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ISOTOPIC FRACTIONATION PROCESS OF URANIUM

Filed March 18, 1952

2 Sheets-Sheet 1

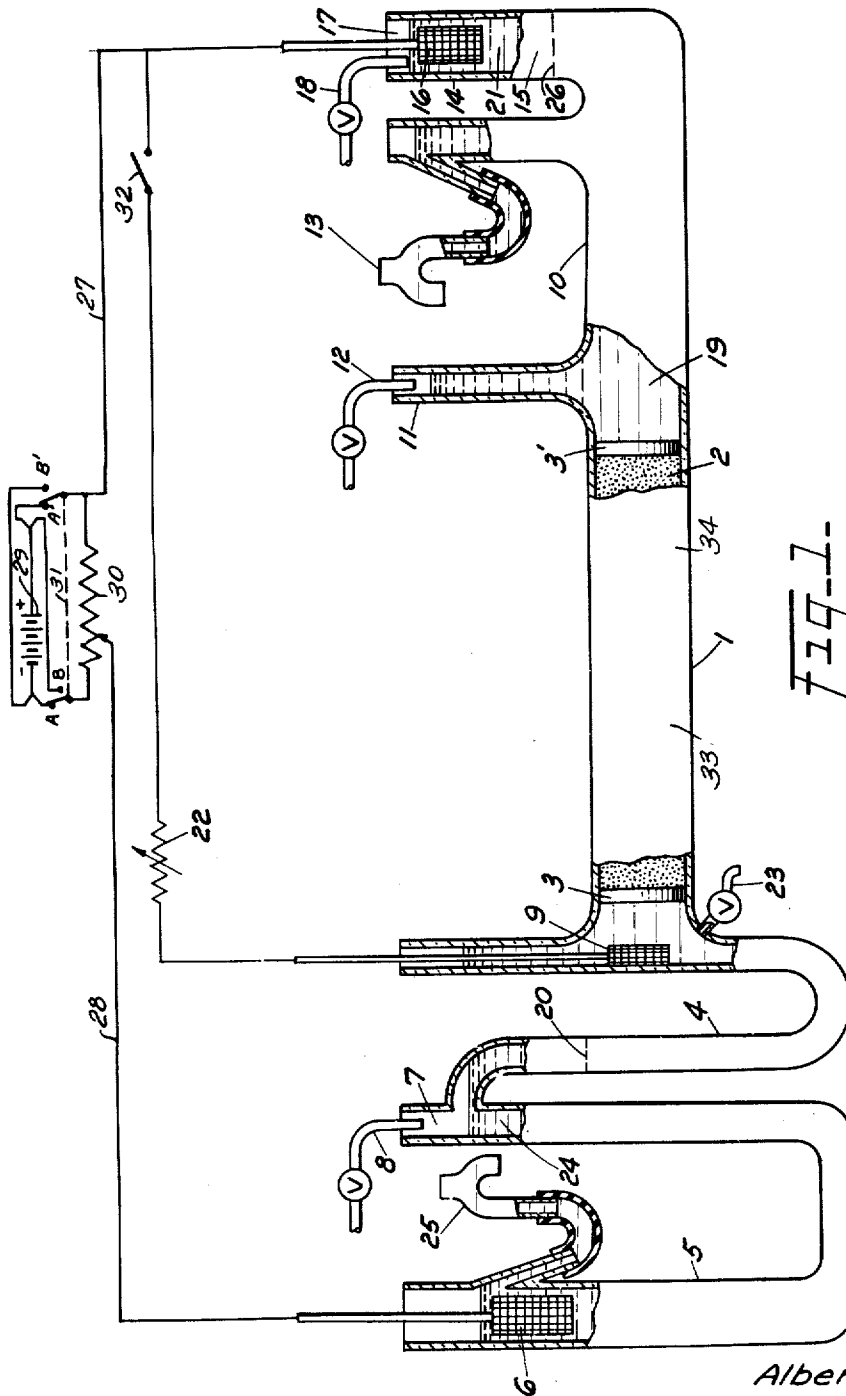


FIG. 1--

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2 Sheets-Sheet 2

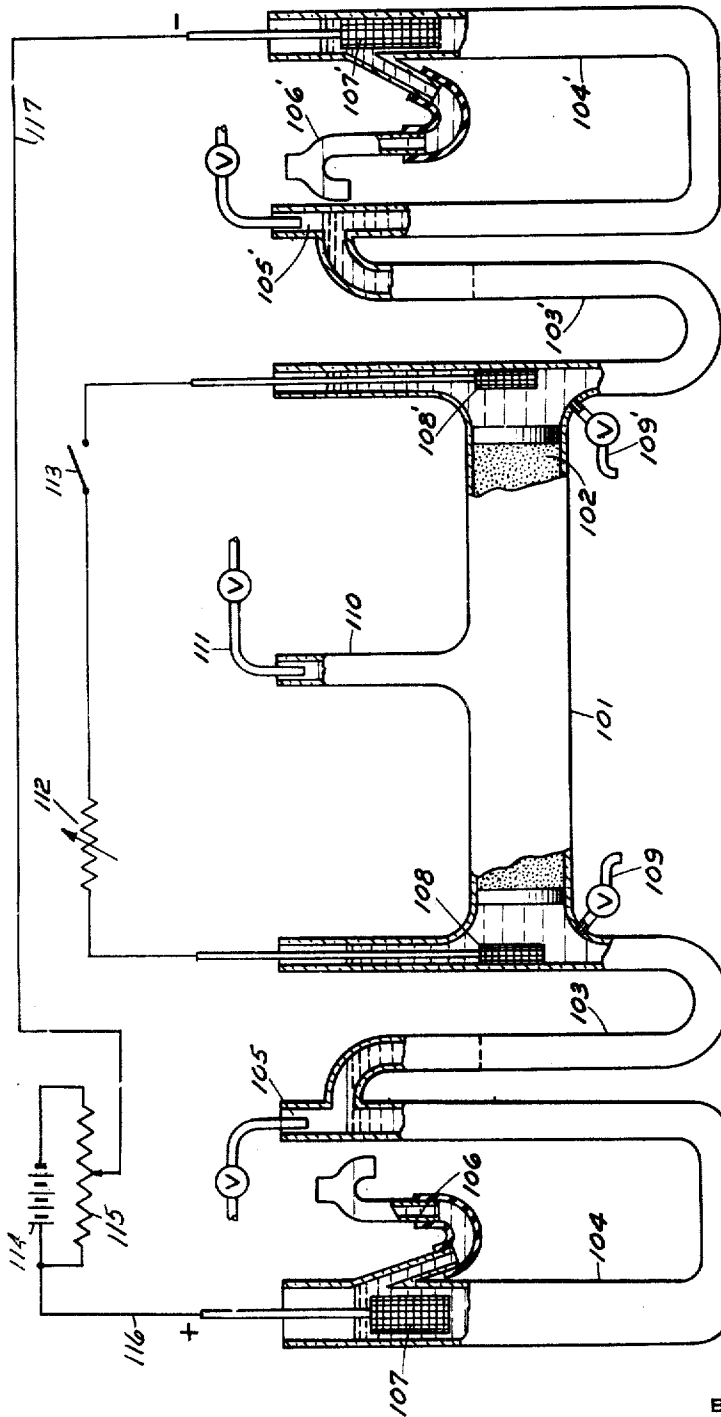


Fig. 2-

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2,813,064

## ISOTOPIC FRACTIONATION PROCESS OF URANIUM

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19 Claims. (Cl. 204—1.5)

The present invention relates in general to fractionation and enrichment of uranium with respect to one or more particular isotopes thereof, and more particularly to a new and improved continuous counter-current electrolytic migration process for the purpose, particularly adapted to such fractionation and enrichment with respect to  $^{235}\text{U}$  and  $^{238}\text{U}$ .

As is known, isotopic enrichment of uranium has become of great importance. Of particular interest is the separation of natural uranium, which comprises ca. .07%  $^{235}\text{U}$  and ca. 99.3%  $^{238}\text{U}$  into fractions richer in  $^{235}\text{U}$ , and other fractions richer in  $^{238}\text{U}$ —toward ultimate virtually complete isolation of each isotope by successive fractionations. Widely developed for this purpose have been various physical methods, including gaseous diffusion, electromagnetic separation, and thermal diffusion. While such physical methods have proven capable of effecting enrichment on a production scale, they are exceedingly complex and are beset with myriad technical difficulties. It has, therefore, been highly desirable that simpler and easier alternative effective means be found for the purpose.

In this direction, there has been continuing concurrent interest in chemical methods of isotopic fractionation. However, while in the past a number of chemical techniques have been devised for accomplishing isotopic enrichment, their effectiveness has, in the main, been limited to merely those elements having atomic weights not substantially above 40 to 60. One such chemical method, of particular interest to the present case, was previously developed by A. K. Brewer, S. L. Madorsky, J. W. Westhaver, et al., at the National Bureau of Standards, for the fractionation of potassium isotopes,  $^{39}\text{K}$  and  $^{41}\text{K}$ , from one another. [Cf. Journal of Research of the National Bureau of Standards, vol. 38, pp. 137-189, (1947).] The Brewer and Madorsky process is based upon a discovered isotopic differentiability between  $^{39}\text{K}$  and  $^{41}\text{K}$  in the electrolytic migration of otherwise-identical dissolved potassium cations in aqueous solution. That is, it was found that under electrolysis, the lighter  $^{39}\text{K}^+$  ion migrates toward the cathode slightly faster than the identically-charged, but heavier,  $^{41}\text{K}^+$  ion. To apply this discovery to the fractionation of potassium isotopes, an electrolytic operation was devised wherein an electrolyte, in a horizontal electrolytic cell packed with a porous bed, is flowed as a continuous stream, from the cathode to the anode, at a rate precisely between the rates of electrolytic migration of the  $^{39}\text{K}^+$  and the  $^{41}\text{K}^+$  ions in the system. Upon electrolyzing under such conditions, the more-rapidly-electromigrating  $^{39}\text{K}^+$  ions make headway, against the flowing electrolyte stream, toward the cathode, while the slower  $^{41}\text{K}^+$  ions cannot keep pace and are carried slowly back toward the anode. Thus  $^{39}\text{K}^+$  tends to be concentrated toward the cathode, and  $^{41}\text{K}^+$  toward the anode.

To prevent the potassium cations from contacting the electrode toward which they concentrate and form thereby undesirably engaging in electrode reaction, and at the

same time to provide a gauge means whereby electrolyte solution velocity might be intelligently adjusted, use is made of an ingenious adaptation of an electrokinetic boundary (cf. MacInnes, Principles of Electrochemistry, pp. 68-80, Reinhold, 1939). That is, for example, where the source of potassium is a solution of KCl, the electrolyte solution flowed from cathode to the anode would be aqueous HCl—an electrolyte having the same anion as the potassium salt, but a cation of higher ionic-mobility than  $\text{K}^+$ . Upon electrolyzing, the forefront of the potassium ions migrating upstream may—especially in a vertical portion of the cell—be delineated by a sharp, self-maintaining, and visible boundary. Such boundary forms by virtue of a difference in ionic mobility between the hydrogen ions and potassium ions present. The hydrogen ions of the added HCl, carried by the electrolyte stream, tend, by virtue of their positive charge and higher ionic mobility, to migrate toward the cathode at a faster rate than the  $\text{K}^+$  ions. Thus the faster-migrating  $\text{H}^+$  ions, as a moving body, stay ahead of the body of slower  $\text{K}^+$  ions, with the plane of juncture between two bodies constituting the electrokinetic boundary. The boundary automatically maintains itself definite and sharp: the slower, trailing  $\text{K}^+$  ions tend to lag, thereby reducing solution concentration behind the boundary, and concomitantly increasing electrolytic potential drop per unit distance behind the boundary; any of the faster hydrogen ions straying behind the boundary immediately encounter the stronger electrolytic field and are forthwith accelerated forward through the boundary, while any slower  $\text{K}^+$  ions straying forward across the boundary enter the weaker electrolytic field, languish, and lag back behind the boundary. So pronounced is the phenomenon, that the plane of the boundary is readily visible by virtue of the sharp difference in indices of refraction between the two bodies of ions. The electrolyte flow rate is adjusted to maintain the boundary stationary, thereby reducing the net spatial transfer of  $\text{K}^+$  ions to zero. Under such conditions the desired  $^{39}\text{K}^+$  isotopic ions remain almost stationary, but as a body slowly drift upstream toward the boundary to replace the  $^{41}\text{K}^+$  ions slowly washed downstream from that region. After a suitable build-up period, to afford time for  $^{39}\text{K}^+$  to preferentially congregate toward the boundary,  $^{39}\text{K}$ -enriched solution from just below the boundary may be slowly withdrawn.

Toward the anode, a similar boundary may be utilized at the trailing end of the body of  $\text{K}^+$  ions. In this instance, a body of cations of ionic mobility lower than that of the  $\text{K}^+$  ions is introduced at the anode, forming a boundary, maintainable stationary, against which  $^{41}\text{K}^+$  will concentrate.

Such operation proved to be eminently effective in concentrating either  $^{39}\text{K}$  or  $^{41}\text{K}$  alone, or both  $^{39}\text{K}$  and  $^{41}\text{K}$  in one operation. For concentration of only  $^{39}\text{K}$ , a source of natural potassium ions is continuously maintained in the proximity of the anode, while  $^{39}\text{K}^+$  ions are concentrated at a boundary near the cathode. On the other hand, for concentrating only  $^{41}\text{K}$ , the source of natural  $\text{K}^+$  ions is continuously maintained at the cathode, with  $^{41}\text{K}^+$  concentration taking place at a boundary near the anode. Use of a boundary near each electrode, and introducing the source of natural  $\text{K}^+$  about midway between them, affords simultaneous concentration of  $^{39}\text{K}^+$  and  $^{41}\text{K}^+$  at the respective cathode and anode boundaries. In practice, such operation has proven effective, for example, in increasing  $^{39}\text{K}:^{41}\text{K}$  ratio, at the cathode boundary, from its normal value of 14.2 to so much as 24, in 500 hours of operation.

The success so realized in potassium isotope enrichment then prompted attempts to apply the operation to the isotopic enrichment of uranium. For this, aqueous

uranyl nitrate solutions were subjected to a like electrolytic operation, under analogous electrolytic conditions, in the interest of similarly concentrating the lighter  $^{235}\text{UO}_2^{++}$  ions toward the cathode, and the heavier  $^{238}\text{UO}_2^{++}$  ions toward the anode. However, great difficulty was encountered in effecting any isotopic concentration at all, doubtless because of the very small relative difference in the ionic weights between the pair of isotopic ions—it seemed that here again was a manifestation of the generality that chemical means for isotopic enrichment tend not to be practically feasible for elements having atomic weights above the range of 40 to 60. There was obtained, though, experimental indication that the lighter  $^{235}\text{UO}_2^{++}$  tended to concentrate slightly toward the cathode, and the heavier  $^{238}\text{UO}_2^{++}$  to concentrate slightly toward the anode.

The hereinabove discussed methods for fractionating isotopes on the basis of a difference in cathodic electrolytic migrational velocity between a lighter (faster) isotope and a heavier (slower) isotope, both present in dissolved ionic form identical other than for isotopic constitution, comprise the concepts and inventions of others, and do not, per se, constitute a part of the present invention. Details of such prior methods are more fully set forth in published papers, as for example:

Science, 104, pages 156-7, (August, 1946);

Journal of Research of the National Bureau of Standards, 38, pages 137-189, (1947); 39, pages 141-147, 397-409, (1947); 41, pages 41-44, (1948); and copending application:

Serial No. 432,185, filed February 25, 1942, in the names of Samuel Leo Madorsky and Aubrey Keith Brewer, for Process for the Separation of Isotopic Ions, now U. S. Patent No. 2,645,610, issued July 14, 1953). Accordingly, reference is made to these sources for further details concerning such previously-developed operations.

Following the aforementioned electrolytic migration work, there has been an increasing desire that new, effective means, especially chemical means, be found for more simply and easily fractionating and enriching uranium with respect to its individual isotopes, particularly on large scale and in continuous operation.

Accordingly one object of the present invention is to provide a new and improved process for the enrichment of uranium with respect to one or more particular isotopes thereof.

Another object is to provide such a process which is fundamentally chemical in nature, and wherein all operations are conducted in aqueous solution.

A further object is to provide such a process which is readily adapted to multi-stage operation, but which does not require extensive chemical recovery and reconversion of uranium between separate stages.

Still another object is to provide such a process adaptable to concentrating, in particular, either  $^{235}\text{U}$  or  $^{238}\text{U}$ , or both at the same time.

Still a further object is to provide such a process which is of practical fitness and suitability appropriate for large scale application, and which is of a truly continuous nature.

Yet another object is to provide such a process adapted to affording substantially complete separation, recovery, and isolation, of individual isotopic species of uranium from other isotopic species thereof.

Additional objects will become apparent hereinafter.

As the basis for the present invention, applicant has discovered that upon subjecting a mixture of tetravalent and hexavalent uranium cations in dissolved aqueous solution to the action of an electrolytic current, while flowing a stream of an aqueous acidic electrolyte from cathode to anode at a velocity between that of cathodic electrolytic migration of the faster (lighter and more highly positively charged)  $\text{U}^{+4}$  ions and the slower (heavier and less positively charged)  $\text{UO}_2^{++}$  ions, not only is there achieved a concentration of  $\text{U}^{+4}$  toward the

cathode and  $\text{UO}_2^{++}$  toward the anode, but, most significantly, there concomitantly obtains a definite and vigorous concentration of  $^{235}\text{U}$  toward the anode and of  $^{238}\text{U}$  toward the cathode. It is striking that in this isotopic concentration, it is the heavier isotope that is concentrated toward the cathode, and the lighter toward the anode—exactly the opposite of the directions in which concentration obtained in the previous Brewer, Madorsky, and Westhaver operations. Thus, the phenomenon involved must be exceptionally forceful, since it not only completely overrides and cancels the Brewer et al. effect, but goes much farther in effecting pronounced isotopic concentrations toward the opposite electrodes. Hence, in accordance with the present invention, a new and improved method for enriching uranium with respect to one or more particular isotopes thereof comprises subjecting a mixture of uranous and uranyl cations, the isotopic constitution of which cations comprises  $^{235}\text{U}$  and  $^{238}\text{U}$ , in dissolved aqueous, acidic solution, to the action of an electrolytic current passed between an anode and cathode in an electrolytic cell, thereby inducing the uranous and uranyl ions to electrolytically migrate toward the cathode, with the electrolytic migration of the uranous ions being characteristically at a faster rate than that of the uranyl ions, while passing a stream of aqueous, acidic electrolyte solution from the cathode to the anode at a velocity between the cathodic electrolytic migrational velocity of the faster uranous and slower uranyl ions, thereby washing uranyl ions toward the anode while the faster uranous ions make headway upstream in migrating toward the cathode, consequently concentrating uranous ions toward the cathode and uranyl ions toward the anode, and therewith concomitantly concentrating  $^{235}\text{U}$  toward the anode and  $^{238}\text{U}$  toward the cathode. Propitiously, the relative difference between the cathodic electromigrational velocities of  $\text{U}^{+4}$  and  $\text{UO}_2^{++}$  was found to be much, much greater than that between uranous or potassium cations identical other than in isotopic constitution—as could be expected on the basis that  $\text{U}^{+4}$  has twice as much positive electrical charge as  $\text{UO}_2^{++}$ . So, in the present process, the ions being concentrated toward a particular electrode—instead of standing virtually motionless, as in the previous process alluded to hereinbefore, with merely a slight drift toward the electrode in gradual replacement of the counterpart ions being slowly carried away—dynamically surge toward their particular electrode goal. Besides speeding operations, the much greater difference in electromigrational rates lends itself to easier control; precise balance and delicate adjustment requirements are considerably relaxed.

In further accordance with the present invention, it has also been found that isotope enrichment by this operation may be markedly intensified and hastened by continuously oxidizing the upstream-migrating uranous ions to hexavalent state at a point just short of the cathode, and continuously reducing the downstream-receding uranyl ions, just short of the anode. Immediately upon such oxidation or reduction, the uranium ions reverse direction and move back toward the opposite electrode; this results in two ionic streams—one of uranous and the other of uranyl ions—each coursing substantially the full length of the cell countercurrent to the other, and each stream being "refluxed," by the oxidation or reduction, as it nears each electrode. Significantly, under such reflux, not only does the concentration of  $^{235}\text{U}$  toward the anode and  $^{238}\text{U}$  toward the cathode continue, but the degree of isotopic enrichment afforded by given cell size and electrolytic conditions is actually substantially increased, and the rapidity with which the cell operation provides such enrichment is considerably accelerated. Continuous operation may be achieved by means of continuously tapping off isotopically-enriched uranium solution from the extremity of the dissolved uranium ion body nearest the goal-electrode for the desired isotope. Also the operation is adapted to concentrate either  $^{235}\text{U}$  or  $^{238}\text{U}$ , or both simultaneously,

depending on whether the uranium feed solution is introduced in the proximity of one or other electrode, or midway between them. Representative of the eminent efficacy throughout these various adaptations, one small experimental cell, having an effective length of only eight inches, in 1400 hours under total reflux, effected increase of  $^{235}\text{U}$  concentration in natural uranium from 0.7111% to 0.7171%. Being of such efficiency, the present process clearly affords substantial practical advantages in uranium isotope enrichment.

In conducting the present operation, it is again desirable that the electrolytic cell be elongated, predominantly horizontal, and that a substantial part of its operative portion be packed with a fine-pored bed. Likewise, it is highly advantageous to apply the electrokinetic boundary phenomenon, as alluded to hereinabove, to prevent the bulk of the uranium ions from contacting the anode or cathode, and to provide a simple gauge means for enabling appropriate adjustment of electrolyte solution flow velocity and/or electrolytic potential between anode and cathode. For refluxing, the necessary oxidation or reduction of uranium may effectively and advantageously be effected electrolytically; an appropriately-charged auxiliary electrode is disposed just inside a particular one of the boundaries to effect rapid and complete local oxidation or reduction without complicating the basic operation with introduction of oxidants, reductants, or other undesirable ions, and without otherwise interfering with uranium oxidation state at distant points in the cell.

A more comprehensive and detailed insight into the present process is quickly afforded by consideration of the particular apparatus and operation preferred and employed by applicant. While conducting the present invention in accordance with the foregoing general outline is not limited to any specific design of the electrolytic apparatus, the electrolytic systems illustrated in the appended drawings have proven to be particularly efficacious for the purpose.

In the drawings:

Fig. 1 illustrates an electrolytic cell adapted to the concentration of  $^{238}\text{U}$  selectively, and alternatively adaptable to the concentration of  $^{235}\text{U}$  selectively.

Fig. 2 is a partially-cross-sectional illustration of a cell adapted to the fractionation and simultaneous separate concentration of both  $^{235}\text{U}$  and  $^{238}\text{U}$ .

Both cells are operable continuously and may be utilized with, or without, applying reflux.

Referring to the electrolytic cell arranged for the concentration of  $^{238}\text{U}$ , shown in Figure 1, an elongated, horizontal, tubular electrolytic-migration compartment 1, is filled with a chemically-inert, porous packing material, e. g. a bed of tiny glass beads, 2, maintained in place by inert, porous plugs, e. g. porous fritted-glass discs 3,3', at both ends. Contiguous with one end of the migration compartment 1, and communicating therewith, is a boundary level tube 4, extending vertically upward, which in turn leads to a cathode compartment 5, having disposed therein a cathode 6, and being provided with a precisely adjustable liquid overflow spout 25. Intermediate the cathode 6, and the boundary level tube 4, the cathode compartment is provided with a port 7, having extending therein a liquid delivery pipe 8, for affording introduction of liquid into the cathode compartment. In the boundary tube 4, near its point of communication with the migration compartment 1, an auxiliary electrode 9, is disposed. At the opposite end of the migration compartment 1, contiguously extending therefrom, and in communication therewith, is a feed compartment 10, comprising, in order away from the migration compartment, a feed solution introduction port 11, into which a feed delivery tube 12, extends, and a precisely adjustable feed compartment overflow spout 13. The feed compartment communicates, at its far end, with an anode compartment 14, initially turned upward to provide a bound-

ary region 15, and has disposed in its upper extremity an anode 16. Also beyond the boundary region, the anode compartment is provided with a liquid introduction port 17, into which extends a liquid delivery pipe 18. The system, from a point part way down the vertical portion of boundary tube 4, on through the packed migration compartment 1, further through feed compartment 10, and on to a point part way up the vertical boundary portion 15, of the anode compartment 14, contains an aqueous acidic uranium solution 19, comprising uranous and uranyl ions. The cathode compartment 5, and the remainder of the boundary tube 4, contains a catholyte solution 24, immersing the cathode 6, and forming a boundary 20, with the uranium solution in the vertical portion of boundary tube 4. The remaining unfilled portion of the anode compartment 14, is filled with an anolyte solution 21, which immerses the anode 16, and forms a boundary 26 with the uranium solution in vertical boundary portion 15. For impressing appropriate electromotive potential between the anode 16 and the cathode 6, there is connected across said anode and cathode, through an anode lead 27 and a cathode lead 28, a potentiometer circuit permitting reversal of polarity comprising a source of electromotive force 29, a potentiometer 30, and, therebetween, a double-pole-double-throw reversing switch 31 which when thrown in its A—A' position provides proper polarity for rendering anode 16 anodic with respect to the cathode 6 and which is adapted by simply being thrown to its B—B' position to reverse the polarity so as to render the left-hand principal electrode 6 anodic with respect to the right-hand principal electrode 16. Auxiliary electrode 9, is electrically connected with the anode 16, through a variable electrical resistance 22 and a switch 32. A product solution outlet spout 23 is provided in the proximity of the auxiliary electrode. For convenience in reference hereinafter, the electrolytic-migration compartment 1, may be considered as comprising a left-hand portion 33 and a right-hand portion 34. The entire apparatus, other than the electrodes, the variable resistance, and electrical connections, is constituted of substantially chemically-inert and electrically-nonconducting material.

In operation of the Fig. 1 apparatus for concentration of  $^{238}\text{U}$ , electromotive force provided by the potentiometer circuit, comprising source of electromotive force 29, reversing switch 31 thrown in its A—A' position, and potentiometer 30, is impressed between the cathode 6 and the anode 16, via the cathode lead 28 and the anode lead 27, whereupon electrolytic current passes through the cell therebetween. A continuous stream of aqueous acidic solution of uranous and uranyl cations, comprised of  $^{235}\text{U}$  and  $^{238}\text{U}$ , is introduced into the feed compartment, through feed delivery pipe 12 and port 11, whence it constantly flushes through the feed compartment, passing out the feed compartment overflow spout 13, maintaining migration compartment 1, and the portion of the boundary tube 4, up to the boundary 20, filled with uranium solution. A constant stream of catholyte solution 24 is introduced through liquid delivery pipe 8, into port 7, whence it constantly flushes through the cathode compartment 5, passing out the overflow spout 25. The catholyte solution 24, is constituted of an aqueous acidic solution, less dense than the uranium solution, of strong electrolyte, the anion of which is identical with the anion of the uranium compound employed, and the cation of which has a substantially greater ionic mobility than the uranous ion, and will engage in a simple cathode reaction. For example, where chloride is the anion of the uranium solution, the catholyte solution would preferably comprise aqueous hydrochloric acid. Having the above outlined characteristics, an electrokinetic boundary 20, will readily form. The cathode compartment overflow spout 25 is adjusted to a level substantially higher than the feed solution overflow spout 13, thereby establishing a substantial hydraulic gradient between the cathode compartment and the

feed compartment, thereby producing a substantial liquid flow from the first electrode compartment 5 through the migration compartment 1, to the feed compartment 10, and out the feed compartment overflow spout 13. Although the solution flows, the hydrogen ions of the HCl in the first electrode solution migrate upstream toward the cathode 6, the bulk never getting downstream any farther than the boundary 20, which also represents the forefront of the upstream-migrating mass of uranium ions. The electrolyte solution flow rate is so adjusted, by adjusting the relative heights of the overflow spouts, that the boundary 20—conveniently visible—remains stationary in boundary tube 4. The anolyte solution 21, is constituted of an aqueous acidic solution, less dense than that of the uranium solution 19, of a strong electrolyte, the anion of which is identical with that of uranium compound and engages in a simple anode reaction, and the cation of which has an ionic mobility substantially lower than that of the uranyl ion, (for example, aqueous LiCl solution), and is introduced through liquid pipe 18, through port 17. With the switch 32 open so that the auxiliary electrode 9 is disconnected from the anode lead 27, the mixed  $UO_2^{++}$  and  $U^{+4}$  solution flushing through the feed compartment provides a constant source of uranium ions in unchanging isotopic ratio.  $U^{+4}$  tends to migrate upstream through the packing 2, in migration tube 1, while  $UO_2^{++}$  is swept downstream and back out into the feed compartment, with the result that  $U^{+4}$  and concomitantly  $^{238}U$  are concentrated in the region of the upstream porous plug 3.

Alternatively, to employ reflux in such operation of the Fig. 1 system, a positive potential somewhat lower than that of the anode 16, is impressed upon auxiliary electrode 9, by maintaining switch 32 closed thereby connecting it to the anode 16 through variable resistance 22. Furthermore, for operation under reflux, the uranium solution employed for constant flushing through the feed compartment is in that case constituted of merely  $U^{+4}$ , rather than a mixture of  $U^{+4}$  and  $UO_2^{++}$ . Under such conditions, the  $U^{+4}$  ions migrate upstream through the packing; upon reaching the auxiliary electrode 9, the  $U^{+4}$  ions are oxidized to  $UO_2^{++}$  which are thereupon washed slowly downstream back through the packing.  $UO_2^{++}$  ions leaving the packing into the feed compartment are washed out through the feed compartment overflow spout 13. It will be noticed, that, ordinarily, in the course of adjusting the relative heights of the overflow spouts so as to maintain the boundary 20—conveniently visible—stationary in the boundary tube 4, a somewhat different electrolyte solution flow velocity is required to maintain the boundary stationary, when operating the auxiliary electrode, than when not. The result, again, is that uranium ions in the vicinity of the auxiliary electrode become progressively more enriched in  $^{238}U$ . Finally, after allowing an appropriate initial build-up time for  $^{238}U$  to concentrate,  $^{238}U$ -enriched uranium solution, as the product, may be slowly and continuously tapped from the vicinity of auxiliary electrode 9, through product outlet spout 23.

Alternative operation of the cell in Figure 1 for concentration of  $^{235}U$  is much the same as that just described for concentration of  $^{238}U$ . However, the polarity of electrical potential impressed across the electrodes 6 and 16, is reversed by throwing the reversing switch 31 into the B'-B' position. Upon such change, the left-hand electrode 6 becomes, and operates as, an anode, and the right-hand electrode 16 becomes, and operates as, a cathode; correspondingly, the electrode lead 27 acts as a cathode lead and the electrode lead 28 operates as an anode lead. Electrolyte solution flow direction is reversed also; in this instance the flow is from the right-hand electrode compartment (now the cathode compartment) 14, through the feed compartment 10, on through migration compartment 1, to the left-hand electrode compartment (now the anode compartment) 5, and out

the left-hand electrode compartment overflow spout (now the anode compartment overflow spout) 25. Such flow is produced by adjusting the level of feed compartment overflow spout 13 substantially higher than that of the other spout 25. The solutions used to immerse the left-hand electrode (now the anode) 6, and the right-hand electrode (now the cathode) 16, are reversed, such that the solution such as HCl is used as the right-hand electrode solution (now the catholyte) 21, and the solution such as LiCl is employed as the left-hand electrode solution (now an anolyte) 24. With reflux, the uranium feed solution employed is  $UO_2^{++}$ , rather than  $U^{+4}$ . Again, the product, in this case  $^{235}U$ -enriched uranium solution, may, after a suitable build-up time, be continuously tapped from product outlet spout 23.

Referring to Figure 2, the cell for concentration of both  $^{235}U$  and  $^{238}U$ , simultaneously, is similar in structure and operation with the above systems for separation of  $^{235}U$  and  $^{238}U$  separately, and, in effect, represents a combination of the two. As in the apparatus illustrated in Figure 1, a horizontal, elongated tubular electromigration compartment 101, packed with a porous bed 102, is provided. However, the apparatus extending from each end of the migration compartment 101, is identical with that which extended from the end, toward the left-hand electrode compartment 5, of migration compartment 1 in Figure 1. Thus, the apparatus has symmetrically disposed at both ends of migration tube 101: boundary tubes 103, 103'; electrode compartments 104, 104', with electrode solution inlet ports 105, 105', and electrode solution overflow spouts 106, 106', and containing an anode 107 and a cathode 107'; auxiliary electrodes 108, 108', and product solution outlet spouts 109, 109'. Communicating with the top of migration tube 101, and intermediate its ends, is a vertical feed standpipe 110, into the top of which extends feed solution delivery pipe 111. Auxiliary electrodes 108 and 108', are electrically connected together through a variable resistance 112 and a switch 113. For impressing appropriate electromotive potential between the anode 107 and the cathode 107', a potentiometer circuit comprising a source of electromotive force 114, and a potentiometer 115, is connected across said anode and cathode through an anode lead 116 and a cathode lead 117.

In operation, an electromotive force is impressed between the anode 107 and the cathode 107'. Again, the solutions filling the electrode compartments are appropriately an aqueous acidic solution such as HCl in the cathode compartment 104', and an aqueous acid solution such as LiCl in the anode compartment 104. Flow of electrolyte solution is from cathode compartment 104' to the anode compartment 104—right to left—and is produced and controlled by appropriate relative adjustment of electrode compartment overflow spouts 106, 106'. The feed uranium solution, added through feed solution delivery pipe 111, and standpipe 110, is an aqueous acidic solution, preferably proportioned about 50%  $U^{+4}$  and 50%  $UO_2^{++}$ ; different proportions, or exclusively one or the other, of the uranous or uranyl states may be utilized, but a preponderance of the feed uranium in uranous state favors  $^{235}U$  concentration at the expense of  $^{238}U$ , while a preponderance of uranyl conversely favors  $^{238}U$  concentration. Again, boundaries—to be maintained stationary—are formed in boundary tubes 103 and 103'. Under such conditions,  $U^{+4}$ , and concomitantly  $^{238}U$ , concentrate to the vicinity of the right-hand auxiliary electrode 108', while  $UO_2^{++}$ , and concomitantly  $^{235}U$ , concentrate toward the left-hand auxiliary electrode 108. For reflux, it is necessary merely, in view of the electrolytic potential drop through the cell, to connect the auxiliary electrodes together through a variable resistance 112 by maintaining switch 113 closed to provide appropriate charges thereon for the desired oxidation and reduction. Here, the left-hand auxiliary electrode 108, being maintained somewhat cathodic with respect to the

anode, may be termed a "canode," and the right-hand auxiliary electrode 108', being maintained somewhat anodic with respect to the cathode, may be termed an "anode."  $U^{+4}$  ions migrating upstream, upon encountering the anode, are oxidized to the uranyl state, whence they are slowly washed back downstream through the packing bed 102;  $UO_2^{++}$  ions being washed from the other end of the packed bed, upon encountering the canode, are reduced to  $U^{+4}$ , whence they reverse direction and commence migrating upstream through the packing again. After an appropriate build-up time,  $^{235}U$ -enriched uranium solution may be continuously tapped at the left-hand product solution outlet spout 109, while  $^{238}U$ -enriched uranium solution may be continuously tapped from the right-hand product solution discharge spout 109'. Introduction of the uranium feed solution into standpipe 110 at a rate just equal to withdrawal of product through the outlet spouts 109, 109', maintains the material balance of the system.

More generally speaking, while the compositions of suitable uranium solutions for effecting the present invention are subject to considerable variation, certain solution conditions are recognized as particularly desirable. Since the uranium ions, in the operation, migrate upstream through a flow of electrode solution introduced into the cathode compartment, the solution conditions to which the uranium is subjected depend not only upon the composition of the uranium feed solution employed, but as well upon the specific composition of the cathode electrode solution used. Broadly, the satisfactory condition for the migrating uranium ions is in aqueous, acidic solution of a dissolved uranium salt, having an anion of preferably a strong acid. Naturally, anions of the dissolved uranium salt, as well as any other extraneous material permitted in the solution, should be of such nature as not seriously to oxidize or reduce the uranium cations, precipitate the uranium, or otherwise deleteriously interfere, through their own particular activity, with the electromigration operation. The chloride anion, being eminently satisfactory in these respects, is preferred for the purpose; accordingly, the particular preferred feed solution is an aqueous, acidic chloride solution of uranium in appropriate valence state, and the particularly preferred electrode solution introduced to the cathode compartment is aqueous hydrochloric acid. In order that the solution may be effectively electrolyzed, it should meet the customary requirement of including a sufficient concentration of strong electrolyte to provide a reasonable magnitude of electrolytic conductance; in this case, the uranium chloride salt is the electrolyte, with concentrations of fractional molarity, particularly 0.01 to 1.0 molar, and especially 0.1 molar, being preferred. Throughout the operation, the uranium-containing solutions should be maintained moderately acidic, since uranium tends disadvantageously to hydrolyze, polymerize, and precipitate as hydroxide and peruranate compounds at higher pH's. For avoiding these adverse hydrolytic effects, at the uranium concentrations alluded to, pH's no higher than ca. 1.5 are desirable. On the other hand, it has been found that the rapidity and intensity of the isotopic concentration effect involved is markedly favored by higher (i. e., less acidic) pH's—seemingly, the higher the pH the better. Upon balancing these two conflicting pH requirements, the preferred pH range is about 1 to 1.5, with pH 1 appearing to be the practical optimum. In the interest of avoiding spurious oxidation or reduction of uranium, it appears advisable to avoid exposure of the dissolved uranium in the system to air, as far as practicable.

In the electrolytic system employed, it is highly important that the electrolyte solution flow velocity be maintained substantially uniform over the entire cross-section of the electrolytic migration compartment. In an open tube, liquid velocity would tend to have a parabolic distribution across the cross-section—maximum

velocity at center, decreasing to virtually zero velocity adjacent the walls. This is avoided by constituting the migration compartment of a multiplicity of capillary flow paths, which may most conveniently be provided by constituting the compartment of a bed of fine-mesh packing. While comminuted, non-reactive, and non-conductive mineral materials, such as sand, are suitable, tiny glass beads have proven to be much more elegant and satisfactory; ca. 100 mesh is the apparent optimum. Being so packed, the particular shape of the cross-section of the migration tube is unimportant, so long as the cross-section is fully enclosed and the cross-sectional area remains substantially constant over the length of the compartment. Horizontal disposition of the migration compartment is particularly preferable, toward mitigating interference by thermal convection and diffusion arising from non-uniform heating of the solution by the electrolytic current. In view of such undesirable thermal effects, electrolytic current should be limited to low amperages to avoid excessive heating of the solution; electrolytic currents the order of 0.1 amp/sq. in., and a little lower, through the migration compartment have been found appropriate. Furthermore, the efficiency of the operation is improved by maintaining the migration compartment, or better the entire cell, at a constant temperature—say room temperature, preferably 18° C.—by such means as jacketing, or immersing, the apparatus in water or other liquid maintained at constant temperature. For the electrodes, both principal and auxiliary, inert metals are generally suitable, with shiny platinum gauze being preferable.

For the solutions employed in the electrode compartments, preferred as fully meeting the aforementioned requirements therefor are aqueous HCl for the cathode compartment and aqueous, acidic LiCl for the anode compartment. With these, the predominant electrode reactions are  $H^+$  reduction with hydrogen evolution at the cathode, and  $Cl^-$  oxidation with chlorine evolution at the anode. Since at equilibrium, the equivalent concentrations of a pair of migrating cations, across an electrokinetic boundary, are in direct proportion with their cation transference numbers, the concentrations of solutions in the electrode compartments appropriate for maintaining the uranium solution in the central portion of the cell at its preferred concentration level, are readily calculable. Precise adjustment of electrode solution concentrations is unwarranted, though, since the system will automatically bring itself into equilibrium by relative movement of the boundaries; it is merely desirable that the HCl equivalent concentration be somewhat greater, and the LiCl concentration somewhat smaller, than that of the uranium solution. From an electrolytic current efficiency standpoint, it is desirable that the hydrogen ion concentration in the anode compartment solution be maintained as low as practicable, to avoid waste of electrolytic current by an excessive degree of cathodic migration of hydrogen ions through the migration compartment. However, in view of the requirement of low pH to avoid uranium hydrolysis and precipitation, the anode compartment solution should be maintained at about pH 1 to 1.5 to continuously supply, across the anode boundary, upstream-migrating hydrogen ions to thereby maintain adequate  $H^+$  throughout the entire migration compartment to prevent uranium precipitation. In controlling the operation, the boundaries normally tend to move out of position so slowly that occasional manual adjustment of the electrolyte solution flow rate, and/or impressed electrolytic potential, is sufficient for reliable control. Automatic boundary control means, such as described in the Bureau of Standards Papers cited supra, though, afford added convenience.

In applying electrolytic refluxing, each auxiliary electrode employed should be of such generous proportions and so disposed in close proximity to an extremity of the migration compartment as to effectively intercept and

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alter the oxidation state of virtually all uranium ions leaving that compartment. Electrical current flow through the auxiliary electrode circuit of about  $\frac{1}{4}$  that through the migration compartment has been found adequate. For sustaining such current, the auxiliary electrode reactions comprise, in addition to uranium oxidation or reduction, hydrogen evolution at the canode and chlorine evolution at the anode; accordingly electrolytic-gas escape means disposed vertically above the auxiliary electrodes best be provided.

Concerning efficacy in enrichment, it has been found, particularly under reflux, that the degree of enrichment afforded qualitatively increases with increase in length of the migration compartment. Also, as in other refluxed systems (e. g. continuous distillation) degree of enrichment increases with decrease in the proportionate rate of withdrawal of product. Moreover, the system is ideally adapted to an arrangement involving a succession of cells, each further enriching the product from the cell below it; advantageously, the product solution may be directly passed into the next cell, without any intermediate processing being necessary. A most practical application of such succession of cells comprises a cascade of cells, each concentrating both  $^{235}\text{U}$  and  $^{238}\text{U}$  as in Figure 2. In such arrangement, the feed to any one cell in the succession comprises a mixture of the  $^{235}\text{U}$ -enriched top product from the upper "rectifying" end of the next cell below, and the  $^{238}\text{U}$ -enriched bottom product from the lower "stripping" end from the next cell above.  $^{235}\text{U}$ , then, concentrates toward one end of the cascade while  $^{238}\text{U}$  concentrates toward the other; product is withdrawn at each end of the cascade, and the original uranium feed solution is introduced at some intermediate cell in the succession.

Further illustration of the quantitative aspects and preferred conditions and procedures of the present method is provided in the following specific example. In the example, a protracted run directed to concentrating uranium-235 in accordance with the present method was made.

## EXAMPLE

Apparatus substantially as illustrated in Figure 1 was applied to the concentration of uranium-235 from a chloride solution of uranium of natural isotopic constitution, by employing the procedure hereinbefore described for  $^{235}\text{U}$  concentration. The particular pH's, concentrations, dimensions and other operating conditions employed are outlined in Table 1 below. At the outset, the anode compartment 5 over to boundary 20, anode end of the migration compartment 33 over to boundary 20, cathode end 34 of the migration compartment and feed compartment 10 over to boundary 26, and the cathode compartment 14 were filled with LiCl,  $\text{UCl}_4$ ,  $\text{UO}_2\text{Cl}_2$ , and HCl, solutions respectively, and the flushing actions through the overflow spouts were commenced. To constitute the flushing actions, in more detail, a continuous stream of aqueous LiCl solution was introduced into port 7 through liquid delivery pipe 8, whence it passed through the left-hand compartment (here the anode compartment) 5, and on through the liquid overflow spout 25; a continuous stream of aqueous  $\text{UO}_2\text{Cl}_2$  solution was introduced into feed solution induction port 11, through feed delivery tube 12, whence it passed through feed compartment 10, and on out through the feed compartment overflow spout 13; and a continuous stream of HCl was introduced into the liquid introduction port 17 through liquid delivery pipe 18, whence the aqueous component thereof passed down through the right-hand extremity of the feed compartment 10, and on through the feed compartment overflow spout 13. Appropriate electrolytic potential was impressed across the anode (in this case 6) and cathode (in this case 16) as by throwing the reversing switch 31 to its B-B' position, and electrolytic current through the auxiliary electrode circuit was ad-

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justed by means of the variable resistor 22. The feed solution overflow spout 13 was raised to commence electrolyte solution flow toward the anode, and manipulated until the lithium-uranium boundary in the boundary tube 4 appeared and became stationary (cf. Getman and Daniels, "Outlines of Physical Chemistry," 7th edition, page 406, John Wiley, New York, 1943; typical ionic mobilities are of the order of 2 centimeters per hour at 25° C. and a potential gradient of one volt per centimeter). The LiCl solution overflow (through spout 25) at the anode was collected and analyzed daily to determine the amount, if any, of uranium lost through the lithium-uranium boundary; representative daily analyses are tabulated in Table 2 below. After approximately 1400 hours operation, the solutions in the proximity of the canode 9, and that in the feed compartment 19, were sampled and isotopically analyzed for uranium-235 and 238. Samples were also obtained from within the anode half 33, and the cathode half 34, of the packing, and were similarly analyzed. The analyses are tabulated in Table 3 below.

Table 1  
OPERATING CONDITIONS

|    |   |  |         |
|----|---|--|---------|
| 25 | LiCl.....                                 | 0.20 M (changed to 0.15 M after 13th day). | pH 1.00 |
|    | HCl.....                                  |  | pH 0.35 |
|    | $\text{UO}_2\text{Cl}_2$ .....            | 0.10 M                                     | pH 1.25 |
|    | $\text{UCl}_4$ .....                      | 0.10 M                                     | pH 0.70 |
| 30 | Packing material.....                     | Ballotini Glass Beads (nominal 100 mesh).  |         |
|    | Diameter of packing.....                  | 1.2 inches.                                |         |
|    | Length of packing.....                    | 8.0 inches.                                |         |
|    | Potential across packing.....             | 40 volts.                                  |         |
|    | Current through packing.....              | 0.082 amps.                                |         |
|    | Potential across cell <sup>1</sup> .....  | 350 volts.                                 |         |
|    | Current through cell.....                 | 0.082 amps.                                |         |
| 35 | Potential across external resistance..... | 40 volts.                                  |         |
|    | Current through external resistance.....  | 0.16 amps.                                 |         |
|    | Time of operation.....                    | 1,408 hours.                               |         |

<sup>1</sup> During operation the potential across the cell rose from 260 to 350 volts

Table 2  
REPRESENTATIVE DAILY LOSSES OF URANIUM

| Day     | Uranium Loss (mg.) |
|---------|--------------------|
| 45      |                    |
| 1.....  | 29.3               |
| 6.....  | 11.8               |
| 11..... | 22.8               |
| 16..... | 5.8                |
| 21..... | 2.9                |
| 26..... | 7.0                |
| 31..... | 5.0                |
| 50      |                    |
| 45..... | 2.2                |
| 55..... | 5.0                |

Table 3  
PERCENT  $^{235}\text{U}$  THROUGHOUT CELL

| Solution from—               | Percent of U Represented $^{235}\text{U}$ |
|------------------------------|---|
| 60                           |   |
| Feed.....                    | 0.7111                                    |
| Cathode Half of Packing..... | 0.7122                                    |
| Anode Half of Packing.....   | 0.7162                                    |
| Proximity of Canode.....     | 0.7171                                    |

The definite enrichment afforded by a packed migration compartment length so short as only 8 inches is clearly evidenced. Also noteworthy is the marked decrease in the small uranium loss through the lithium-uranium boundary realized upon 25% reduction in  $\text{Li}^+$  concentration.

To alternatively effect concentration of  $^{238}\text{U}$ , exactly the same apparatus, solutions, concentrations, pH's, dimensions, and other conditions specified in the example are employed, with the exceptions that: the polarity of the potential impressed between the anode and the cathode is reversed, the LiCl and HCl solutions are inter-



changed to correspond with the interchange of cathode with anode, a  $\text{UCl}_4$ , pH 1.25, solution is employed as the feed, and the solution introduced to the vicinity of the auxiliary electrode at the outset is 0.70 pH  $\text{UO}_2\text{Cl}_2$  solution. As a second alternative, the same conditions may be directly applied to the simultaneous concentration of both  $^{235}\text{U}$  and  $^{238}\text{U}$ , employing apparatus as illustrated in Figure 2, by employing a 16' packing length, a feed solution comprising a  $\text{UO}_2\text{Cl}_2$ - $\text{UCl}_4$  mixture in 1:1 molar ratio, and slightly higher impressed electrode potentials to maintain specified amperages. In either alternative, isotopic enrichment of the order of that demonstrated in the example is realized.

Although this invention has been described with particular emphasis upon its very important application to the enrichment of natural uranium in  $^{235}\text{U}$  and/or  $^{238}\text{U}$ , it is inherently of much wider applicability. The present method is also well adapted to the enrichment of uranium initially in isotopic proportion other than that found in nature. For instance, the fact that it may be carried out in glassware apparatus makes it eminently suited for application to the final enrichment of  $^{235}\text{U}$  after its initial enrichment and isolation from the bulk of other isotopes by means of other conventional production procedures. Also, a particularly promising application is in the recovery and reconversion of uranium depleted in  $^{235}\text{U}$  from the waste products of nuclear reactors. Upon use of natural uranium for fuel in nuclear reactors, the isotopic proportion of  $^{235}\text{U}$  is generally reduced below that found in nature. In partial or complete reconversion of this  $^{235}\text{U}$ -depleted uranium back to uranium of natural isotopic proportion, the present operation has direct application. Furthermore, it may also be applied to the concentration of other uranium isotopes, as lighter  $^{234}\text{U}$  or  $^{233}\text{U}$ , which would concentrate toward the anode, while heavier isotopes, as  $^{238}\text{U}$ , concentrated toward the cathode. In addition, the method may also be applied to other elements, especially in the transuranic realm, which have a pair of high positive valence states, and different isotopes which will concentrate toward different electrodes during countercurrent electrolytic migration of cations of those valence states. Various additional applications of the hereinbefore-disclosed methods will become apparent to those skilled in the art. It is therefore to be understood that all matters contained in the above description and example are illustrative only and do not limit the scope of the present invention.

What is claimed is:

1. A new and improved method for effecting elevation in isotopic proportion, with respect to at least one isotope, of uranium initially isotopically comprising a lighter and a heavier isotope, which comprises forming from said uranium an aqueous, acidic solution of uranous and uranyl ions each in substantial proportion, subjecting the uranous and uranyl ions both in substantial proportion in said solution to the action of an electrolytic current passed between an anode and cathode, thereby inducing said uranous and uranyl ions to electrolytically migrate toward the cathode, with the electrolytic migration of the uranous ions being characteristically at a faster velocity than that of the uranyl ions, while passing a stream of aqueous, acidic electrolyte solution from the cathode to the anode at a velocity between the cathodic electrolytic migrational velocities of the faster uranous ion and slower uranyl ion, thereby washing uranyl ions toward the anode while the uranous ions make headway upstream in migrating toward the cathode, consequently concentrating uranous ions toward the cathode and uranyl ions toward the anode, and therewith concomitantly concentrating said lighter uranium isotope toward the anode and said heavier uranium isotope toward the cathode, and thereupon separately recovering at least one of the preferentially-isotopically-abundant portions of the uranium solution resultingly obtaining nearest each of said electrodes.

2. A new and improved process for effecting elevation

in isotopic proportion, with respect to at least one isotope, of uranium initially isotopically comprising uranium-235 and uranium-238, which comprises forming from said uranium an aqueous, acidic solution of uranous and uranyl ions each in substantial proportion, subjecting the uranous and uranyl ions both in substantial proportion in said solution to the action of an electrolytic current passed between an anode and cathode, thereby inducing said uranous and uranyl ions to electrolytically migrate toward the cathode, with the electrolytic migration of the uranous ions being characteristically at a faster velocity than that of the uranyl ions, while passing a stream of aqueous, acidic electrolyte solution from the cathode to the anode at a velocity between the cathodic electrolytic migrational velocities of the faster uranous ion and slower uranyl ion, thereby washing uranyl ions toward the anode while the uranous ions make headway upstream in migrating toward the cathode, consequently concentrating uranous ions toward the cathode and uranyl ions toward the anode, and therewith concomitantly concentrating uranium-235 toward the anode and uranium-238 toward the cathode, and thereupon separately recovering at least one of the preferentially-isotopically-abundant portions of the uranium solution resultingly obtaining nearest each of said electrodes.

3. A new and improved process for effecting elevation in isotopic proportion, with respect to uranium-235, of uranium initially isotopically comprising uranium-235 and uranium-238, which comprises forming from said uranium an aqueous, acidic solution of uranous and uranyl ions each in substantial proportion, subjecting the uranous and uranyl ions both in substantial proportion in said solution to the action of an electrolytic current passed between an anode and cathode, thereby inducing said uranous and uranyl ions to electrolytically migrate toward the cathode, with the electrolytic migration of the uranous ions being characteristically at a faster velocity than that of the uranyl ions, while passing a stream of aqueous, acidic electrolyte solution from the cathode to the anode at a velocity between the cathodic electrolytic migrational velocities of the faster uranous ion and the slower uranyl ion, thereby washing uranyl ions toward the anode while the uranous ions make headway upstream in migrating toward the cathode, consequently concentrating uranyl ions toward the anode, and therewith concomitantly concentrating uranium-235 toward the anode, and thereupon separately recovering the portion of the uranium solution preferentially abundant in uranium-235 resultingly obtaining nearest the anode.

4. A new and improved process for effecting elevation in isotopic proportion, with respect to uranium-238, of uranium initially isotopically comprising uranium-235 and uranium-238, which comprises forming from said uranium an aqueous, acidic solution of uranous and uranyl ions each in substantial proportion, subjecting the uranous and uranyl ions both in substantial proportion in said solution to the action of an electrolytic current passed between an anode and cathode, thereby inducing said uranous and uranyl ions to electrolytically migrate toward the cathode, with the electrolytic migration of the uranous ions being characteristically at a faster velocity of that of the uranyl ions, while passing the stream of aqueous, acidic electrolyte solution from the cathode to the anode at a velocity between the cathodic electrolytic migrational velocities of the faster uranous ion and the slower uranyl ion, thereby washing uranyl ions toward the anode while the uranous ions make headway upstream in migrating toward the cathode, consequently concentrating uranous ions toward the cathode, and therewith concomitantly concentrating uranium-238 toward the cathode, and thereupon separately recovering the portion of the uranium solution preferentially abundant in uranium-238 resultingly obtaining nearest the cathode.

5. A new and improved process for isotopically fractionating uranium initially isotopically comprising urani-

um-235 and uranium-238, simultaneously into separate fractions one preferentially-isotopically-abundant in uranium-235 and the other preferentially-isotopically-abundant in uranium-238, which comprises forming from said uranium an aqueous, acidic solution of uranous and uranyl ions each in substantial proportion, subjecting the uranous and uranyl ions both in substantial proportion in said solution to the action of an electrolytic current passed between an anode and cathode, thereby inducing said uranous and uranyl ions to electrolytically migrate toward the cathode, with the electrolytic migration of the uranous ions being characteristically at a faster velocity than that of the uranyl ions, while passing a stream of aqueous, acidic electrolyte solution from the cathode to the anode at a velocity between the cathodic electrolytic migrational velocities of the faster uranous ion and slower uranyl ion, thereby washing uranyl ions toward the anode while the uranous ions make headway upstream in migrating toward the cathode, consequently concentrating uranous ions toward the cathode and uranyl ions toward the anode, and therewith concomitantly concentrating uranium-235 toward the anode and uranium-238 toward the cathode, and thereupon separately recovering the portion of the uranium solution preferentially abundant in uranium-235 resultingly obtaining nearest the anode, and the portion of the uranium solution preferentially abundant in uranium-238 resultingly obtaining nearest the cathode.

6. The process of claim 2 wherein said aqueous acidic solution of uranous and uranyl ions is an aqueous acidic solution of fractional molarity of uranous chloride and uranyl chloride, with a pH of 1.5.

7. The process of claim 2 wherein said electrolytic current is of a magnitude of approximately 0.1 ampere per square inch.

8. The process of claim 2 wherein said passing of a stream of aqueous, acidic electrolyte solution from the cathode to the anode is effected by the continuous introduction at the cathode, under a substantial hydrostatic head with respect to that of the anode, of an aqueous, acidic solution, of density less than that of said uranium solution, of a strong electrolyte having an anion identical with that of said uranium solution, and having a cation of greater ionic mobility than that of said uranous and uranyl ions, thereby establishing in a sequential section of the course of said stream flowing vertically downward in proceeding from said cathode toward said anode an electrokinetic boundary downstream from the cathode, demarking the common plane of the forefront of the upstream-migrating body of uranous ions, and of the downstream end of the similarly upstream-migrating body of cations of said electrolyte solution introduced at the cathode, and maintaining the resulting boundary stationary, by adjustment of said velocity of the electrolyte solution flowing from the cathode toward the anode, representing a zero net spatial transfer of uranium ions in said body of uranium ions in said flowing electrolyte solution stream immediately downstream from said boundary.

9. The process of claim 2 wherein said anode is maintained continuously immersed in an aqueous acidic solution, of density less than that of said uranium solution, of a strong electrolyte having an anion identical with that of said uranium solution, and having a cation of ionic mobility smaller than that of said uranous and uranyl ions, thereby establishing, in a sequential section of the course of said stream flowing vertically upward in proceeding from said cathode toward said anode, an electrokinetic boundary, demarking the common plane of the trailing end of the body of said downstream-washing uranyl ions, and of the forefront of the upstream-electromigrating cations of said solution immersing said anode, and maintaining the resulting boundary stationary, by adjustment of said velocity of the electrolyte solution flowing from the cathode toward the anode, representing a

zero net spatial transfer of uranium ions in said body of uranium ions in said flowing electrolyte solution stream immediately upstream from said boundary.

10. The process of claim 2 wherein said uranium ions of one oxidation state, in their migration toward a particular said electrode, are, at a location in close approach to said electrode, converted, by changing their oxidation state, to the other said uranium ions of different oxidation state, thereby inducing the so-converted ions to reverse direction and commence moving toward the opposite electrode.

11. The process of claim 2 wherein said uranium ions of one oxidation state, in their migration toward a particular said electrode, are, at a location in close approach to that electrode, converted, by electrolytically changing their oxidation state, to the other said uranium ions of different oxidation state, thereby inducing the electrolytically converted ions to reverse direction and commence moving toward the opposite electrode.

12. A new and improved process for effecting elevation in isotopic proportion, with respect to uranium-238, of uranium initially isotopically comprising uranium-235 and uranium-238, which comprises: forming from said uranium an aqueous, acidic solution of uranous and uranyl ions each in substantial proportions; subjecting the uranous and uranyl ions both in substantial proportion in said solution to the action of an electrolytic current passed between an anode and cathode, thereby inducing said uranous and uranyl ions to electrolytically migrate toward the cathode, with the electrolytic migration of the uranous ions being characteristically at a faster velocity than that of the uranyl ions, while passing a stream of aqueous, acidic electrolyte solution from the cathode to the anode at a velocity between the cathodic electrolytic migrational velocities of the faster uranous ion and slower uranyl ion, by means of continuously introducing at the cathode, under a substantial hydrostatic head with respect to that at the anode, an aqueous acidic electrolyte solution, of density less than that of said uranium solution, having an anion identical with that of said uranium solution, and having a cation of lesser ionic mobility than that of said uranium ions, thereby washing uranyl ions toward the anode while the uranous ions make headway upstream in migrating toward the cathode, and further thereby establishing, in a sequential section of the course of said stream flowing vertically downward in proceeding from said cathode toward said anode, an electrokinetic boundary demarking the common plane of the forefront of the body of upstream-migrating uranium ions, and of the tail end of the likewise upstream-migrating body of cations of said electrolyte solution introduced at the cathode; maintaining the resulting boundary stationary, by adjustment of said velocity of the electrolyte solution flowing from the cathode to the anode, representing a zero net spatial transfer of uranium ions in said body of uranium ions in said flowing stream of electrolyte solution immediately downstream from said boundary; continuously electrolytically oxidizing upstream-migrating uranous ions, as they closely approach said boundary, to uranyl ions, which thereupon reverse direction and are washed downstream toward the anode, consequently concentrating uranium-238 against said boundary, and thereupon recovering uranium solution preferentially abundant in uranium-238 resultingly obtaining adjacent the downstream side of said boundary.

13. A new and improved process for effecting elevation in isotopic proportion, with respect to uranium-235, of uranium initially isotopically comprising uranium-235 and uranium-238, which comprises: forming from said uranium an aqueous, acidic solution of uranous and uranyl ions each in substantial proportion; subjecting the uranous and uranyl ions both in substantial proportion in said solution to the action of an electrolytic current passed between an anode and cathode, thereby inducing said uranous and uranyl ions to electrolytically migrate

toward the cathode, with the electrolytic migration of the uranous ions being characteristically at a faster velocity than that of the uranyl ions, while passing a stream of aqueous, acidic electrolyte solution from the cathode to the anode at a velocity between the cathodic electrolytic migrational velocities of the faster uranous ion and the slower uranyl ion, thereby washing uranyl ions toward the anode while the uranous ions make headway upstream in migrating toward the cathode; maintaining said anode immersed in an aqueous acidic solution, of density less than that of said uranium solution, of a strong electrolyte having an anion identical with that of said uranium solution, and having a cation of ionic mobility greater than that of said uranium ions, thereby establishing, in a sequential section of the course of said stream flowing vertically upward in proceeding from said cathode toward said anode, an electrolytic boundary demarking the common plane of the tail end of the upstream-migrating body of uranium ions, and of the forefront of the likewise upstream-migrating body of cations of said electrolyte solution immersing the anode; maintaining said boundary stationary, by adjustment of said velocity of the stream of aqueous acidic electrolyte solution passed from the cathode to the anode, representing zero net spatial transfer of uranium ions in said body of uranium ions in said flowing stream of electrolyte solution immediately upstream from said boundary; electrolytically reducing downstream-washing uranyl ions, as they closely approach that boundary, to uranous ions, which thereupon reverse direction and commence moving upstream toward the cathode; consequently concentrating uranium-235 against said boundary; and thereupon recovering uranium solution preferentially abundant in uranium-235 resultingly obtaining adjacent the upstream side of said boundary.

14. A new and improved process for isotopically fractionating uranium, initially isotopically comprising uranium-235 and uranium-238, simultaneously into a fraction preferentially-isotopically-abundant in uranium-235 and another fraction preferentially-isotopically-abundant in uranium-238, which comprises: forming from said uranium an aqueous, acidic solution of uranous and uranyl ions each in substantial proportion; subjecting the uranous and uranyl ions both in substantial proportion in said solution to the action of an electrolytic current passed between the anode and cathode, thereby inducing said uranous and uranyl ions to electrolytically migrate toward the cathode, with the electrolytic migration of the uranous ions being characteristically at a faster velocity than that of the uranyl ions, while passing from the cathode to the anode at a velocity between the cathodic electrolytic migrational velocities of the faster uranous ions and slower uranyl ions a stream of aqueous, acidic electrolyte solution, effected by continuously introducing at the cathode under a substantial hydrostatic head with respect to that of the anode, an aqueous acidic solution, of density less than that of said uranium solution, of a strong electrolyte having an anion identical with that of said uranium solution, and having a cation of greater ionic mobility than that of the said uranium ions, thereby washing uranyl ions toward the anode while the uranous ions make headway upstream in migrating toward the cathode, and further thereby establishing, in a sequential section of the course of said stream flowing vertically downward in proceeding from said cathode to said anode, a first electrokinetic boundary, demarking the common plane of the forefront of the body of upstream-migrating uranium ions, and of the trailing end of the likewise upstream-migrating body of cations of said electrolyte solution introduced at the cathode; maintaining said anode immersed in a second aqueous, acidic solution, of density less than that of said uranium solution, of a strong electrolyte having an anion identical with that of said uranium solution, and having a cation of ionic mobility less than that of said uranium ions, thereby establishing, in a sequential section of the course of said stream flowing verti-

cally upward in proceeding from said cathode to said anode, a second electrokinetic boundary, delineating the common plane of the trailing end of the upstream-migrating body of uranium ions, and of the forefront of the likewise upstream-migrating body of cations of said second electrolyte solution; maintaining both said boundaries simultaneously stationary, by adjustment of said velocity of the stream of aqueous, acidic electrolyte solution passing from the cathode to the anode, such condition representing zero net spatial transfer of uranium ions between said boundaries; continuously electrolytically oxidizing upstream-migrating uranous ions, as they closely approach said first electrokinetic boundary, to uranyl ions, which thereupon reverse direction and commence moving toward the anode; continuously electrolytically reducing downstream-receding uranyl ions, as they closely approach said second electrokinetic boundary, to uranous ions, which thereupon reverse direction and commence moving upstream toward the cathode; consequently concentrating uranium-238 against said first electrokinetic boundary, and uranium-235 against said second electrokinetic boundary; and thereupon separately recovering uranium solution preferentially abundant in uranium-238 resultingly obtaining adjacent the downstream side of said first electrokinetic boundary, and uranium solution preferentially abundant in uranium-235 resultingly obtaining adjacent the upstream side of said second electrokinetic boundary.

15. The process of claim 12 wherein said uranium solution comprises a chloride solution, approximately 0.01 to 1.0 M and having a pH substantially within the range of pH 1 to 1.5, said electrolytic current is substantially 0.1 ampere per square inch, and said aqueous, acidic solution of strong electrolyte introduced at the cathode is aqueous hydrochloric acid.

16. The process of claim 13 wherein said uranium solution comprises a chloride solution, approximately 0.01 to 1.0 M, and having a pH substantially within the range of pH 1 to 1.5, said electrolytic current is substantially 0.1 ampere per square inch, and said aqueous, acidic solution of strong electrolyte immersing the anode is an aqueous, acidic lithium chloride solution of fractional molarity and having a pH of approximately pH 1.

17. The process of claim 14 wherein said uranium solution comprises a chloride solution, approximately 0.01 to 1.0 M, and having a pH substantially within the range of pH 1 to 1.5, said electrolytic current is substantially 0.1 ampere per square inch, said aqueous, acidic solution of strong electrolyte introduced at the cathode is aqueous hydrochloric acid, and said aqueous, acidic solution of strong electrolyte immersing the anode is an aqueous, acidic lithium chloride solution of fractional molarity and having a pH of approximately pH 1.

18. The process of claim 2 wherein the said passing of a stream of aqueous, acidic electrolyte solution from the cathode to the anode comprises passing said stream through a horizontally-disposed, substantially-chemically-inert, electrically-non-conductive, porous bed at a velocity between the cathodic electrolytic migration of velocities through said bed of the faster uranous ion and the slower uranyl ion thereby washing uranyl ions through said bed toward the anode while the uranous ions make headway upstream through said bed in migrating toward the cathode.

19. The process of claim 2 wherein said passing of a stream of aqueous, acidic electrolyte solution from the cathode to the anode comprises passing said stream through a horizontally-disposed porous bed of glass beads of substantially 100-mesh size at a velocity between the cathodic electrolytic migration velocities through said bed of the faster uranous ion and slower uranyl ion, thereby washing uranyl ions through said bed toward the anode while the uranous ions make headway up stream through said bed in migrating toward the cathode.

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