958 J. M. CARTER ET AL 2,855,270

PROCESS OF RECOVERING URANIUM

Filed Oct. 20, 1944 5 Sheets-Sheet 3

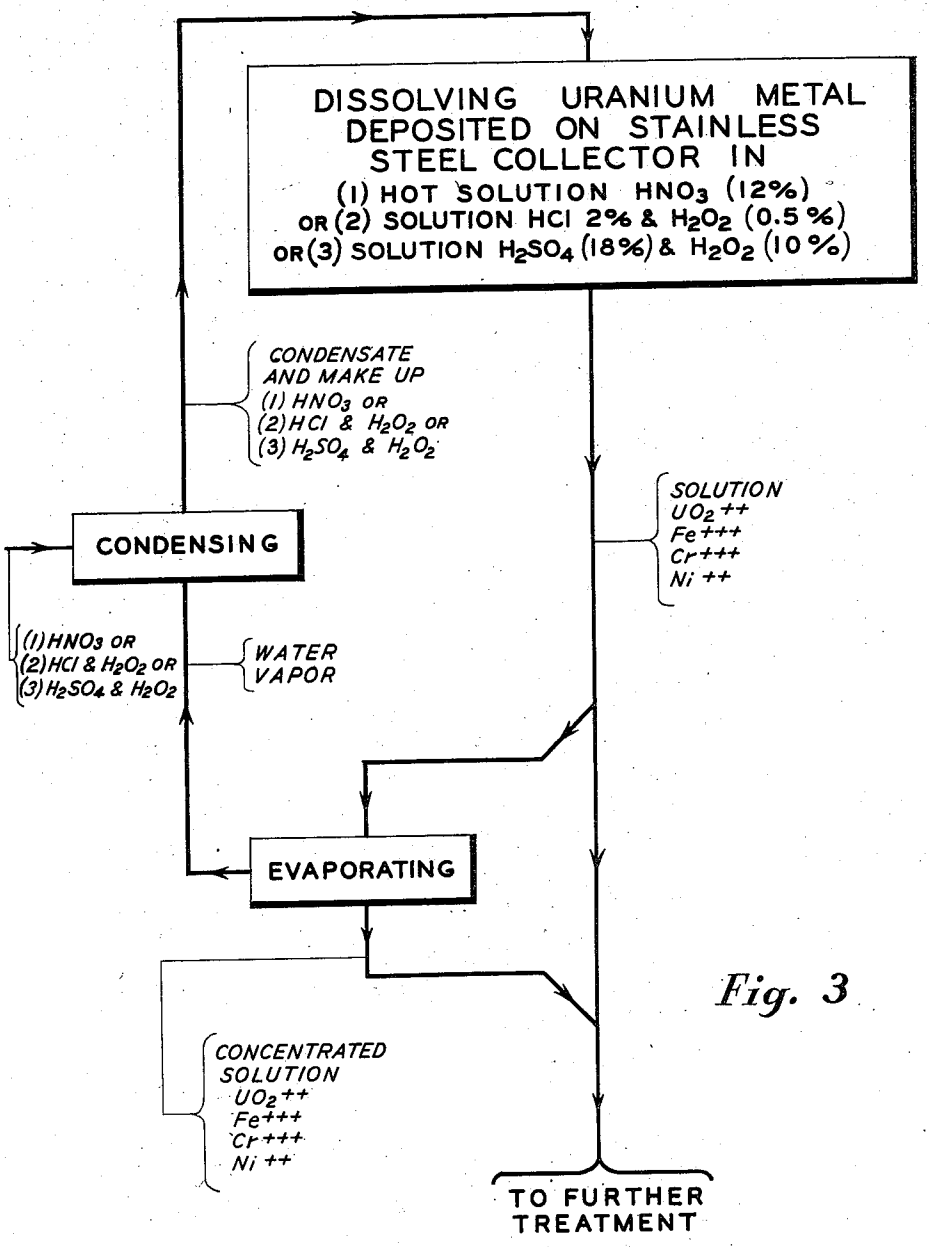


Fig. 3

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PROCESS OF RECOVERING URANIUM

Filed Oct. 20, 1944 5 Sheets-Sheet 4

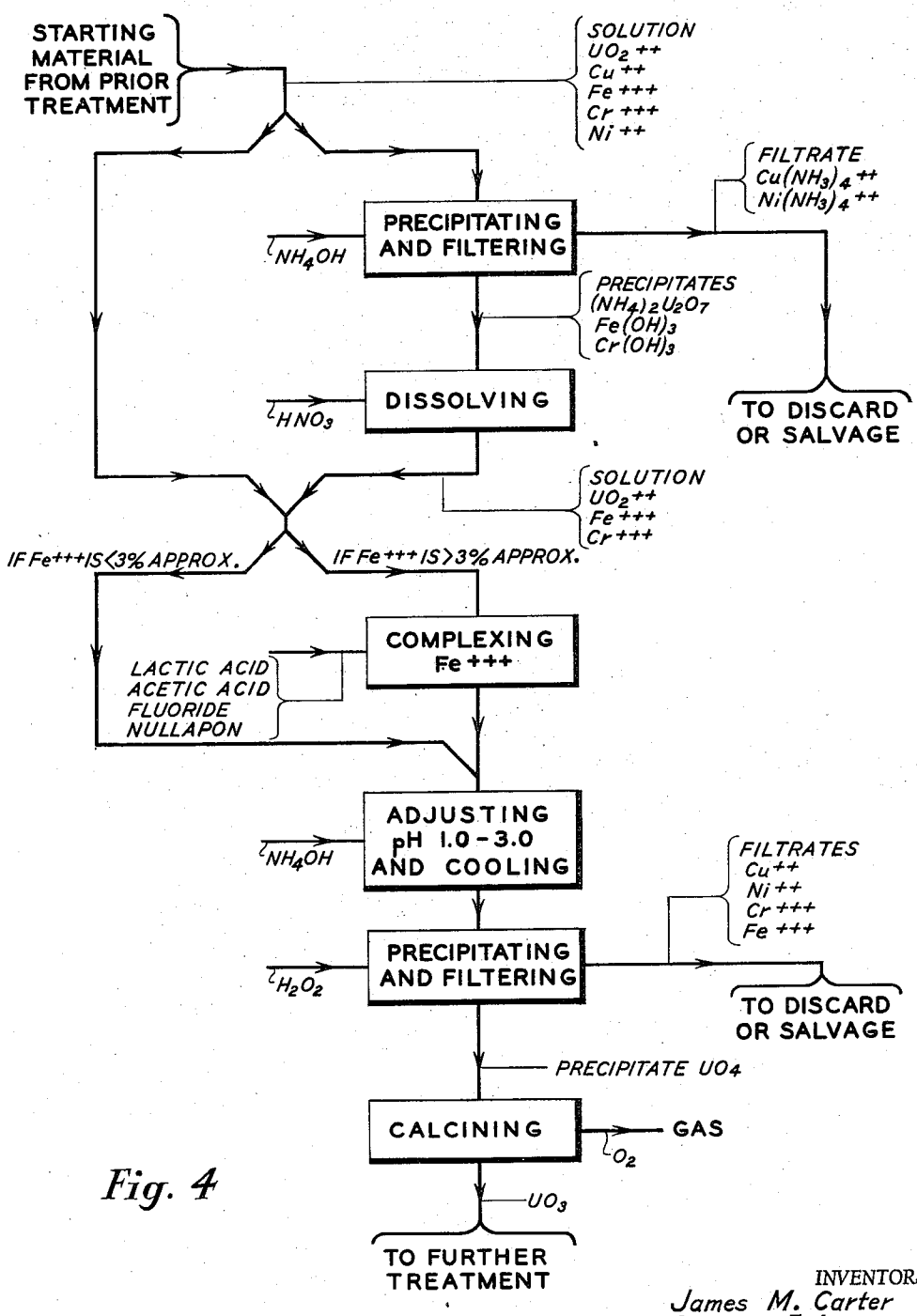


Fig. 4

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Oct. 7, 1958 J. M. CARTER ET AL 2,855,270

PROCESS OF RECOVERING URANIUM

Filed Oct. 20, 1944 5 Sheets-Sheet 5

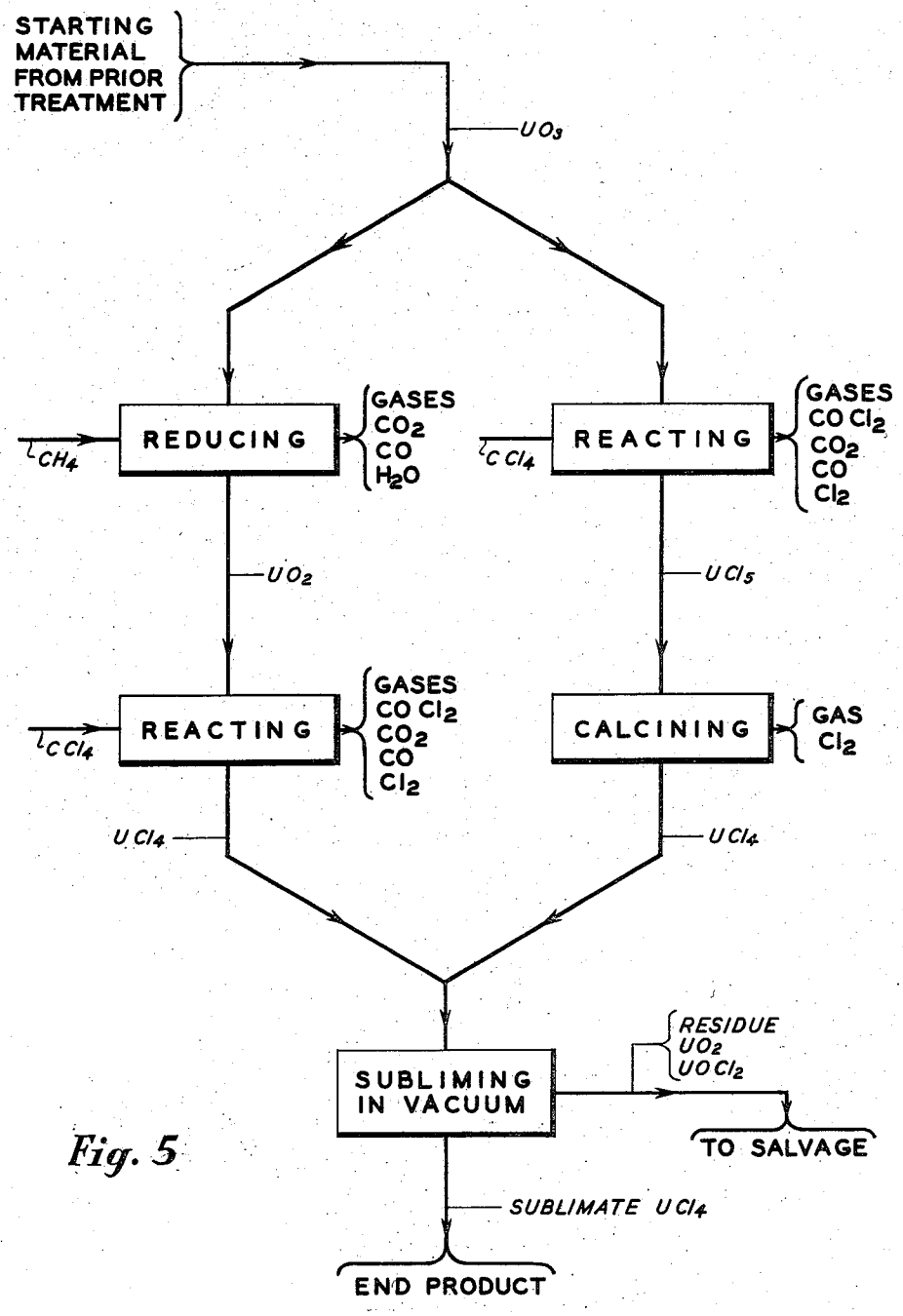


Fig. 5

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United States Patent Office

2,855,270

Patented Oct. 7, 1958

2,855,270

PROCESS OF RECOVERING URANIUM

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Application October 20, 1944, Serial No. 559,624

8 Claims. (Cl. 23—14.5)

The present invention relates to processes of producing 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, now Patent No. 2,758,006.

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 an 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 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 still 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 as uranium peroxide away from metal impurities in the wash solution.

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 is a perspective view, partly broken away, of a calutron in conjunction with which there may be carried out the process of the present invention; Fig. 2 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. 3 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. 4 illustrates a further portion of the flow diagram of the present process, indicating the purification of the recovered uranium; and Fig. 5 illustrates a still further portion of the flow diagram of the present process, indicating the ultimate conversion of the purified uranium back to UCl_4.

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, 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 the 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.

Referring now more particularly to Fig. 1, there is illustrated a representative example of a calutron **10** of the character noted, which comprises magnetic field structure including upper and lower pole pieces **11** and **12**, provided with substantially flat parallel spaced-apart pole faces, and a tank **13** disposed between the pole faces of the pole pieces **11** and **12**. The pole pieces **11** and **12** carry windings, not shown, which are adapted to be energized in order to produce a substantially uniform and relatively strong magnetic field therebetween, which magnetic field passes through the tank **13** and the various parts housed therein. The tank **13** is of tubular configuration, being substantially crescent-shaped in plan, and comprising substantially flat parallel spaced-apart top and bottom walls **14** and **15**, upstanding curved inner and outer walls **16** and **17**, and end walls **18** and **19**. The end walls **18** and **19** close the opposite ends of the tubular tank **13** and are adapted to be removably secured in place, whereby the tank **13** is hermetically sealed. Also, vacuum pumping apparatus, not shown, is associated with the tank **13**, whereby the interior of the tank **13** may be evacuated to a pressure of the order of 10^{-5} to 10^{-4} mm. Hg. Preferably, the component parts of the tank **13** are formed of steel, the bottom wall **15** thereof resting directly upon the pole face of the lower pole piece **12**, and the top wall **14** thereof being spaced a suitable distance from the pole face of the upper pole piece **11**, whereby the top and bottom walls **14** and **15** constitute in effect pole pieces with respect to the interior of the tank **13**, as explained more fully hereinafter.

The removable end wall **18** carries an insulator **20** which supports an upstanding charge block **21**, provided with a hollow central cavity **22** constituting a charge receiving pocket surrounded by rather thick side walls. Electrical heating elements **23** are embedded in the side walls of the charge block **21** and are adapted to be connected to a suitable source of current, whereby the charge block **21** may be appropriately heated, the charge block **21** being formed of cast steel or the like. Also, the charge block **21** is provided with a removable cover, not shown, and supports a tubular member **24** which in turn supports an arc block **25** formed of carbon or graphite. The arc block **25** is substantially C-shaped in plan, an upstanding slot **26** being formed in the wall thereof remote from the charge block **21**. Thus, the arc block **25** is of hollow construction, having a central arc cavity **27** formed therein, the arc cavity **27** formed in the arc block **25** communicating through the tubular member **24** with the cavity **22** formed in the charge block **21**.

Also, the removable end wall **18** carries an insulator **28**, disposed above the insulator **20**, which supports horizontally projecting cathode structure **29**, including a filamentary cathode **30** adapted to be connected to a suitable source of current. The cathode structure **29** projects over the upper end of the charge block **21**, whereby the filamentary cathode **30** overhangs and is aligned with respect to the upper end of the cavity **27** formed in the arc block **25**. Further, an anode **31** is arranged below and in alignment with respect to the lower end of the cavity **27** formed

in the arc block 25, the anode 31 being supported by the charge block 21. The filamentary cathode 30 and the cooperating anode 31 are adapted to be connected to a suitable source of current.

Ion accelerating structure, including a pair of upstanding plates 32 formed of carbon or graphite, is supported by insulating structure, not shown, carried by the removable end wall 18. The pair of upstanding plates 32 are arranged in spaced-apart relation in order to define a slit 33 therebetween, arranged in substantial alignment with respect to the slot 26 formed in the wall of the arc block 25. A suitable source of voltage is adapted to be connected between the arc block 25 and the ion accelerating structure, including the plates 32, for a purpose more fully explained hereinafter.

The removable end wall 19 carries an insulator 34 which supports an upstanding collector block 35 formed of stainless steel or the like and provided with two laterally spaced-apart cavities or pockets 36 and 37 which communicate with aligned slots 38 and 39 formed in the wall of the collector block 35 disposed remote from the removable end wall 19. Alternatively, the collector block may be fabricated of steel plate and the inner surfaces of the pockets 36 and 37 lined with stainless steel plates. It is noted that the pockets 36 and 37 are adapted to receive two constituent isotopes of an element which have been separated in the calutron 10, as explained more fully hereinafter. Finally, the inner wall 16 carries a number of insulators 40 which support a tubular liner 41 formed of copper or the like, rectangular in vertical cross-section, disposed within the tank 13 and spaced from the walls 14, 15, 16 and 17 thereof. One end of the tubular liner 41 terminates adjacent the accelerating structure, including the plates 32; and the other end of the tubular liner 41 terminates adjacent the collector block 35; the tubular liner 41 constituting an electrostatic shield for the high-velocity ions traversing the curved paths between the slit 33 formed by the plates 32 of the ion accelerating structure and the slots 38 and 39 formed in the collector block 35, as explained more fully hereinafter.

In view of the above description, it will be understood that the parts of the calutron 10 carried by the removable end wall 18 constitute a source unit, and the end of the tank 13 disposed adjacent the source unit constitutes the source region of the calutron. Similarly, the parts of the calutron carried by the removable end wall 19 constitute a collector unit, and the end of the tank 13 disposed adjacent the collector unit constitutes the collector region of the calutron.

Considering now the general principle of operation of the calutron 10, a charge comprising a compound of the element to be treated is placed in the charge pocket 22 in the charge block 21, the compound of the element mentioned being one which may be readily vaporized. The cover, not shown, is then secured on the charge block 21 and the end walls 18 and 19 are securely attached to the open ends of the tank 13, whereby the tank 13 is hermetically sealed. The various electrical connections are completed and operation of the vacuum pumping apparatus, not shown, associated with the tank 13 is initiated. When a pressure of the order of 10^{-5} to 10^{-4} mm. Hg is established within the tank 13, the electric circuits for the windings associated with the pole pieces 11 and 12 are closed and adjusted, whereby a predetermined magnetic field is established therebetween, traversing the tank 13. The electric circuit for the heating elements 23 is closed, whereby the charge in the charge pocket 22 in the charge block 21 is heated and vaporized. The vapor fills the charge pocket 22 and is conducted through the tubular member 24 into the cavity 27 formed in the arc block 25. The electric circuit for the filamentary cathode 30 is closed, whereby the filamentary cathode 30 is heated and rendered electron-emissive. Then the electric circuit between the filamentary cathode 30 and the anode 31 is closed, whereby an arc discharge is struck therebetween, electrons proceeding from the filamentary cathode 30 to the anode 31. The electrons proceeding from the filamentary cathode 30 to the anode 31 break up the molecular form of the compound of the vapor to a considerable extent, producing positive ions of the element which is to be enriched with a selected one of its isotopes.

The electric circuit between the arc block 25 and the ion accelerating structure, including the plates 32, is completed, the plates 32 being at a high negative potential with respect to the arc block 25, whereby the positive ions are attracted and accelerated to the voltage impressed between the arc block 25 and the ion accelerating structure. More particularly, the positive ions proceed from the interior of the cavity 27 formed in the arc block 25, through the slot 26 formed in the wall thereof, and across the space between the plates 32 and the adjacent wall of the arc block 25, and thence through the slit 33 formed between the plates 32 into the interior of the tubular liner 41. The high-velocity positive ions form a vertical upstanding ribbon proceeding from the cavity 27 formed in the arc block 25 through the slot 26 and the aligned slit 33 into the tubular liner 41.

The collector block 35, as well as the tubular liner 41, is electrically connected to the ion accelerating structure, including the plates 32, whereby there is an electric field-free path for the high velocity positive ions, disposed between the plates 32 and the collector block 35 within the tubular liner 41. The high-velocity positive ions entering the adjacent end of the liner 41 are deflected from their normal straight-line path and from a vertical plane, passing through the slot 26 and the slit 33, due to the effect of the relatively strong magnetic field maintained through the space within the tank 13 and the liner 41 through which the positive ions travel, whereby the positive ions describe arcs, the radii of which are proportional to the square roots of the masses of the ions and consequently of the isotopes of the element mentioned. Thus, relatively light ions, a relatively light isotope of the element, describe an interior arc of relatively short radius and are focused through the slot 38 into the pocket 36 formed in the collector block 35; whereas relatively heavy ions, a relatively heavy isotope of the element, describe an exterior arc of relatively long radius and are focused through the slot 39 into the pocket 37 formed in the collector block 35. Accordingly, the relatively light ions are collected in the pocket 36 and are de-ionized to produce a deposit of the relatively light isotope of the element therein, while the relatively heavy ions are collected in the pocket 37 and are de-ionized to produce a deposit of the relatively heavy isotope of the element therein.

After all of the charge in the charge pocket 22 formed in the charge block 21 has been vaporized, all of the electric circuits are interrupted and the end wall 18 is removed so that another charge may be placed in the pocket 22 and subsequently vaporized in the manner explained above. After a suitable number of charges have been vaporized in order to obtain appropriate deposits of the isotopes of the element in the pockets 36 and 37 of the collector block 35, the end wall 19 may be removed and the deposits of the collected isotopes in the pockets 36 and 37 in the collector block 35 may be reclaimed.

Of course, it will be understood that the various dimensions of the parts of the calutron 10, the various electrical potentials applied between the various electrical parts thereof, as well as the strength of the magnetic field between the pole pieces 11 and 12, are suitably correlated with respect to each other, depending upon the mass numbers of the several isotopes of the element which is to be treated therein. By way of illustration, it is noted that when the calutron 10 is employed in order to produce uranium, the compound of uranium which is suggested as a suitable charge in the charge block 21 is UCl_4, as this compound may be readily vaporized and the mol-

ecular form of the vapor may be readily broken up to form positive ions of uranium with great facility.

More particularly, the minor fraction of the UCl_4 vapor is ionized to form positive atomic ions including U^+, U^{++}, Cl^+ and Cl^{++}; and positive molecular ions including Cl_2^+, Cl_2^{++}, UCl_4^+, UCl_4^{++}, UCl_3^+, UCl_3^{++}, UCl_2^+, UCl_2^{++}, UCl^+ and UCl^{++}. Of these atomic and molecular ions only the singly ionized atomic ions U^+ have the required ratio between mass and charge such that they are focused through the slots **38** and **39** into the pockets **36** and **37** formed in the collector block **35**; the atomic ions U^+ of masses 234 and 235 focusing through the slot **38** into the pocket **36**, and the atomic ions U^+ of mass 238 focusing through the slot **39** into the pocket **37**, as previously noted.

The doubly ionized atomic ions U^{++} have such a ratio between mass and charge that they are deflected along an arc of shorter radius into engagement with the inner wall of the liner **41**, where they are de-ionized to form a deposit thereon. The singly and doubly ionized atomic ions Cl^+ and Cl^{++} and the singly and doubly ionized molecular ions Cl_2^+ and Cl_2^{++} have such small ratios between mass and charge that they are deflected along arcs of very short radii into engagement with the inner wall of the liner **41** adjacent the source region, where they are de-ionized to form neutral chlorine molecules, which gas is subsequently pumped from the tank **13** due to the operation of the vacuum pumping apparatus previously noted. Similarly, the doubly ionized molecular ions UCl_4^{++}, UCl_3^{++}, UCl_2^{++} and UCl^{++} have intermediate ratios between mass and charge such that they are deflected along arcs of intermediate radii into engagement with the inner wall of the liner **41** intermediate the source region and the collector region, where they are de-ionized to form a deposit thereon. Finally, the singly ionized molecular ions UCl_4^+, UCl_3^+, UCl_2^+ and UCl^+ have large ratios between mass and charge, such that they are deflected along arcs of large radii into engagement with the outer wall of the liner **41** intermediate the source region and the collector region, where they are de-ionized to form a deposit thereon.

The residue of UCl_4 deposited on the parts of the calutron disposed in the source region thereof, principally upon the liner, is recovered by a water wash process, whereby various impurities including copper, iron, chromium, nickel and carbon are introduced in the wash solution, due to the fact that the various parts of the calutron which are thus washed with water are formed of the materials mentioned.

Considering now the details of the recovery of the UCl_4 residue from the parts of a calutron disposed in the source region thereof, reference is made to the portion of the flow diagram illustrated in Fig. 2. 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 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 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 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 stored for further treatment.

Considering now the details of the recovery of the metallic uranium, reference is made to the portion of the flow diagram illustrated in Fig. 3. The inner surfaces of the first pocket of the collector of the calutron 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 the first 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^{++}.

A suitable acid wash solution which may be employed for the purpose mentioned comprises an aqueous solution containing HNO_3 (approximately 12%). Another suitable acid wash solution comprises an aqueous solution containing HCl (approximately 2%) and H_2O_2 (approximately 0.5%). A further suitable acid wash solution comprises an aqueous solution containing H_2SO_4 (approximately 18%) and H_2O_2 (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 comprise 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 makeup 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 first 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 stored for further treatment.

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. 4. In the event that the solution contains a reasonably large amount of copper and nickel, the solution is subjected to a preliminary ammonia treatment in order to eliminate a majority, if not substantially all, of the impurities mentioned; otherwise this step is omitted. Assuming that the ammonia treatment is to be employed, the solution is treated 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 away from most of the copper and nickel in 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 washed with water containing about 1% NH_4OH and 1% NH_4NO_3 in order to eliminate occluded copper and nickel ammonia complex ions. The filtrate containing the copper and nickel ammonia complex ions is then discarded or subjected to salvage treatment in order to recover any uranium contained; and the initially purified precipitate of

$$(NH_4)_2U_2O_7$$

$Fe(OH)_3$ and $Cr(OH)_3$ is dissolved in dilute HNO_3, whereby a solution is obtained containing the following ions: UO_2^{++}, Fe^{+++} and Cr^{+++}.

The original composite solution, or the solution obtained after the preliminary ammonia treatment described above, is then analyzed in order to determine the ferric ion content thereof. In the event it is determined that the Fe^{+++} ion content of the solution mentioned is greater than approximately 3% the ferric ion in the solution is complexed by the introduction of an agent which forms complex ion with ferric ion; on the other hand, in the event it is determined that the Fe^{+++} contained is less than approximately 3%, the last mentioned treatment is omitted. Assuming that the solution contains greater than approximately 3% Fe^{+++} ion, this ion is complexed by the addition to the solution of an appropriate agent such as lactic acid, acetic acid, fluoride ion, or "Nullapon." The addition of the agent mentioned to the solution complexes the ferric ion, thereby eliminating the normal catalytic action of the ferric ion upon H_2O_2 and consequently catalytic decomposition of the hydrogen peroxide in the subsequent purification. It will be understood that the presence of an appreciable amount of uncomplexed ferric ion in the solution will affect catalytic decomposition of hydrogen peroxide, thereby preventing complete precipitation of uranium peroxide, as explained more fully below.

Now assuming that a solution is obtained that contains UO_2^{++}, Cu^{++}, Ni^{++}, Cr^{+++}, and Fe^{+++} ions, which is conditioned for purification by the hydrogen peroxide precipitation step, this solution may be an original wash solution or a solution which has been derived after preliminary ammonia treatment, as explained above; either of which solutions may or may not have been treated with the ferric ion complexing agent. In any case, the solution does not contain undue amounts of copper or nickel impurities or uncomplexed ferric ion in an amount greater than approximately 3%. The solution mentioned is fairly acid in view of its derivation and the pH thereof is adjusted within the approximate range 1.0 to 3.0, and preferably within the range 1.5 to 3.0, by the addition of NH_4OH thereto. The acidified solution is then cooled to a temperature in the range of about 0° to 10° C., and preferably to approximately 5° C., and hydrogen peroxide, which may conveniently be in the form of a 30% solution of H_2O_2, is added to the solution in excess, so that there is more than enough H_2O_2 to precipitate all of the uranium as the peroxide, $UO_4 \cdot 2H_2O$. The solution is kept cool and is permitted to remain in a quiescent state until substantially complete settling of the uranium peroxide has taken place. Thereafter, the solution is filtered and the precipitate is washed with an aqueous solution that is approximately 2% in NH_4NO_3 and 3% in H_2O_2. The filtrate containing the copper, nickel, chromium and iron impurities is then discarded or subjected to salvage treatment in order to recover any uranium contained and the purified $UO_4 \cdot 2H_2O$ precipitate is calcined to UO_3 at approximately 325° C., whereby O_2 gas is given off incident to the calcination. The purified uranium in the compound form UO_3 is then stored for further treatment or commercial use, as previously noted.

Considering now the details of the ultimate conversion of the batch of UO_3 to UCl_4, reference is made to the portion of the flow diagram illustrated in Fig. 5. The uranium trioxide may be converted by alternative processes into crude UCl_4. In accordance with one process the UO_3 is first reduced to UO_2 by heating with CH_4 at approximately 450° C., whereby CO_2, CO gases and water vapor are given off incident to the reduction. The uranium dioxide is then 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. In accordance with an alternative process the UO_3 may be reacted directly with CCl_4 in the liquid phase in an autoclave at a temperature of approximately 140° to 160° C. and at a pressure of approximately 200 pounds per square inch gauge in order to produce UCl_5, whereby $COCl_2$, CO_2, CO and Cl_2 gases are given off incident to the reaction. The uranium pentachloride thus produced is then calcined or decomposed to produce crude UCl_4 by heating to approximately 350° C., whereby Cl_2 gas is given off incident to the calcination.

In any case, the crude uranium tetrachloride produced by either of the alternative processes indicated above 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.

The present process of recovering uranium from solutions is very effective in view of the fact that it is quite versatile. Thus, not only may uranium be reclaimed from a solution containing the impurities mentioned, copper, iron, chromium and nickel, but the 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 solutions derived from the different calutrons.

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

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 for recovering uranium values from deposits formed on a metallic surface comprising treating said deposits to produce an oxidized acidic solution containing the uranium together with impurities of the group consisting of copper, iron, chromium, nickel, manganese and zinc, adjusting the pH of the solution within the approximate range 1.5 to 3.0, treating the acid solution with hydrogen peroxide to precipitate the uranium as uranium peroxide away from the metal impurities in the solution, separating the uranium peroxide precipitate from the metal impurities in the filtrate, and then calcining the uranium peroxide precipitate to produce uranium trioxide.

2. The process for recovering uranium values from deposits formed on a metallic surface comprising treating said deposits to produce an oxidized acidic solution containing the uranium together with impurities of the group consisting of copper, iron, chromium, nickel, manganese and zinc, treating said solution with ammonia to precipitate the uranium and the iron and chromium away from the other metal impurities which remain in the solution, separating the precipitate from the solution, dissolving the precipitate in acid, whereby the solution contains uranyl and ferric and chromic ions, adjusting the pH of the solution within the approximate range 1.5 to 3.0, treating said solution with hydrogen peroxide to precipitate the uranium as uranium peroxide away from the iron and chromium impurities in the solution, and then separating the uranium peroxide precipitate from the solution.

3. In a process for recovering uranium values from deposits formed on a metallic surface, the steps comprising producing from said deposits an oxidized acidic solution containing said uranium values together with impurities including at least one material selected from the group consisting of copper, iron, chromium, nickel, manganese and zinc, adjusting the pH of the solution to within the range 1.0 to 3.0, then adding hydrogen peroxide to the solution to precipitate the uranium as uranium peroxide away from the impurities in the solution, and separating the uranium peroxide from the solution.

4. The process for recovering the uranium values from deposits formed on a metallic surface containing materials of the group consisting of copper, iron, chromium, nickel, manganese and zinc, comprising treating said deposits with an oxidizing acidic solvent to produce a solution containing the uranium together with said materials as impurities, adjusting the pH of the solution to the range of about 1.0 to 3.0, cooling the solution to a temperature in the range of about 0° to 10° C., then precipitating the uranium as uranium peroxide away from the impurities in the solution by the addition of hydrogen peroxide, and separating the uranium peroxide from the solution.

5. In a process of recovering uranium values from deposits formed on a metallic surface including the steps of producing an oxidized acidic solution containing the uranium together with impurities including more than about 3% of ferric ion, adjusting the pH of the solution to the range of about 1.0 to 3.0, precipitating the uranium as uranium peroxide away from the impurities in the solution by means of hydrogen peroxide, and separating the uranium peroxide from the solution; the step comprising, complexing the iron in the solution prior to said precipitation step to prevent the ferric ion catalyzed decomposition of the hydrogen peroxide employed therein.

6. The process as defined in claim 3, wherein said deposits comprise the residue of a water-soluble uranium compound formed with a metallic surface, and, in which, water is the solvent employed in producing said oxidized acidic solution.

7. The process as defined in claim 3, wherein said deposits comprise the residue of uranium tetrachloride formed on a metallic surface, and, in which, water is the solvent employed in producing said oxidized acidic solution.

8. The process as defined in claim 4, wherein said deposits comprise metallic uranium deposits formed with said metallic surface.

References Cited in the file of this patent

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