

[54] **RECOVERY OF URANIUM FROM HCl
DIGESTED PHOSPHATE ROCK SOLUTION**

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[58] Field of Search **423/6, 7, 8, 9, 10, 15,**
423/18, 20, 260, 319, 321, 253; 23/312 P,
312 ME

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[57]

ABSTRACT

Uranium is recovered from a solution containing phosphoric acid, uranium in the hexavalent state and a chloride salt from the group consisting of alkali metal chloride, alkaline earth metal chloride, ammonium chloride and mixtures thereof, such as a solution obtained by hydrochloride acid digestion of phosphate rock. The phosphoric acid is extracted from the solution before the uranium is recovered from the remaining constituents thereof. Extraction degradation and emulsification of the organic layer previously employed in organic solvent extraction methods are eliminated, and the uranium is recovered at low cost and in a highly efficient manner.

11 Claims, No Drawings

RECOVERY OF URANIUM FROM HCl DIGESTED PHOSPHATE ROCK SOLUTION

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the recovery of uranium from a phosphoric acid containing solution, and more particularly to a process for extracting phosphoric acid from the solution before the uranium is recovered.

2. Description of the Prior Art

The demand for uranium is continuously increasing, but relatively few extensive high grade uranium deposits have been found. Fortunately, many phosphate rocks contain small amounts of recoverable uranium. The tonnage of phosphate rock consumed during manufacture of phosphoric acid is considerable. Hence, it is apparent that a substantial amount of uranium could be made available therefrom by provision of an efficient, economical method of recovery. Unless uranium is recovered during manufacture of phosphoric acid, it has been estimated that more than two thousand tons of uranium from this source will be lost each year. The need for such a method of recovery cannot be overstated, since future growth of electric power generation by nuclear means depends to a large extent on an economical source of uranium fuel.

The methods which have enjoyed, perhaps, the widest use in recovering uranium from phosphate rock during manufacture of phosphoric acid are of the types disclosed in U.S. Pat. Nos. 2,761,758, 2,859,092 and 2,866,680. In each of those methods uranium is recovered directly from the product acid, but to date considerable problems inherent in the use of such methods have not been solved. The coprecipitation method of U.S. Pat. No. 2,761,758 is time consuming for relatively large volumes of phosphoric acid, is multistep, and requires recycle procedures. Organic extractants, such as the ethyl phosphates employed in the solvent extraction methods of U.S. Pat. Nos. 2,859,092 and 2,866,680, tend to degrade so as to require constant addition of make-up amounts. Moreover, emulsification of the organic layer in the aqueous phase of such solvent extraction methods necessitates additional stripping procedures to prevent solvent loss.

Ion exchange, normally a preferred separation method when applicable, has been found not useful for methods of the types described above. The hexavalent uranium present in the phosphoric acid forms an anionic complex which is an improper target for cation exchange. Phosphorus-containing ions present in the product acid are readily adsorbed by anion exchange resins, with the result that the selectivity of such resins for uranium complexes is substantially decreased. For the above reasons, methods of the type described have generally resulted in lower efficiencies and higher costs for recovering uranium than have been considered commercially acceptable.

SUMMARY OF THE INVENTION

The present invention provides an economical and efficient method for recovering uranium present in a solution containing phosphoric acid, uranium in the hexavalent state and a chloride salt from the group consisting of alkali metal chloride, alkaline earth metal chloride, ammonium chloride and mixtures thereof, such as that obtained by hydrochloric acid digestion of phosphate rock. In accordance with the present inven-

tion, the phosphoric acid is extracted before the uranium is recovered from the solution. This is accomplished by contacting the solution with a reductant capable of converting the uranium from a hexavalent to a tetravalent state. After the solution has been reduced in this manner, it is brought into contact with an organic extractant capable of separating the phosphoric acid therefrom. Thereafter, the uranium is recovered from the remaining constituents of the solution.

It has been found that significant advantages result from extracting the phosphoric acid from the solution and then recovering the uranium from the remaining constituents thereof. The numerous steps and recycle procedures required by coprecipitation methods are avoided. Problems such as extractant degradation and emulsification of the organic layer previously employed in solvent extractant methods are eliminated. Upon extraction of the phosphoric acid, the uranium is readily converted from the tetravalent to the hexavalent state and adsorbed from the solution in a highly efficient manner by contacting the remaining constituents thereof with an ion exchange resin. Adsorption of uranium is substantially complete, i.e. at least about 95 percent by weight of the uranium is adsorbed. Moreover, the uranium is adsorbed by the resin as a complex chloride ion, so that the adsorbing column can be economically regenerated with water. For the above reasons, recovery of the uranium results in higher efficiencies and lower costs than those incurred by operations wherein the solution from which the uranium is recovered contains phosphoric acid.

The invention will be more fully understood and further advantages will become apparent when reference is made to the following detailed description of the preferred embodiments of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Most phosphoric acid-containing solutions, including those obtained during various stages of superphosphate and industrial phosphoric acid manufacture as by-products and as intermediate products, contain uranium. As a consequence, the present invention will function with most types of phosphoric acid-containing solutions. For illustrative purposes, the invention is described in connection with a solution obtained by hydrochloric acid digestion of phosphate rock. However, solutions differing very considerably in composition from the latter solution either in relative concentrations or in the types of ions present can also be satisfactorily processed by the invention. Moreover, it is contemplated that phosphate may be added to acidic uranium solutions and the uranium recovered by the process of the invention. In each of these phosphoric acid-containing solutions, the necessity for recovering uranium in an economical and efficient manner is readily apparent.

The starting material may be any solution containing phosphoric acid, uranium in the hexavalent state and chloride salt from the group consisting of alkali metal chloride, alkaline earth metal chloride, ammonium chloride and mixtures thereof. Of course, the starting material can contain uranium in each of the hexavalent and tetravalent states. A common starting material is the solution obtained by hydrochloric acid digestion of phosphate rock, during the conversion of the rock into fertilizer. The method of obtaining such solution is well

known to those skilled in the art. Generally, an aqueous slurry of such rock is introduced into an acidulating vessel wherein it is treated with hydrochloric acid to form a solution containing phosphoric acid, uranium and chloride salts, principally as calcium chloride. The solution is then transferred to a reducing vessel wherein it is brought into contact with a reductant capable of converting the uranium from the hexavalent to the tetravalent state. After the solution has been reduced in this manner, it is transferred to an extracting vessel wherein it is caused to contact an organic extractant capable of removing the phosphoric acid therefrom. It was discovered that uranium in the tetravalent state is not separated from the solution during extraction of the phosphoric acid, but instead remains in the resulting solution, comprising an aqueous brine phase, from which it is recovered in a highly efficient manner, as by passing the solution through an anion exchange resin.

The concentration of the uranium present in the starting solution can vary considerably, as in the order of from about 10–2000 parts by weight of uranium per million parts by weight of solution, and preferably from about 100–1000 parts by weight of uranium per million parts of solution. Uranium in the tetravalent state tends to become insoluble at concentrations higher than about 2000 parts by weight uranium per million parts by weight of solution, with the result that a tetravalent uranium dihydrogen phosphate precipitate is formed which interferes with the extraction of the phosphoric acid and leads to uranium losses through deposition of solids in the extraction equipment. The concentration of phosphoric acid present in the starting solution generally ranges from about 1–50 weight percent of the solution, and preferably from about 5–30 weight percent thereof. Concentrations of phosphoric acid below about one percent by weight of the solution tend to result in precipitation of tetravalent uranium phosphate. At concentrations of the phosphoric acid above about 50 percent by weight of the solution, the solubility of the chloride salt decreases rapidly and extraction of the phosphoric acid is reduced.

In addition to promoting extraction of the phosphoric acid, the chloride salt forms a complex with uranium which is retained by the resin in the ion exchange column, whereby the column can be economically regenerated with water. The required amount of chloride salt will, of course, vary depending upon the type of salt present and such considerations will be understood by those skilled in the art. Generally, solutions obtained by hydrochloric acid digestion of phosphate rock already contain a sufficient quantity of chloride salts, principally as calcium chloride. As a result no chloride salt has to be added to such solutions. During extraction, distribution of phosphoric acid into the organic phase increases directly with the chloride salt concentration. At chloride salt concentrations above about 30 percent by weight of the solution, the chloride salt tends to enter the organic phase. Calcium chloride concentrations below about 5 percent by weight of the solution tend to hinder separation of the tetravalent uranium and the phosphoric acid during the extraction step. Accordingly, for most effective separation of the tetravalent uranium and phosphoric acid during extraction of the latter, the calcium chloride concentration should range from about 5–30 percent by weight of the solution.

The reductant employed to convert the uranium from a hexavalent to a tetravalent state should not hinder extraction of phosphoric acid by adversely affecting either the phosphoric acid or the organic solvent. Moreover, such reductant should be oxidized to a form whereby the reductant (1) does not interfere with recovery of uranium from the brine phase in which the uranium is retained during extraction of the phosphoric acid, or (2) is readily separable from the brine phase. Reductants which have been found particularly effective for the method of the present invention include elementary iron, elementary aluminum, hydrogen sulfide, sodium hydrosulfite and formaldehyde-sodium sulfoxylate. The preferred reductant is hydrogen sulfide since its oxidation product, elementary sulfur, is readily separated from the solution prior to extraction of the phosphoric acid therefrom.

Reduction of the uranium from the hexavalent to the tetravalent state can be conveniently carried out at temperatures ranging from about 10°C. to the boiling point of the solution and preferably from about 40°C. to 100°C. Generally, the uranium is associated with relatively large proportions of iron, thus the Fe/U weight ratio in a HCl-phosphate rock digest liquor is approximately 50. Moreover, all the iron must be reduced to the divalent state before any U can be reduced to the tetravalent state. As a result, the amount of reductant required is controlled by the iron rather than the uranium. Since the reduction step is relatively slow when weak reductants are employed, a catalyst, such as a soluble copper salt (e.g. copper sulfate or chloride), may be added to increase the rate of the reduction reaction. The copper catalyst has been found to be effective when added in an amount ranging from about 0.005 to 0.05 mole copper per mole of hexavalent uranium, and preferably about 0.01 mole copper per mole of hexavalent uranium.

The extractant used to separate phosphoric acid from the solution must be phosphoric acid-miscible and brine-immiscible. Moreover, the extractant must not separate the tetravalent uranium from the solution. Good results have been obtained using organic extractants such as butanols (e.g. 2-methyl-1-propanol), pentanols (e.g. 3-methyl-1-butanol), trialkylphosphates having alkyl groups containing from 2 to 8 carbon atoms (e.g. tri-n-butylphosphate), and N,N-disubstituted amides which are derived from monocarboxylic acids having 1 to 3 carbon atoms (e.g. N,N-dibutyl acetamide), as well as from mixtures of the foregoing extractants individually or in combination with kerosene or other hydrocarbons. Best results are obtained using butanols and pentanols diluted with kerosene or heptane. The amount of extractant used may vary depending on the concentration of phosphoric acid in the solution as well as the type of extractant. Generally, the amount of extractant used ranges from about 5 to 20 parts by weight per part of the phosphoric acid, and preferably from about 10 to 15 parts per part thereof.

As indicated, after the phosphoric acid has been extracted from the solution, the uranium can be efficiently and economically recovered from the remaining solution comprising an aqueous brine phase. The brine solution is transferred to an oxidizing vessel wherein the constituents thereof are brought into contact with an oxidant capable of converting the uranium from the tetravalent to the hexavalent state. When oxidation of

the uranium is substantially complete, the brine solution is directed through an ion exchange column wherein it contacts an anion exchange resin such as Dowex-1 (a registered trademark of the Dow Chemical Company for an anion exchange resin made from a styrene-divinylbenzene copolymer), Amberlite IRA-400 (a registered trademark of Rohm and Haas Company for an anion exchange resin comprising an insoluble cross-linked polymer), Permutit S (a registered trademark of Permutit Company for a basic anion exchange resin), or the like. Due to the presence of the chloride salt, the uranium tends to form anionic uranyl chloro-complexes which, upon contact with the resin, are substantially adsorbed. The adsorbed uranyl chloro-complexes are removed from the column by means of a solvent and uranium is then recovered from the resulting solution in a manner hereinafter described.

The oxidant which can be used to convert the uranium from the tetravalent to the hexavalent state include any oxidant which does not prevent or interfere substantially with the separation of uranium by the anion exchange resin. As discussed hereinafter, the amount of oxidant used should be no greater than that sufficient to convert the tetravalent uranium to the hexavalent state. Typical oxidants suitable for use with the present invention include soluble trivalent iron salts (e.g. ferric chloride), sodium chlorate, sodium hypochlorite, sodium chlorite and elementary chlorine. Elementary chlorine and sodium chlorate are inexpensive, easily handled and form reduction products which do not interfere with the separation of uranium by the anion exchange resin. For this reason, the latter oxidants are preferred.

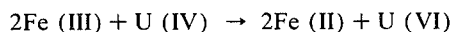
The oxidation step can be carried out at atmospheric pressure and at temperatures ranging from about 10°C. to the boiling point of the solution, and preferably from about 40°C. to 100°C. At temperatures lower than about 10°C., the chloride salt commences to precipitate from the solution and the oxidation rate is retarded, thereby inconveniently prolonging the oxidation step.

The efficiency of the anion exchange resin depends on the chloride ion concentration of the solution. Good results have been obtained with 3-10 molar chloride ion solutions. The best results are obtained with 4-9 molar chloride ion solutions.

Generally, the starting solution contains a trivalent iron salt present in an amount ranging from about 1000 parts by weight of salt per million parts by weight of solution. During reduction of the uranium from the hexavalent to the tetravalent state, the trivalent iron is reduced to the divalent state, and consequently, remains in the aqueous phase of the solution during extraction of the phosphoric acid therefrom. To prevent oxidation of this iron to a trivalent state and coadsorption thereof with the uranium as FeCl_4^- during passage of the aqueous phase (brine solution) through the adsorbing column, the amount of oxidant used to convert the uranium from tetravalent to the hexavalent state must be carefully controlled. For this reason, the quantity of oxidant employed should be no greater than that sufficient to convert the tetravalent uranium to the hexavalent state. A suitable means of control is by electrode potential measurements. Over-oxidation of the solution is easily corrected by introduction of a sufficient quantity of sulfur dioxide to convert the iron from the trivalent to the divalent state. Advantageously, the presence

of sulfur dioxide in the solution does not reduce the uranium therein to a tetravalent state.

The uranium can, alternatively, be recovered from the brine solution by separating the solution into a plurality of portions. A first portion of the solution is brought into contact with an oxidant of the type described, the oxidant being present in sufficient quantity that each of the uranium and the iron contained therein become fully oxidized. Thus oxidized, the first portion is combined with a second portion of the solution in an amount sufficient to selectively oxidize substantially all of the uranium of the second portion from the tetravalent to the hexavalent state. By appropriate apportionment of the first and second portions of the solution according to the formula



a resultant stream is produced having its uranium and iron constituents in the form best suited for the adsorption step.

Uranium adsorbed by the ion exchange resin can be removed therefrom by washing the resin with a solvent such as water or dilute hydrochloric acid. During the washing step the hexavalent uranium is dissolved by and enters the resulting solution in the form of uranyl chloride (UO_2Cl_2).

One method of recovering uranium from the solution comprises the steps of neutralizing the solution with limestone to a pH of about 4, removing trace impurities such as iron from the solution, as by filtering, introducing a sufficient quantity of ammonia to cause precipitation of hexavalent uranium in the form of the compound ammonium diuranate $(\text{NH}_4)_2\text{U}_2\text{O}_7$, separating such compound from the solution, as by filtering, washing the compound and calcining it to produce uranium trioxide (UO_3). Another method of removing uranium from the solution comprises the steps of evaporating the solution so as to bring the uranium concentration thereof to at least about one percent by weight of the solution, contacting the solution with a sufficient amount of a reductant, such as a hydroxylamine salt (e.g. hydroxylamine hydrochloride, hydroxylamine sulfate $(\text{NH}_2\text{OH} \cdot \text{H}_2\text{SO}_4)$) to reduce the uranium therein from a hexavalent to a tetravalent state, contacting the reduced solution with a sufficient amount of hydrogen fluoride (HF) and ammonium fluoride (NH_4F) to precipitate uranium from the solution in the form of crystalline ammonium uranous pentafluoride (NH_4UF_5), and separating (as by filtering), washing and calcining the precipitate to form uranium tetrafluoride (UF_4). The above-described process for recovering the uranium in a desirable form (UF_4) is described in detail in U.S. Pat. No. 3,681,035, assigned to Allied Chemical Corporation.

In a specific embodiment of the present invention, a solution obtained from hydrochloric acid digestion of phosphate rock was found to contain from about 5-15 percent by weight phosphoric acid (H_3PO_4), 20-30 percent by weight calcium chloride (CaCl_2), 1-2 percent by weight hydrochloric acid (HCl), 0.3 to 1.5% by weight ferric chloride (FeCl_3), and 50-200 parts by weight uranium per million parts by weight of solution. The solution was treated at 80°C. with a sufficient quantity of hydrogen sulfide to reduce substantially all of the iron and uranium present therein to the divalent and tetravalent states, respectively. An extractant composed of a mixture of pentanols and kerosene was then

introduced into the solution, whereby 99.8 percent by weight of phosphoric acid was extracted therefrom. The remaining constituents of the solution, comprising an aqueous uranium-containing brine phase were then separated into two portions. A first portion was fully oxidized upon contact with sodium chlorate (NaClO_3). Thereafter, a second portion of the brine phase was combined with a sufficient amount of the first portion thereof to oxidize substantially all of the tetravalent uranium in the second portion from the tetravalent to the hexavalent state and to simultaneously reduce an equivalent amount of the trivalent iron in the first portion to the divalent state. With the iron and uranium constituents of the resultant solution in the form best suited for adsorption, the solution was directed through an ion exchange column wherein it was brought into contact with an anion exchange resin. Uranium adsorbed onto the resin was then removed therefrom by washing the column with dilute hydrochloric acid. The slightly acidic solution which resulted was then treated with hydroxylamine sulfate $(\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4$ to reduce the uranium to the tetravalent state. Hydrogen fluoride and ammonium fluoride were then introduced into the solution, whereby the uranium was separated from the solution in the form of ammonium uranous pentafluoride. The ammonium uranous pentafluoride precipitate was washed and then calcined at 350°C . to produce uranium tetrafluoride.

The method described hereinabove can, of course, be modified in numerous ways without departing from the invention. The extractant can be recycled after separation of phosphoric acid from the solution. Moreover, the ammonium fluoride removed from the precipitated ammonium uranous pentafluoride by calcination can be recycled for use in forming the ammonium uranous pentafluoride precipitate. Such modifications are intended to fall within the scope of the present invention. It is, accordingly, intended that all matter disclosed in connection with the foregoing method should be interpreted as illustrative and not in a limiting sense.

The following examples, in which parts and percentages are by weight, are presented to provide a more complete understanding of the invention. The specific techniques, conditions, materials, proportions and reported data set forth to illustrate the principles and practice of the invention are exemplary and should not be construed as limiting the scope of the invention.

EXAMPLE 1

A reaction vessel equipped with a mechanical stirrer was charged at atmospheric pressure with an aqueous slurry of phosphate rock, hydrochloric acid and sodium chloride. The resultant starting solution contained 25 percent calcium chloride, 13.1 percent phosphoric acid, 1.8 percent hydrochloric acid and 66 parts uranium (essentially in the hexavalent form) per million parts of solution. These constituents were heated with vigorous stirring to a temperature of 80°C . The stirring was continued, 0.55 gram of sodium hydrosulfite was added to the solution and the temperature of the solution was maintained at 80°C . for 15 minutes, during which time substantially all of the uranium was reduced from the hexavalent to the tetravalent state.

The reduced solution was divided into ten one-liter portions. An extractant was prepared by saturating a mixture of 80 percent isobutanol and 20 percent n-heptane with water at 50°C . Substantially all of the

phosphoric acid was extracted from the solution by contacting each one liter portion thereof with the same volume of the extractant in five successive stages at a temperature of 50°C . Hydrochloric acid removed from the solution during extraction of the phosphoric acid was replaced after each stage of the extraction process by contacting the aqueous phase thereof with 50 milliliters of concentrated aqueous (37 percent) hydrochloric acid.

The aqueous phases of the solution were then combined to produce 11.5 liters of uranium-containing brine solution. The brine solution was found to contain 80 percent of the uranium present in the starting material.

EXAMPLE 2

An acidulation tower equipped with a mechanical stirrer was charged with a water based slurry of ground Florida phosphate rock containing 235 parts uranium (essentially in the hexavalent form) per million parts of phosphate rock. The slurry was contacted with a stream of hydrochloric acid vapor moving in a direction countercurrent to that of the slurry. The acid-insoluble residue was removed by settling and filtration. An acidulate solution was thereby formed which contained 26.7 percent calcium chloride, 13.1 percent phosphoric acid, 1.8 percent hydrochloric acid, 0.8 percent ferric chloride, 0.7 percent aluminum chloride, 0.8 percent fluorine and 66 parts uranium (essentially in the hexavalent form) per million parts of solution. These constituents were heated with vigorous stirring to a temperature of 80°C . The stirring was continued, the temperature was maintained at 80°C . and hydrogen sulfide was directed through the acidulate solution until the electromotive potential developed between platinum and saturated calomel electrodes immersed therein decreased from an initial value of +0.52 volt to from about +0.15 to 0.20 volt. When the latter voltage was developed between the electrodes, substantially all of the iron and uranium present in the solution had been converted to the divalent and tetravalent states, respectively.

The reduced acidulate solution was divided into ten one-liter portions. An extractant was prepared by saturating a mixture of 80 percent isobutanol and 20 percent n-heptane with water at 50°C . Substantially all of the phosphoric acid was extracted from the acidulate solution by contacting each one-liter portion thereof with the same volume of the extractant in five successive stages at a temperature of 50°C . Hydrochloric acid removed from the solution during extraction of the phosphoric acid was replaced after each stage of the extraction process by contacting the aqueous phase thereof with 50 milliliters of concentrated aqueous (37 percent) hydrochloric acid.

The aqueous phases were then combined to produce 11.5 liters of a brine solution containing 24.1 percent calcium chloride, 0.1 percent phosphoric acid, 2.0 percent hydrochloric acid, 0.6 percent ferrous chloride, 0.6 percent aluminum chloride, 0.7 percent fluorine and 50 parts uranium per million parts of solution. As indicated by the composition of the brine solution, more than 99 percent of the phosphoric acid was extracted from the acidulate solution, while the brine solution contained substantially all of the calcium chloride, aluminum chloride, and fluorine, 84 percent of the uranium and 90 percent of the iron thereof. More-

over, the uranium and iron contained by the brine solution was reduced to the tetravalent and divalent states, respectively.

The brine solution was then transferred to an oxidizing vessel wherein it was brought into contact with a 30 percent aqueous solution of sodium chlorate. Contact between the sodium chlorate and the aqueous phase of the solution was continued at a temperature of 50°C. until the electromotive potential developed between the platinum and saturated calomel electrodes immersed therein increased for an initial value of +0.20 volt to a value of +0.30 volt. When the latter voltage was developed between the electrodes, substantially all of the uranium present in the solution had been converted to the hexavalent state. As a precautionary measure, the solution was then brought into contact with 2 liters of sulphur dioxide gas for each gram of sodium chlorate employed to ensure that substantially all of the iron remained in the divalent state during oxidation of the uranium to the hexavalent state.

The latter solution was fed to an ion exchange vessel having a 20 millimeter column of 50-100 American Standard Mesh Dowex-1-X4 anion exchange resin in chloride form. Passage of the solution through the column was continued at a temperature of 50°C. and at a flow rate of 5 milliliters per minute until the uranium concentration in the effluent from the column increased to about that of the feed solution. The column was scrubbed with 40 milliliters of a 7 molar hydrochloric acid solution, passed therethrough at a flow rate of 10 milliliters per minute. Seventy milliliters of water were then passed through the column at a flow rate of 3 milliliters per minute to strip the uranium from the column. An aqueous solution of uranyl chloride resulted which contained 520 milligrams of uranium in each 70 milliliters of solution.

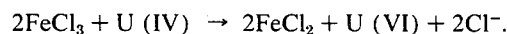
To the resulting solution were added 0.19 gram of 100 percent hydrogen fluoride, 0.89 gram of ammonium fluoride, 0.32 gram of hydroxylamine acid sulfate, a trace of copper sulfate (CuSO_4) and one drop of 37% concentrated hydrochloric acid (as a catalyst). The solution was then boiled for 15 minutes during which time 90% of the uranium contained therein precipitated in the form of ammonium uranous pentafluoride.

The ammonium uranous pentafluoride was filtered from the solution, washed and then calcined at 350°C. After a few minutes substantially all of the ammonium fluoride was volatilized and pure uranium tetrafluoride was obtained.

EXAMPLE 3

An 11.5 liter uranium-containing brine solution was prepared from 10 liters of an acidulate solution containing 26.7 percent calcium chloride, 13.1 percent phosphoric acid, 1.8 percent hydrochloric acid, 0.8 percent ferric chloride, 0.7 percent aluminum chloride, 0.8 percent fluorine and 66 parts uranium (essentially in the hexavalent form) per million parts of solution by the solvent extraction process of Example 2. A first portion of the uranium-containing brine solution having a volume of 0.5 liter was heated to 80°C. The temperature of the solution was maintained at that level for 3 minutes, during which time chlorine gas was passed therethrough at the rate of 0.5 liter per minute to oxidize all the uranium and iron therein to the hexavalent and trivalent states, respectively. After being oxidized,

the first portion of the uranium-containing brine solution, containing all of its iron in the form of ferric chloride, was added to the remaining 11.0 liters (second portion) of the solution at 50°C. whereby all of the uranium of the second portion was oxidized to the hexavalent state according to the formula



The first and second portions thus combined were processed in the manner described in Example 2. The uranium tetrafluoride recovered represented more than 90% of the uranium present in the acidulate solution.

Having thus described the invention in rather full detail it will be understood that these details need not be strictly adhered to but that various changes and modifications may suggest themselves to one skilled in the art, all falling within the scope of the invention as defined by the subjoined claims.

What is claimed is:

1. A process for recovering uranium from a solution containing phosphoric acid, uranium in the hexavalent state and a chloride salt selected from the group consisting of alkali metal chloride, alkaline earth metal chloride and ammonium chloride, comprising the steps of:

- contacting the solution with a reductant capable of converting said uranium from the hexavalent to the tetravalent state;
- contacting said reduced solution with an organic extractant capable of separating said phosphoric acid from the reduced solution and leaving said tetravalent uranium in said reduced solution; and
- recovering said tetravalent uranium from said reduced solution.

2. A process as recited in claim 1 wherein said solution is obtained by hydrochloric acid digestion of phosphate rock.

3. A process as recited in claim 1 wherein said uranium is recovered from said remaining constituents of said solution by:

- contacting said remaining constituents with an oxidant capable of converting said uranium from the tetravalent to the hexavalent state;
- contacting the oxidized solution with an anion exchange resin capable of adsorbing said uranium;
- removing said uranium from said anion exchange resin by means of a solvent; and
- recovering said uranium from the resulting solution.

4. A process as recited in claim 1 wherein said reductant is selected from the group consisting of elementary iron, elementary aluminum, hydrogen sulfide, sodium hydrosulfite and formaldehydesodium hydrosulfoxylate.

5. A process as recited in claim 1 wherein the reduction step is carried out at a temperature ranging from about 10°C. to the boiling point of said solution.

6. A process as recited in claim 1 wherein the extractant is selected from the group consisting of butanols, pentanols, trialkylphosphates having alkyl groups containing from 2 to 8 carbon atoms, N,N-disubstituted amides derived from monocarboxylic acids having 1 to 3 carbon atoms, and mixtures thereof with each other and with hydrocarbons.

7. A process as recited in claim 3 wherein the oxidant is selected from the group consisting of trivalent iron

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salts, sodium chlorate, sodium hypochlorite, sodium chlorite and elementary chlorine.

8. A process as recited in claim 3 wherein the oxidation step is carried out at a temperature ranging from about 10°C. to the boiling point of the solution.

9. A process as recited in claim 3 wherein said oxidized solution is a 3 to 10 molar chloride ion solution.

10. A process as recited in claim 3 wherein said uranium is recovered from the solution of step d by:

- a. neutralizing said solution;
- b. contacting said solution with a sufficient quantity of ammonia to precipitate a hexavalent uranium-containing compound therefrom; and
- c. washing and calcining said compound to produce uranium trioxide.

11. A process as recited in claim 3 wherein said ura-

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nium is recovered from the solution of step d by:

- a. evaporating said solution so as to bring the uranium concentration thereof to at least about 1 percent by weight of the solution;
- b. contacting said solution with a sufficient amount of a reductant to reduce the uranium therein from the hexavalent to the tetravalent state;
- c. contacting the reduced solution with a sufficient amount of hydrogen fluoride and ammonium fluoride to precipitate the uranium from said solution in the form of crystalline ammonium uranous pentafluoride; and
- d. separating, washing and calcining the precipitate to form uranium tetrafluoride.

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