Potentiality of Alcoholic Purification of Abu-Zaabal Impure Phosphoric Acid for Selective Ion Exchange Recovery of Uranium

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Abstract

A suggested procedure was studied for recovering of uranium selectively from the Abu Zaabal impure phosphoric acid assaying about 46% P2O5, and about 3% iron. This procedure involves the application of an alcoholic precipitation step for most impurities by using isopropyl alcohol and cationic resin where uranium was kept in the acid phase by a prior oxidation step. After distillation of alcohol for recycling, the uranium in the purified phosphoric acid was properly reduced to U4+ and recovered via the Chinese cation exchange resin namely; amino phosphonic (D4O4). Displacing Fe2+ from the resin, washing the resin with aqueous ammonia, eluting the resin with carbonate – bicarbonate solution and precipitating uranium from the elute as UO22H2O.

Keywords: Uranium; Abu Zaabal; Alcoholic precipitation; Amino phosphonic resin D4O4

Introduction

Generally, uranium is found in natural phosphate in the concentrations ranged from 0.005%–0.02% [1]. It was reported that 6.34 million tons of uranium exist in phosphate throughout the world [2]. Besides the phosphorous value, phosphate rocks whose world’s resources are estimated to be about 18000 million tons can indeed be considered as a secondary resource for some interesting metal values e.g., U and REEs. Technologically, U extraction from wet process phosphoric acid (WPPA) has been developed by the solvent extraction technique using some organophosphate compounds up to the commercial scale. Wetering and Janssen [3] have also studied a new and considerably cheaper process (precipitation method) and have even claimed that it would be considerably cheaper in a manner to replace the still exclusively based solvent extraction expensive methods. This is due to the pre-purification step of phosphoric acid which is necessary to assist phase separation besides the subsequent acid treatment step in order to prevent the attack of the Auber lining of the phosphoric acid evaporation equipment.

Several other methods for uranium recovery from phosphoric acid have been proposed e.g., U precipitation through replacement of calcium in the calcium sulfate hemi hydrate or dehydrate (gypsum) or else via liquid emulsion membranes [4]. However, the latter still too expensive as in the case with solvent extraction. In this regard, it has to be also indicated that solvent extraction of U cannot be applied in the direct production high concentration acid >45% P2O5, and about 3% iron. This procedure involves the application of an alcoholic precipitation step for most impurities by using isopropyl alcohol and cationic resin where uranium was kept in the acid phase by a prior oxidation step. After distillation of alcohol for recycling, the uranium in the purified phosphoric acid was properly reduced to U4+ and recovered via the Chinese cation exchange resin namely; amino phosphonic (D4O4). Displacing Fe2+ from the resin, washing the resin with aqueous ammonia, eluting the resin with carbonate – bicarbonate solution and precipitating uranium from the elute as UO22H2O.
uranium in the purified phosphoric acid was properly reduced and recovered via the Chinese cation exchange amino phosphonic resin (DIO). The latter is a chelating resin in the big pure styrene cross linking copolymerization - two vinyl sphere introduce amino acid chelating genes. It can finish the exchange - adsorption capabilities no matter what pH value. This product has the large capacity of exchange 2.4 mmol/l, exchange speed, good mechanical strength, etc. It was shown that the amino phosphoric acid DIO gives a promising sorption/elution behaviour working in small column extraction of U from phosphoric acid solution.

Experimental

Materials

Chemicals and reagents: In the present work the applied miscible solvent IPA has been supplied by Fine Chem. Ltd, India. The other chemicals and reagents used for preparing the working phosphoric acid besides those used for chemical analysis have mostly been of analytical grade.

Abu Zaabal crude H₃PO₄ acid specification: The working crude H₃PO₄ acid of Abu Zaabale Company produced through sulphuric acid route. The chemical analysis of the acid shown that it contains many undesirable elements [15]. In order to improve the purity of Abu Zaabale concentrated phosphoric acid humic materials, fluoride and sulphates must be decrease. Table 1 show the composition of Abu Zaabal crude H₃PO₄ acid.

Methods

Analytical procedures: Several analytical procedure were performed in order to determine the purity and the concentration of the pure phosphoric acid. The cations in this medium were detected with Atomic Absorption Spectroscopy, GBC 932 AA. Phosphoric acid concentration was detected with acid base titration against 0.1 N NaOH while the precipitated P₂O₅ was detected using Spectrophotometer method.

Control analysis of impurities: For uranium analysis in the different working experimental stream solutions, the oxidimetric titration method using ammonium metavanadate has been applied. For this purpose, a prior uranium reduction was performed by (NH₄)₂Fe(SO₄)₂ in the presence of diphenylamine sulfonate indicator until it changes to a slightly violet colour [16] U (g/l)=T.V1/V. 1000 where V1: volume taken of NH₄VO₃ solution (ml) V: sample volume (ml) T: concentration of NH₄VO₃ to U (g/ml).

Control analysis of REEs: For the REEs analysis in the different working experimental stream solutions, the REEs content was spectrophotometrically determined by Arsenazo III as a complexing agent and the absorbance was measured at 650 nm against proper standard solutions [17] using a Lambda UV/VIS spectrophotometer (Perkin-Elmer, USA) [18,19].

Determination of fluorine: The present work determination of soluble sulphate was performed by using turbid metric method using BaCl₂. In this method, sulphate is precipitated as BaSO₄ and the resultant turbidity was compared with that produced in a series of chemical standards of known concentrations according to sulphate calibration curve.

Determination of fluoride: Fluoride ion concentration in the working and purified phosphoric acid was measured by the ion selective electrode technique where 0.05 ml of sample was taken with 0.45 ml of sodium acetate tri-hydrate to adjust the pH of the sample at 5.0. This was followed by the addition of the TISAB to adjust the ionic strength of the solution and which was then diluted and made up to volume with bi-distilled water to 500 ml in a plastic flask. From the latter, 50 ml was taken and its fluoride ion concentration was measured by the ion selective electrode (Jenway, UK).

Recovery procedures

Commercial acid pre-treatment

Removal of humic matters: In this regard, it was found interesting to subject the provided acid to a pre-treatment procedure. Humus matters tend to dissolve with the organic phase as the base, like dissolve like. So, the commercial phosphoric acid has involved its clarification using clay (12 g for 1 l, 1580 gm crude WPPA 48% P₂O₅). This is done at room temperature with 400 rpm mixing speed and half an hour mixing time. After clay treatment the commercial acid was then subjected to sulphate precipitation.

Sulphate precipitation: Using 42.6 gm calcium carbonate for precipitating the excess sulphuric acid in 1580 gm crude phosphoric acid. The precipitation of sulphate occurred while mixing and keeping the working acid at more than 600 mv using 0.4 ml H₂O₂ in order to prevent the partial precipitation of uranium with calcium sulphate formation.

Control analysis ofREEs: For the REEs analysis in the different working experimental stream solutions, the REEs content was spectrophotometrically determined by Arsenazo III as a complexing agent and the absorbance was measured at 650 nm against proper standard solutions [17] using a Lambda UV/VIS spectrophotometer (Perkin-Elmer, USA) [18,19].

Determination of sulfate: In the present work determination of soluble sulphate was performed by using turbid metric method

| Component | Wt % | Component | ppm |
|-----------|------|-----------|-----|
| P₂O₅      | 48.2 | U         | 74  |
| SO₄       | 2.60 | Ca        | 54  |
| Fe        | 2.73 | Cd        | 9.7 |
| F         | 0.48 | V         | 260 |
| Mn        | 0.155 | REEs | 560 |

Table 1: Composition of the Abu Zaabal crude H₃PO₄ acid.
then treated by 5% HCl solution and soaked for 2 h in acid followed by washing and treatment by 4% NaOH and soaked for 2 h. Finally 5% HCl was pour in to the column and good washing by H₂O until pH 7 followed by passing the WPA. Saturation of uranium take place after the passage of 3 L (6BV).

**Elution process:** After saturation, the loaded D₂O₂ resin was then subjected to the elution process. This have been performed by using 30% H₃PO₄ to remove Fe²⁺ while using ammonium carbonate for eluting of uranium.

**Results and Discussion**

**Purification of crude phosphoric acid**

**Composition of H₃PO₄ acid after pre-treated:** In the present work the concentrated commercial phosphoric acid (50% P₂O₅), was used after removal of humic materials, fluoride and sulphate to precipitate the impurities by miscible solvent technique. Table 2 shows the analysis of the pre-treated concentrated working acid accompanied by desulphurization and defluorination as previously mentioned in the experimental part. From this table it could be concluded that the percent of sulphate and fluoride decreased from 2.6, and 0.48 to 0.34 and 0.15 respectively as a result for desulfurization and defluorination.

**Alcoholic purification:** To separate most of the metal values and impurities, it was found convenient to subject the preliminary purified acid to a second purification step using a proper precipitant together with a water miscible solvent (isopropyl alcohol). However, in order to keep uranium soluble in the purified acid / alcohol mixture it was previously oxidized by H₂O₂. From the Table 3 uranium can be kept in the mixture of IPA, uranium and some of the impurities by miscible solvent technique. Table 2 shows the analysis of the partially purified phosphoric acid after IPA treatment.

**Composition of the working acid after precipitation:** The acid after filtration consists of a mixture of IPA, uranium and some of impurity. This acid have been subjected to reduction by iron powder to convert uranium to tetravalent state for passing through D₄O₄ resin for selective separation of uranium. About 3 L of purified acid 40% contains U and Fe 74 and 500 ppm respectively pass over 1.5 ml of D₄O₄ resin after treatment. The flow rate about 0.3 ml/min. the acid effluent was subjected to uranium analysis every 500 ml. The result of adsorption showed that the percent of loading reach to about 75% where the first three sample after analysis of uranium proven that the loading percent 100% otherwise the percent of loading decrease in the latter three sample 75, 50 and 15% respectively. After saturation and washing the resin was subjected to elution process (Table 7).

**Recovery of uranium**

**The loading process:** The pre-treatment of WPA acid which contains uranium in hexavalent state after passing on Amberlite 120 resin have been subjected to reduction by iron powder to convert uranium to tetravalent state for passing through D₄O₄ resin for selective separation of uranium. About 3 L of purified acid 40% contains U and Fe 74 and 500 ppm respectively pass over 1.5 ml of D₄O₄ resin after treatment. The flow rate about 0.3 ml/min. the acid effluent was subjected to uranium analysis every 500 ml. The result of adsorption showed that the percent of loading reach to about 75% where the first three sample after analysis of uranium proven that the loading percent 100% otherwise the percent of loading decrease in the latter three sample 75, 50 and 15% respectively. After saturation and washing the resin was subjected to elution process (Table 7).

**Procedure of elution:** An ion exchange column was loaded with uranium by feeding it with reduced WPA. Loading was continued until saturation of the resin. At this point, the column was loaded with 0.16 g of uranium. After rinsing with water, elution with a solution of ammonium- carbonate 6%. About 200 ml of eluting agent was pass in two fraction after analysis of uranium the first fraction contain about 1000 mg/l where the second contain about 600 mg/l. The color of the solution that emerged from the column was dark brown indicating the presence of organic matter. To precipitate uranium from loaded ammonium- carbonate solution is based on evaporation of the solution until boiling where ammonia and carbon dioxide evolve, as their concentration in the mother liquor decrease until pH 7 at which uranium precipitate as UO₂⁻2H₂O₄ (Figure 2).

**Conclusion**

i. The work presents a new process integrating for partial purification and selective separation of uranium from Egyptian WPA by miscible solvent and D₂O₂ cation exchange linked by active aminophosphonic group as follow

ii. Subjecting crude acid after deflorination and desulfurization processes to oxidation treatment thereby to oxidized uranium to hexavalent state.

iii. Contacting the so- oxidized acid to purification by IPA solvent and ammonium salts precipitation agent.

| Exp. No. | g NH₃ Per/100 g P₂O₅ | Dispersant g/100 g P₂O₅ | State of U | U precipitation |
|---------|----------------------|-------------------------|------------|-----------------|
| 1       | 6                    | 400                     | Oxidized   | <10             |
| 2       | 7                    | 350                     | Oxidized   | <10             |
| 3       | 8                    | 300                     | Oxidized   | <10             |

**Table 3:** Effect of addition precipitating agent on IPA quantity needed to iron precipitation and uranium kept in WPA.

| Component, % | Component, ppm |
|--------------|----------------|
| P₂O₅         | 46.2           |
| Fe           | 8.8            |
| F            | 0.24           |
| U            | 0.565          |
| Cd           | 32             |
| Mn           | 5              |
| Ca           | 139            |
| V            | 27             |
| REEs         | 610            |
| %            | 52.2           |

**Table 4:** Analysis of the components of the partially purified phosphoric acid after IPA treatment.

| Component, % | Component, ppm |
|--------------|----------------|
| P₂O₅         | 52.2           |
| Fe           | 8.8            |
| F            | 0.48           |
| U            | 0.2           |
| Cd           | 5              |
| Mn           | 135            |
| Ca           | 27             |
| V            | 600            |
| REEs         | 1410           |

**Table 5:** Composition of the viscous precipitate after phosphoric acid partially purification.

| Component | Wt. % |
|-----------|-------|
| P₂O₅      | 50.0  |
| U         | 77.0  |
| SO₄       | 0.34  |
| Ca        | 340.0 |
| Fe        | 2.88  |
| Cd        | 10.4  |
| F         | 0.15  |
| V         | 275   |
| Mn        | 0.158 |
| REEs      | 560   |

**Table 2:** The composition of the working acid 50% P₂O₅.
Table 7: Analytical results of Abu-Zaable effluent purified WPA using D4O4 resin (each aliquot sample Vol=500 ml).

| Component, % | Component, ppm |
|--------------|----------------|
| P2O5 | Fe | F | U | Cd | Mn | Ca | V | REES |
| 46.2 | 0.008 | 105 | 74 | 0.3 | 2 | nil | nil | nil |

Table 6: Analysis of the components of the highly purified phosphoric acid after Amberlite IR 120 Resin treatment.

| Component | Component, ppm |
|-----------|----------------|
| Uranium assay mg/l | Uranium adsorption, % |
| (500 ml) | |
| 1 | Nil | 100 |
| 2 | Nil | 100 |
| 3 | Nil | 100 |
| 4 | 18 | 75 |
| 5 | 37 | 50 |
| 6 | 54 | 15 |

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