

Uranium extraction enhancement form phosphoric acid by emulsion liquid membrane

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Abstract This work is mainly concerned with the uranium extraction from phosphoric acid commercially produced by Abu Zaabal Fertilizers and Chemical Co., Egypt. This target would realize a dual purpose where the phosphate ore is considered as an alternative source of uranium besides eliminating its environmental contamination. The applied procedures are that of the new technology of emulsion liquid membrane. Authors have indeed pointed out that the variables explored still leave open to question the roles of stripping at the internal interface as well as the bulk transfer of uranium in the internal phase. For this purpose, two reducing agents are studied as additives to two organic solvent systems; namely the organophosphorous synergistic mixture of D2EHPA/TOPO as well as the tridodecyl amine. The relevant factors have first been optimized upon synthetic uraniferous phosphoric acid solution followed by the application upon the commercial acid after purification. These factors include the concentration of solvent system and the used emulsifier, acid concentration of the external and internal phases besides the nature and concentration of the reductant added to the internal phase. In addition, the permeation time as well as the oxidation state of the external phase was studied. All

these factors have indeed been studied under different mixing speeds ranging from 300 up to 1,000 rpm. Ascorbic acid concentration, 1 % as an additive to the internal phosphoric acid phase (40 % P_2O_5) resulted in 95 % uranium extraction efficiency at the lower speed of 600 rpm.

Keywords Uranium · Emulsion liquid membrane · Phosphoric acid · D2EHPA–TOPO

Introduction

Efforts are being made worldwide to investigate the newer resources of uranium to meet the required demands. Among the secondary resources of uranium, natural phosphates are found to be an important resource for uranium and REE [1]. Phosphate rock is essentially composed of tricalcium phosphate which exists in the form of apatite mineral that could accept various ionic replacements. This is due to the fact that the hexagonal crystal lattice of the apatite mineral is adequately open to permit several cationic and anionic displacements. Among these displacements, U, V, REE, etc. can be found in the rock and where the average uranium concentration varies actually between wide limits but generally in the ranges of 50–200 ppm.

During the acid digestion of phosphate rocks, most of the uranium (~90 %) reports in phosphoric acid and so phosphoric acid become a potential source of uranium [2]. The separation of uranium from phosphoric acid may be carried out using different separation techniques like solvent extraction, extraction chromatography, ion exchange, precipitation, etc. [3–5].

Solvent extraction processes have been reported for the industrial level extraction of U(VI) from phosphoric acid medium by a mixture of di(2-ethylhexyl) phosphoric acid

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(D2EHPA) and a neutral synergist reagent like tri-*n*-butyl phosphate (TBP), di-butyl butyl phosphonate (DBBP), PC88A and DBBP mixture, and tri-*n*-octyl phosphine oxide (TOPO) [1, 6–16]. All these solvent extraction based processes have their own limitations and drawbacks such as solvent degradation, third phase formation, crud formation etc.

According to the report of an Advisory Group Meeting organized by the IAEA in Vienna in March 1987, research and development activities on uranium recovery from phosphoric acid are continuing along three main lines; viz,

1. Improvements on the D2EHPA/TOPO process to further enhance its flexibility and economy.
2. Development of new liquid–liquid extractants.
3. Development of other processes such as ion exchange (using solid ion exchangers), liquid membranes and processes compatible with the hemi- hydrate process for the production of phosphoric acid.

Liquid membranes (LMs) seem to be a promising separation technology. According to Botella and Gasos [17], liquid membranes whether supported by a solid structure (SLM) or in the form of an emulsion (ELM) and froth flotation whether ionic flotation or precipitate flotation seem to be the most promising. A liquid membrane is actually a thin liquid film that would selectively permit the passage of a particular component of a mixture. Both kinds of liquid membranes involving simultaneous extraction and stripping have been applied to the uranium phosphoric acid system using D2EHPA/TOPO and OPPA as extractants. Advantages cited by Botella and Gasos of liquid membranes over solvent extraction and ion exchange are derived mainly from the favorable kinetics and smaller equipment besides the possibility to treat phosphoric acid under more difficult conditions (higher temperature and higher acid concentrations). The use of liquid membrane processes has gained great importance in separation and recovery of toxic, valuable metals from their lean sources as well as treatment of effluents containing low concentration of solute in large volume without generating any secondary waste [18–24].

Emulsion liquid membranes (ELMs) have been studied for the extraction of U(VI) from wet phosphoric acid (WPA) using a mixture of D2EHPA and TOPO [25, 26]. In the field of applying liquid membranes for uranium recovery from strong phosphoric acid that would result in HDH processes, Naiem et al. [27] has been able to prepare a stable emulsion for the strong acid. This was composed of 1 % concentration of each of D2EHPA and TOHPO (tri-octyl hexyl phosphine oxide) in kerosene with 40 % P₂O₅ phosphoric acid as the internal phase in the presence of 3 % Span 80. The obtained uranium extraction efficiency decreased from 78 to 70 % as the P₂O₅ concentration in the external phase increased from

20 to 45 %P₂O₅. El-Hazek and El Sayed [28] employed ELM containing a synergistic mixture of 0.1 mol L⁻¹ D2EHPA + 0.025 mol L⁻¹ TOPO with 4 % span 80 as the surfactant for extraction of U(VI) from dihydrate and hemihydrate wet process phosphoric acid solutions. Use of citric acid as the internal (stripping) phase in ELM led to the simultaneous extraction and recovery of uranium from phosphoric acid solutions. Another study showed that ELM could extract ~90 % U(VI) from phosphoric acid medium in three stages with aqueous/organic phase ratio of 12, without removal of the dissolved organic matter from the phosphoric acid feed solution [29]. The major disadvantage of the ELM is the complications in formation and breaking of the emulsion phase. This can be avoided in SLM based separation process.

The industrially applied processes as well as most of the research works carried so far have actually been applied upon uranium extraction from dihydrate phosphoric acid (28–32 % P₂O₅). Such processes do not indeed work satisfaction in the more concentrated acid (40–42 % P₂O₅) produced by the hemihydrate process. Working with the Egyptian El Sebaiya phosphate ore, Fouad et al. [30] has prepared a concentrated phosphoric acid using directly a mixture of H₂SO₄ and H₃PO₄ for acidulation as a new alternative to the hemihydrate process. In this new alternative, the obtained acid assaying 63.2 % P₂O₅ was prepared. Under oxidizing conditions and using two filtration stages, the P₂O₅ recovery attained 97.5 % while that of U attained 97 %. From 52.7 % P₂O₅, it has been possible to extract 90 % of the uranium content using a new synergistic solvent mixture involving D2EHPA with tri-octyl hexyl phosphoric acid (TOHPO). In the same manner Abdel-Khalek et al. [31] studied the extraction of uranium from Egyptian phosphoric acid with synergistic mixture of di-2-ethyl hexyl phosphoric acid (D2EHPA) and di-butyl butyl phosphonate (DBBP). In the light of these giving; the present work was thus formulated to study the applicability of liquid emulsion membranes for the purification of the locally produced WPPA from the contained uranium.

To realize this objective, two systems of extractants have been used; namely the synergistic mixture of D2EHPA/TOPO and the tridodecyl amine (TDDA). In this study, the different relevant parameters have first been studied upon simulated synthetic phosphoric acid.

Summing up, authors have indeed pointed out that the variables explored still leave open to question the roles of stripping at the internal interface as well as the bulk transfer of uranium in the internal phase. These factors would involve the response to changes in surfactant concentration, internal phase droplet interfacial area and the membrane to internal phase ratio. Besides employing reduced levels of expensive complexing agents in ELM, relative insensitivity to variations of WPPA strength and

favorable response to temperature (60–70 °C) would actually reduce processing limitations.

Experimental

Reagents

All the chemicals and reagents used for preparation of required solutions are chemically pure reagents. A stock solution of synthetic uraniferous phosphoric acid assaying 25 % P₂O₅ was prepared by properly diluting the necessary amount of the chemical grade phosphoric acid (61.7 % P₂O₅). Choice of this assay was due to the fact that the commercial WPPA of Abu Zaabal Co. is produced by the Fison's dihydrate process (about 25 % P₂O₅). On the other hand, a proper weight of A.R. uranyl nitrate hexahydrate (BDH, England) was dissolved in a small amount of slightly acidified water and was so added to the prepared acid to give an assay of 63 ppm U. D2EHPA, TOPO, and TDDA supplied by Aldrich Co. Germany were used as such. Ascorbic acid, Sodium acetate tetra hydrate, Potassium sulfate, and Sodium carbonate (ADWIC, Egypt) were used without any treatment. Silicon dioxide, used in the pretreatment stage, was product of Al Naser co., Egypt. Kerosene (Misr petroleum Ltd., Egypt) was used as a solvent for organic phase.

Purification of Abu Zaabal commercial WPPA

As a matter of fact, Abu Zaabal commercial WPPA is generally black due to its contamination with several impurities derived from the input ore. Therefore, the acid received from the Co. should first be properly treated to eliminate most of these impurities and to convert the acid into the clear green acid suitable for treatment with solvent extraction for uranium recovery. However, the product acid received for the present work was concentrated by evaporation at the plant to attain the assay of merchant grade acid quality (MGA) of 42 % P₂O₅. Accordingly, the received acid was subjected to the following purification steps using 1L of the MGA.

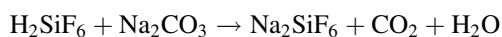
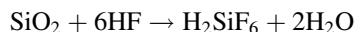
Pre-treatment

The purpose of the pre-treatment step is mainly to eliminate most of the organic and humic matter. Therefore, after addition of about 15 gm of clay (El Nasr Co.), the acid slurry was mechanically stirred for 1 h followed by addition of 2 ml poly acrylamide solution as a flocculant (0.2 gm/100 ml distilled water) and stirring for about

10 min. The acid slurry was then left for settling and the clear acid was separated by decantation.

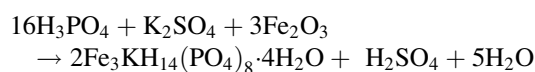
Fluoride and iron separation

To 1 kg of the decanted green acid assaying 0.8 %F⁻, 3.6 gm of SiO₂ powder was added and the slurry was mechanically stirred for about 3 h. This was then followed by a gradual addition of 6.6 gm Na₂CO₃. The added quantities represent indeed the stoichiometric amounts required for the precipitation of sodium fluorosilicate (Na₂SiF₆) according to the following reactions; viz,



Fluoride ion concentration was measured by the ion selective electrode (Jenway, UK).

In a next step, most of the iron content of the working acid (2.3 % Fe) has been directly precipitated by the addition of 28 gm of K₂SO₄ and heating the slurry to 80 °C. Iron would indeed precipitate in the form of a hydrated double phosphate salt according to the following reaction:



After settling, the two formed precipitates (containing fluorine and iron) were properly filtered. Iron concentration in Abu-Zaabal WPPA before and after its precipitation was analyzed using atomic absorption spectroscopy (AAS) (GBC model 932 AA, UK).

Acid polishing and dilution

The filtered acid was finally allowed to pass several times through a carbon column (80 cm × 10 cm diameter) to ensure final separation of any humic matter. The output acid was properly diluted to attain a concentration of 28 % P₂O₅ to resemble that directly resulting from the DH process i.e. before concentration to the MGA by evaporation. Accordingly, the locally produced Abu Zaabal WPPA used in the present work for application of ELM for uranium recovery had the following composition: 28 % P₂O₅, 0.12 % F⁻, 0.9 % Fe, and 42 ppm uranium.

Emulsion liquid membrane (ELM) preparation

In the present work, the organic phase of the emulsion was composed of either D2EHPA or TOPO mixture or tri dodecyl amine (TDDA) in different concentrations that have been dissolved in kerosene. This was followed by adding a certain amount of Span 80 as a surfactant and the obtained

organic phase was adequately stirred for proper mixing. For preparing the W/O/W emulsion in case of D2EHPA/TOPO extraction system, orthophosphoric acid of 40 % P₂O₅ was used as the internal aqueous phase while in case of TDDA extractant, 2 M sodium carbonate was used as the internal aqueous phase. To obtain an emulsion with adequate stability, a mechanical stirrer with a three-blade turbine impeller of 40 mm diameter was used at a mixing speed of 5,000 rpm for 30 min mixing time in a plastic vessel of 200 mm depth and 40 mm diameter. A predetermined volume ratio of 1:1 was maintained for the organic phase to the internal strip phase in all the performed experiments. Emulsification has been performed using the high-speed Cole-Parmer mechanical mixer (homogenizer) model 50003–45. The used stirrer consists actually of a servo-dyne mixer head with stand and a mixer controller.

ELM extraction procedure

Extraction experiments have taken place by well mixing the prepared emulsion with the external aqueous phase containing uranium ions to be extracted in glass vessels of 120 mm depth and 110 mm diameter. In the latter, a mechanical mixer with a three bladed turbine impeller was used at different stirring speeds ranging from 300 to 1,200 rpm. After a proper mixing time, samples were taken from the external phase for uranium analysis by the Arzenazo (III) spectrophotometric method for the synthetic acid and by the oxidimetric metavanadate titration method or the laser method using the uranium analyzer (Laser) model (UK–3) for the commercial acid.

In the present study, different parameters were investigated for uranium extraction by emulsion liquid membrane. Some of the latter are related to the emulsion formation and the others are related to the operation process itself. Factors related to emulsion formation included the concentration of the extractant and surfactant as well as that of the reductant added to the internal aqueous phase of the emulsion. On the other hand, the studied operational parameters included the effects of the mixing speed and time as well as that of the concentration of the feed acid.

Application of the optimum conditions on the commercial phosphoric acid produced by Abu-Zaabal Fertilizers and Chemicals Co. has been done using emulsion liquid membrane containing 4 % D2EHPA–1 % TOPO, 1 % Span 80 and 40 % P₂O₅ with the addition of 1 % ascorbic acid in one case and 300 ppm iron in another case at a mixing speed in the range from 300 to 1,000 rpm.

Determination of emulsion swelling

Emulsion swelling is a phenomenon that occurs during its dispersion operation resulting in an increase of the

emulsion volume and a decrease in the external phase volume. The percent swelling was calculated as the volume ratio of the change in the emulsion volume after the dispersion process to the initial volume according to the following equation:

$$\text{Swelling (\%)} = \frac{V_i - V_i^o}{V_i^o}$$

where V_i is the final volume of emulsion after extraction and V_i^o is the initial volume of emulsion.

Determination of membrane breakage

One of the known ways for membrane breakage determination is the change in the electrolytic solution concentration in the feed phase after extraction. In the present work, the membrane breakage was calculated as a function of the change in the concentration of P₂O₅ in the feed solution after the dispersion operation to the input P₂O₅ concentration according to the following equation:

$$\text{Breakage (\%)} = \frac{C_p^i - C_p^o}{C_p^o} \times 100$$

where C_pⁱ is the P₂O₅ concentration in the feed phase after extraction, and C_p^o is the P₂O₅ concentration in the feed phase before extraction.

Results and discussion

Results involve indeed the permeation of uranium from two carriers, namely D2EHPA/TOPO as a cationic synergistic extractant mixture and the tridodecyl amine (TDDA) as an anionic extractant. As previously mentioned, the relevant extraction conditions for the two working solvent systems have first been studied using synthetic phosphoric acid and the obtained optimum conditions were then applied to Abu Zaabal commercial WPPA. The applied W/O emulsion was prepared with the internal to the organic phase ratio of 1:1 using a mixing speed of 5000 rpm. In the extraction experiments, the ratio of the emulsion to the feed phase was fixed at 1:5 except when studying the effect of the emulsion/feed phase ratio.

Favorable operating conditions for uranium extraction with the ELM

Effect of D2EHPA concentration

The obtained results of uranium extraction% versus D2EHPA concentration under various stirring speeds are shown in Fig. 1. From this figure; it's clear that the extraction

percent is directly proportional to D2EHPA concentration until 4 % as well as to the stirring speed up to 800 rpm. At 4 % D2EHPA concentration and at 800 rpm, the uranium extraction% has actually reached up to 67 %. It can thus be concluded that uranium extraction process by ELM is diffusion controlled where its extraction% increased as the mixing speed increased. However, a further increase of the D2EHPA concentration to 5 % has resulted in a decrease in the uranium extraction% at all stirring speeds except that at 600 rpm. This can indeed be attributed to increase in the emulsion viscosity where large emulsion globules would be formed through increased mixing process; a matter which would result in decreasing the interfacial area available for extraction [32]. The increased uranium extraction percent at 5 % D2EHPA (67 %) and which has been realized at 600 rpm might be interpreted as being the optimum rpm at this D2EHPA concentration. In other words, it can be mentioned that increase in the latter at 300 and 400 rpm has resulted in increasing its viscosity and subsequent formation of larger emulsion globule, however, associated with reasonable mixing speed for increasing diffusion and in turn more permeation of uranium.

On the other hand, using 800 and 1,000 rpm would result in higher extraction rate. This was due to high shear rates that would result in presence of small emulsion globules that increase the surface area of reaction. On the other hand, higher shear rates resulted higher breaking of emulsion that adversely affect the extraction process. Accordingly, 600 rpm can be chosen as the compromise value at the 5 % D2EHPA concentration. The realized maximum uranium extraction of 67 % can however be obtained at 4 % D2EHPA and 800 rpm. Concerning the effect of increasing the D2EHPA concentration upon the emulsion swelling, it

has actually been determined by measuring the increase in the emulsion volume after the dispersion process.

Effect of TOPO concentration

From Fig. 2, it is evident that increasing the TOPO concentration from 1 to 2 % has resulted in a slight increase in uranium extraction efficiency at low mixing speeds of 300 and 400 rpm. Beyond the latter, the increase in uranium permeation was more perceptible. This increase can be interpreted as due to increasing in the functional groups that give more sites to form complexes with uranyl ions at the emulsion/feed interface. Thus, up to 78 % uranium extraction efficiency was attained by increasing TOPO concentration to 2 % at 1,000 rpm. At the lower mixing speed of 300 rpm, increase in TOPO concentration did not have any effect upon uranium extraction. In other words, it can be concluded that the influence of TOPO concentration upon uranium extraction efficiency has actually been observed at the high mixing speeds. On the other hand, increasing the TOPO concentration to 3 % did not however perceptibly improve the uranium extraction.

Effect of surfactant concentration

Surfactants or emulsifiers play indeed an important role in emulsion formation in the liquid membrane technique where its concentration affects greatly both the stability and the viscosity of the formed emulsion. To study its effect, the surfactant concentration was studied in the range of 1–3 % (v/v). In these experiments, the other extraction conditions were kept constant at 4 % D2EHPA, 1 % TOPO

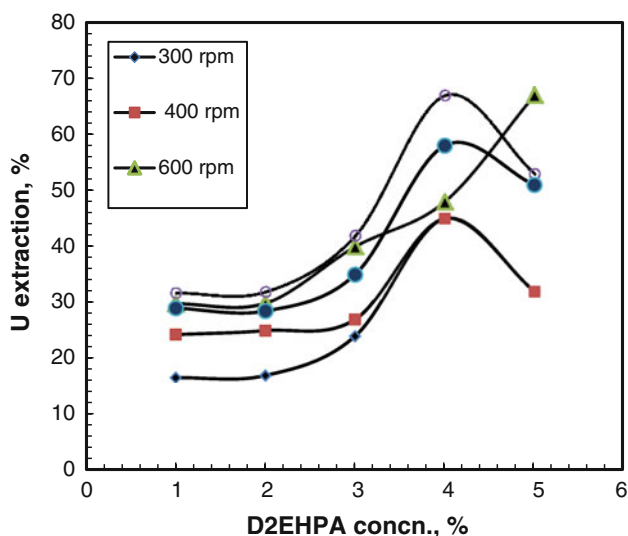


Fig. 1 Uranium extraction from H₃PO₄ acid (25 % P₂O₅) as a function of D2EHPA with 1 % TOPO under different stirring speeds

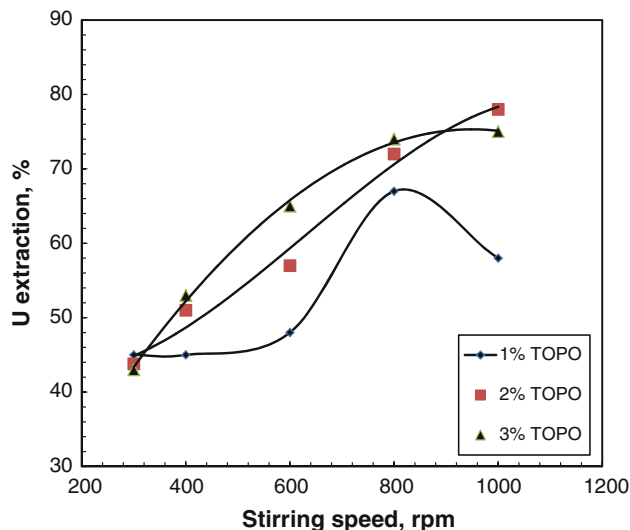


Fig. 2 Uranium extraction from H₃PO₄ (25 % P₂O₅) as a function of TOPO in the synergistic mixture of 4 % D2EHPA under different stirring speeds

and using H_3PO_4 acid (40 % P_2O_5) as the internal solution for a dispersion time of 10 min. The obtained data shown in Fig. 3 show that the uranium extraction efficiency is only slightly affected by changing the Span 80 concentration at lower speeds. This is due to the increase in the emulsion viscosity with increasing Span 80 concentration and in turn formation of emulsion globules of larger volume. The latter would actually result in a smaller interfacial area available for uranyl ions to transfer from the feed phase to the internal phase. However, using a high mixing speed of 800 rpm resulted in a higher extraction efficiency of uranium to 54, 51 and 67 % at 1, 2 and 3 % Span 80 respectively. Further increasing the mixing speed to 1,000 rpm has negatively affected the extraction process; a matter which is most probably due to emulsion breakage.

The role of surfactant concentration can indeed be discussed by the fact that while increasing the Span 80 concentration would increase the emulsion stability, however, this would in the meantime increase the viscosity in a manner to retard the mass transfer through emulsion globules. This result is confirmed from the obtained results were in spite of less stable emulsion at 1 % (increased breakage), a reasonable uranium extraction percent has been attained. The more stable and viscous emulsion of 3 % Span 80 is reflected in a relatively low extraction percent at the lower speeds until 600 rpm. However, at a higher speed of 800 rpm, the uranium extraction efficiency increased up to 67 % due to increased diffusion rate but the decreased

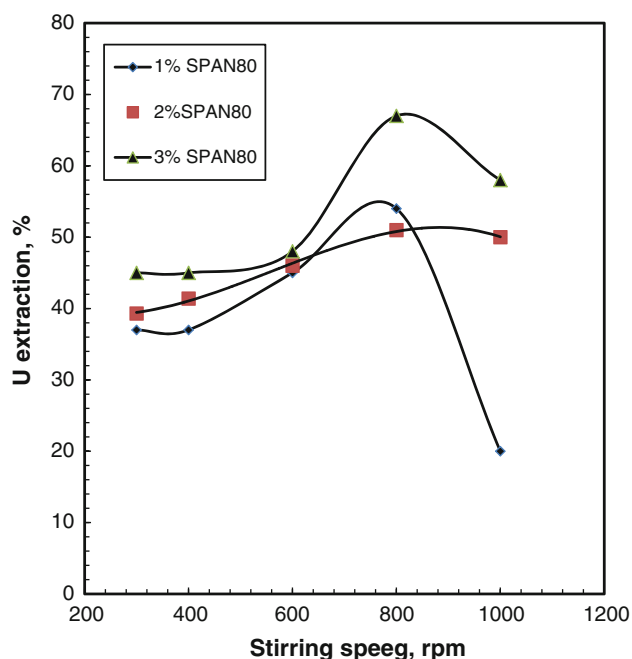


Fig. 3 Uranium extraction from H_3PO_4 (25 % P_2O_5) as a function of Span 80 concentration by a mixture of 4 % D2EHPA–1 % TOPO under different stirring speeds

uranium extraction by further increasing the mixing speed to 1,000 rpm must have resulted from emulsion breakage.

Summing up, it can be concluded that while increasing the surfactant concentration would result in more stable emulsion; this would actually be at the expense of the later required de-emulsification step. Both of the later would indeed require increased costs. Therefore, besides having reasonable extraction efficiency for uranium, working with the lowest possible surfactant level would realize dual economy; namely in its price and in the later de-emulsification step. Accordingly, in all the next ELM extraction experiments, the applied surfactant level would be fixed at only 1 % (v/v) Span 80.

Effect of H_3PO_4 concentration in external phase

For studying the effect of phosphoric acid feed concentration on uranium extraction, several experiments were carried out in which the acid was varied between 28 and 40 % P_2O_5 . The other factors were fixed at 4 % D2EHPA, 1 % TOPO, 1 % Span 80, emulsion/external phase ratio of 1/5, 10 min stirring time, and using 40 % P_2O_5 acid as an internal solution. Figure 4 clearly indicates that the uranium extraction% is greatly dependent upon H_3PO_4 acid concentration in the external acid feed phase. Thus 28 % P_2O_5 acid has been found advantageous especially at the stirring speeds 600 and 800 rpm where the uranium extraction% increased from about 50–71 and 75 % respectively. However, further increase in the acidity has markedly decreased the uranium extraction% down to 42 and 35 % at 32 % P_2O_5 and to only 16 and 15 % at 40 % P_2O_5 under the stirring speeds of 600 and 800 respectively. On the other hand, besides the possibility of back extraction at low stirring speeds, it has to be indicated that uranium permeation% increases by increasing the stirring speed to 600 and 800 rpm. On the contrary, the decreased extraction% by further increasing the latter to 1,000 rpm might be due to back extraction of uranium besides membrane swelling and breakage. These results are indeed expected since through uranium extraction by D2EHPA, hydrogen ions would be liberated to the external aqueous phase; a matter which would not be encouraged by the increasing acidity in the external phase. On the other hand, it is interesting to refer to the better uranium extraction efficiency of 71–75 % at 600–800 rpm when using 28 % P_2O_5 acid. The latter acidity would thus be applied in all the next experiments.

Effect of H_3PO_4 concentration in internal phase

The phosphoric acid concentration in the internal phase has indeed an important role in uranium extraction by ELM. In this study, another concentration of the internal phosphoric acid solution equivalent to 32 % P_2O_5 was studied to be compared with that of 40 % P_2O_5 . The other experimental

conditions was fixed at 4 % D2EHPA, 1 % TOPO, 1 % Span 80 while fixing the external acid feed concentration at 28 % P₂O₅ equivalent, which was proven to be the optimum value. The applied contact or permeation time was fixed at 10 min. The obtained results are represented in Fig. 5. From the latter, it was found that the extraction% of uranium is increased from about 50–71 and 75 % at 600 and 800 rpm mixing speed as the internal acid concentration increased from 32 to 40 % P₂O₅. On the other hand, it was found that increasing the acid concentration in the internal solution from 32 to 40 % P₂O₅ has resulted in increased uranium extraction from 51 to 62 % at 1,000 rpm due to increased shear forces. In this regard, it is interesting to indicate that increasing the internal acid concentration results in increasing the hydrogen ion concentration inside the emulsion globules. Therefore, the reaction at the membrane/internal solution interface (stripping reaction) resulting in the transfer of the uranyl ion inside the globules and the hydrogen ion vice versa to the membrane phase would be increased.

Effect of iron addition

Effect of iron addition to external phase

To investigate the effect of iron on uranium extraction, a simulated 28 % P₂O₅ acid concentration was prepared and

to which iron powder was added in different concentrations varying between 0.4 and 1.2 g/l. In these experiments, the extraction conditions were fixed at the emulsion composition of 4 % D2EHPA, 1 % TOPO and 1 % Span80 in kerosene and using 40 % P₂O₅ acid concentration as the internal solution while the contact time was fixed at 10 min and the stirring speed at 800 rpm.

From the obtained results graphically represented in Fig. 6, it was found that the uranium extraction% was markedly decreased with increasing the amount of iron where from 75 % in its absence down to 20 and 4 % at added iron concentration of 0.4 and 0.8 g/l respectively. This can actually be explained as due to the fact that the added iron will dissolve as the divalent Fe²⁺ state which would in turn reduce the uranyl ion from the more extractable hexavalent species to the much less extractable tetravalent uranium species.

On the other hand, another set of experiments was performed with the addition of an oxidizing agent to present the iron ions in the Fe³⁺ state before being subjected to another permeation experiment under the same conditions. Oxidation has been performed by H₂O₂ addition till obtaining a redox potential of 575 mV where the reduced tetravalent uranium species would be converted to the uranyl ion UO₂²⁺. After a permeation time of 10 min at 800 rpm, it was found that oxidation has been very efficient where the extraction% has remarkably increased and reaches up to 96 % extraction.

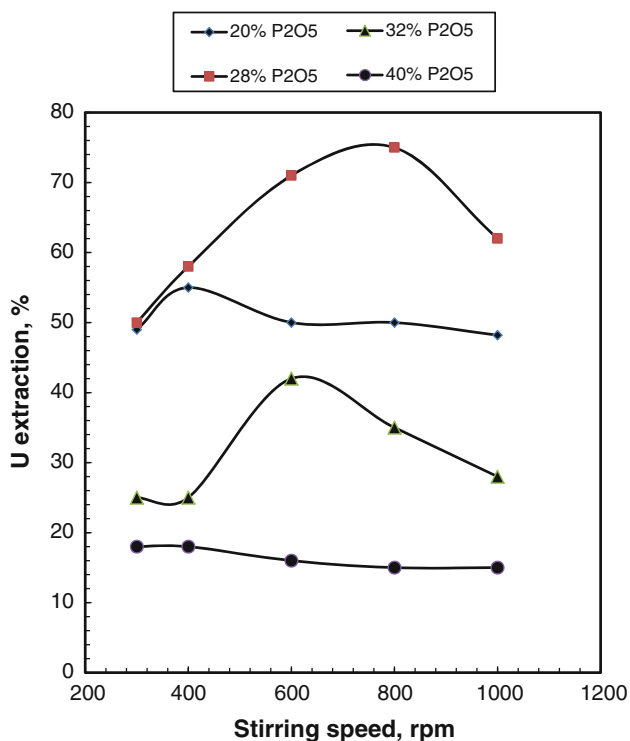


Fig. 4 Uranium extraction from uraniferous H₃PO₄ as a function of different acid concentration under different stirring speeds

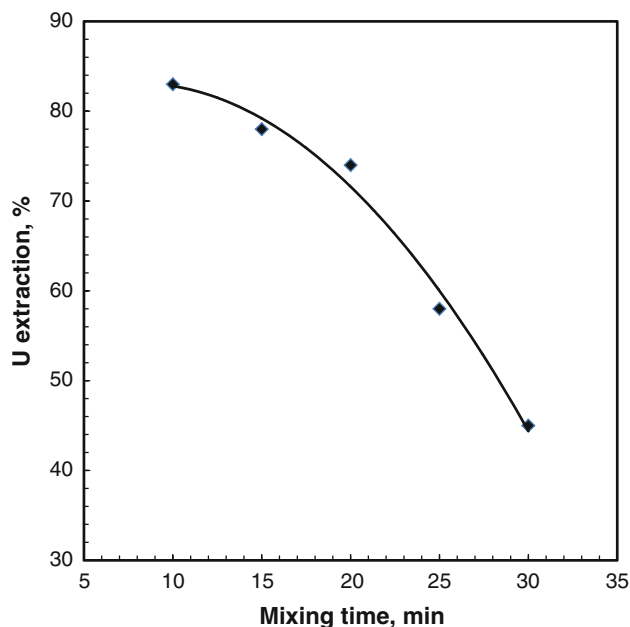


Fig. 5 Effect of internal acid concentration on uranium extraction, from uraniferous H₃PO₄ (28 % P₂O₅) by 4 % D2EHPA, 1 % TOPO and 1 % Span 80 in kerosene

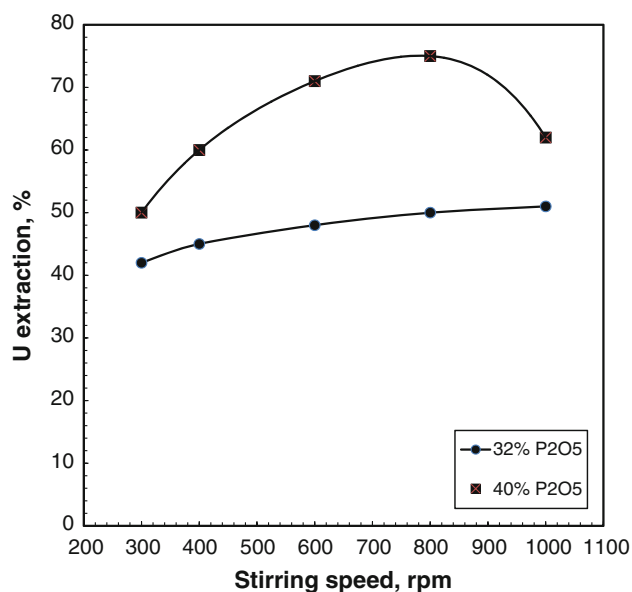


Fig. 6 Effect of iron addition on uranium extraction by from 28 % P₂O₅ equivalent phosphoric acid solution in presence of iron (with and without oxidation)

Effect of iron addition to internal phase

According to Rao and Sagi [33] and Koussi et al. [34] the effect of iron on uranium extraction was studied. To study the effect of iron presence as a reductant in the internal phase, 300 ppm Fe was added to the internal 40 % P₂O₅ acid concentration and the applied emulsion was composed of 4 % D2EHPA, 1 % TOPO and 1 % Span 80 in kerosene while the concentration of the external phosphoric acid was fixed at 28 % P₂O₅. In this experiment, it was found interesting to study the effect of the permeation time and which was varied from 10 to 30 min at 800 rpm mixing speed. From the obtained permeation data represented in Fig. 7, it was found that the presence of 300 ppm Fe in the internal solution increased greatly the extraction efficiency of uranium where it attained about 85 % after 10 min. This is due to the reduction of uranium at the organic ELM-internal phase interface where the uranyl ions would be reduced and trapped in the internal phosphoric acid solution.

Prolongation of the mixing time beyond 10 min has however resulted in a gradual decrease of uranium extraction efficiency to only 45 % at 30 min mixing time. This has actually been interpreted as due to insufficient surfactant concentration in the organic ELM phase (1 % Span 80) for keeping the emulsion stable.

Effect of ascorbic acid incorporation

Effect of ascorbic acid as the internal phase

Since the transfer of uranyl ions from the external phosphoric acid phase into the internal strip phase is the major

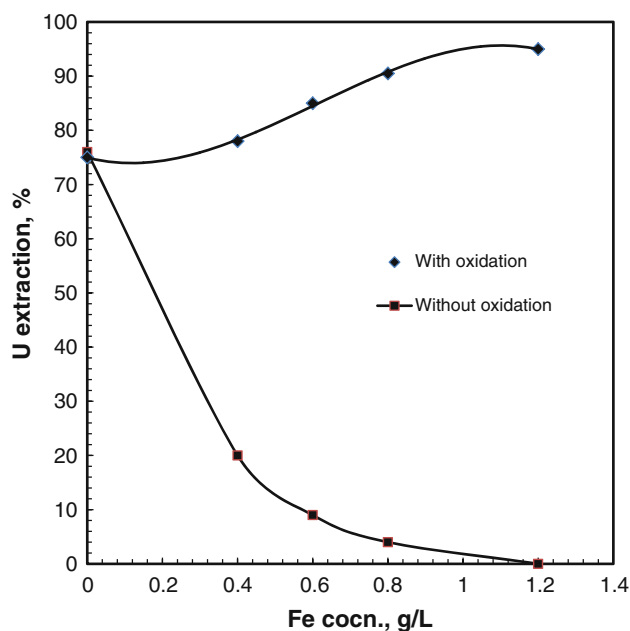


Fig. 7 Uranium extraction from 28 % P₂O₅ acid as a function of the stirring time in presence of 300 ppm iron in the 40 % P₂O₅ internal phase

target in the working ELM process, some experiments were performed to enhance uranium stripping. Ascorbic acid is indeed a weak organic acid that could act as a reducing agent. Accordingly, five extraction experiments have been carried out using an external phosphoric acid assaying 28 % P₂O₅ and an emulsion containing 4 % D2EHPA, 1 % TOPO and 1 % Span80 in kerosene together with 20 % ascorbic acid as the internal phase while the stirring speed was varied between 300 and 1,000 rpm for 10 min.

From the obtained data plotted in Fig. 8, it was observed that ascorbic acid as the internal solution has not been able to achieve the required reduction for UO₂²⁺ from the external phosphoric acid solution even by increasing the stirring speed to 800 rpm. Thus while the extraction efficiency at 300–400 rpm did not exceed 2 %, it increased to only 15 and 25 % at 600 and 1,000 rpm respectively.

On the other hand, it has actually been noticed that after each experiment, the volume of the emulsion was found to decrease by about 30 % from its initial volume indicating that the emulsion prepared by using ascorbic acid as the internal solution is not stable. Accordingly, the decreased uranium extraction must be due to the release of the ascorbic acid to the external phase where it must have reduced the UO₂²⁺ ions to the non extractable tetravalent state.

Effect of ascorbic acid addition to internal phosphoric acid phase

In the present work, it was tried to capture the uranyl ion from the external phosphoric acid feed (28 % P₂O₅) into an

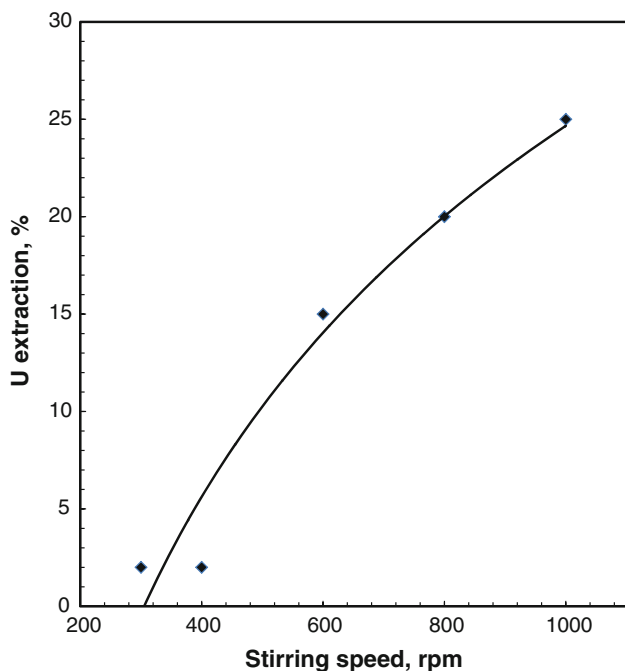


Fig. 8 Uranium extraction from 28 % P₂O₅ solution as a function of the stirring speed using 20 % Ascorbic Acid as internal phase

internal phosphoric acid solution (40 % P₂O₅) containing only the required amount of ascorbic acid as a necessary reducing agent to convert the extracted hexavalent uranium to the non transferable tetravalent uranium ions. For this purpose, five experiments were done using different ascorbic acid concentrations varying from 0.5 to 3 wt% (as additive) in the H₃PO₄ acid internal solution. In these experiments the emulsion liquid membrane phase was composed of 4 % D2EHPA and 1 % TOPO. However, as was revealed from the previous experiments in which ascorbic acid (20 %) was used as the internal phase that the stability of the emulsion prepared by using 1 % Span 80 has not been adequate for the extraction process, the prepared W/O emulsion in these experiments was formed using 3 % Span 80 as the surfactant. The other extraction conditions were fixed at a stirring speed of 600 rpm for 10 min dispersion time. The obtained results are plotted in Fig. 9. Investigation of these results indicate that using ascorbic acid as additive affect significantly the extraction process where the uranium extraction efficiency increased from 38 % with the addition of only 0.5 % ascorbic acid to 91 % by increasing the latter to 3 %. These results cannot be compared with those using phosphoric acid only as the internal phase since in presence of ascorbic acid, emulsion swelling was markedly increased (from 40 to 150 %).

Thus in spite of using 3 % Span 80 as a surfactant, it was found that the emulsion volume increased by increasing the ascorbic acid added to the internal solution from 40 % at only 0.5 wt% and reached up to 150 % at

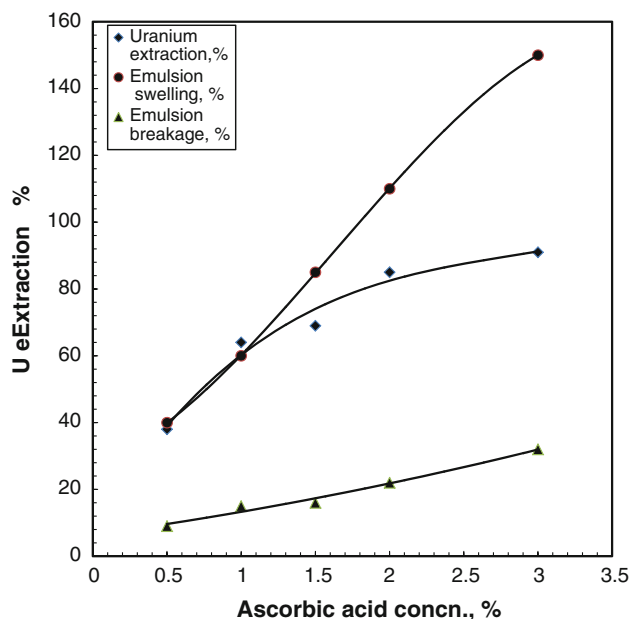


Fig. 9 Effect of ascorbic acid concentration as additive to 40 % P₂O₅ internal acid solution on uranium extraction as well as upon emulsion swelling and breakage

3 wt% ascorbic acid, Fig. 9. In this regard, it might be possible that ascorbic acid addition to the internal solution beside using the high Span 80 % have resulted in increasing the osmotic pressure on the membrane surface; a matter which resulted in increasing the emulsion swelling by water entrainment. In the mean time, the higher emulsion swelling% with the addition of ascorbic acid to the internal phosphoric acid phase was found to also affect the emulsion breakage%. The latter has indeed been increased from 9 to 32 % by increasing the ascorbic acid in the internal phase as additive from 0.5 to 3 wt% respectively (Fig. 9).

Effect of stirring speed on uranium extraction using 1 % ascorbic acid in H₃PO₄ as internal phase (40 % P₂O₅)

From the previous data, it has been ascertained that addition of ascorbic acid to phosphoric acid internal solution has resulted in interesting and promising results of uranium extraction from phosphoric acid feed solutions, however emulsion swelling (and breakage) is very high. To investigate the swelling phenomenon apparently associated with the addition of ascorbic acid to the internal phosphoric acid solution, it was convenient to study the effect of mixing speed since it was proved that water entrainment is indeed a diffusion-controlled behavior. Accordingly, the mixing speed was studied in a number of experiments in which it ranged from 300 to 1,000 rpm and using a membrane phase composed of 1 % ascorbic acid in 40 % P₂O₅ acid as the internal solution together with 4 % D2EHPA, 1 % TOPO

and 3 % Span 80 while the feed acid was fixed at 28 % P_2O_5 . In the mean time and in order to overcome the swelling phenomenon, the dispersion time was reduced to 5 min.

Inspection of the obtained results summarized in Fig. 10, has revealed that increasing the stirring speed from 300 to 800 rpm increased the uranium extraction efficiency from 30 to 89 %. This confirms indeed that the extraction process in the presence of 1 % ascorbic acid as additive is diffusion-controlled. As a matter of fact, increasing the stirring speed would lead to the decreasing of the size of the emulsion globules; a matter which would increase the interfacial surface area and in turn the extraction efficiency would increase. Increasing the stirring speed to more than 800 rpm has however resulted in a negative effect on the extraction process which was decreased to 64 % at 1000 rpm; a matter which is most properly due to emulsion breakage.

On the other hand, from Fig. 10, it is clearly evident that at the lower stirring speeds of 300 and 400 rpm, the prepared emulsion has not at all suffered from any swelling. Increasing the stirring speed to 600 and 800 rpm at the fixed contact time of 5 min has resulted in emulsion swelling to 10 and 25 % respectively. This means that the latter ratio associated with 89 % uranium extraction could indeed be acceptable in liquid membrane systems.

Effect of stirring time on uranium extraction using 1 % ascorbic acid in H_3PO_4 acid internal phase (40 % P_2O_5)

From the foregoing results, it can be concluded that ascorbic acid is indeed a good additive for the H_3PO_4 acid internal solution (40 % P_2O_5) where it has proved to be capable of converting the extracted hexavalent uranium to its non transferable tetravalent state. In these experiments, the applied emulsion contained 4 % D2EHPA, 1 % TOPO and 3 % Span 80 together with H_3PO_4 acid (40 % P_2O_5) as internal solution that contains 1 % ascorbic acid while the external feed solution was 28 % P_2O_5 . To further study the prepared ELM of 1 % ascorbic acid as additive in the internal phosphoric acid (40 % P_2O_5) under these conditions, a number of extraction experiments were performed at the two mixing speeds of 600 and 800 rpm for different contact times (5–30 min). The obtained results are presented in Fig. 11. Investigation of these data revealed that the uranium extraction efficiency at the lower 600 rpm mixing speed has increased from 75 up to 95 % as the mixing time was increased from 5 to 25 min respectively. However, at the higher mixing speed of 800 rpm, the increased contact time was found to have a negative effect upon the extraction% which was decreased from 93 % at 5 min to 70 % at 25 min contact time. These results reflect indeed that the emulsion does not

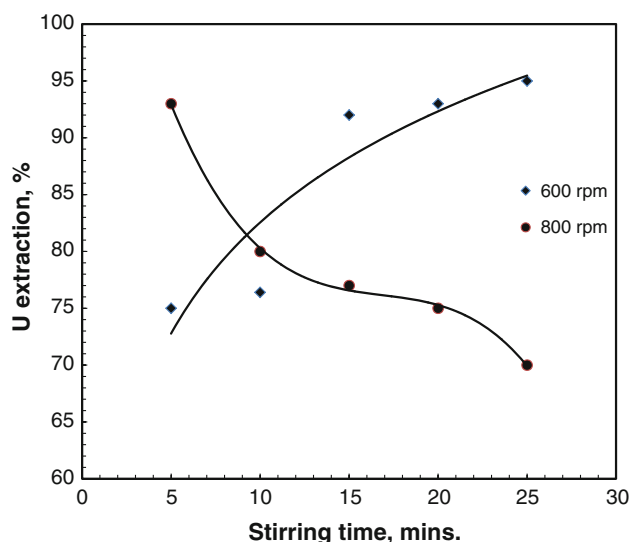


Fig. 10 Effect of stirring speed on uranium extraction using 1 wt% ascorbic acid added to H_3PO_4 (40 % P_2O_5) internal solution from 28 % P_2O_5 phosphoric acid solutions

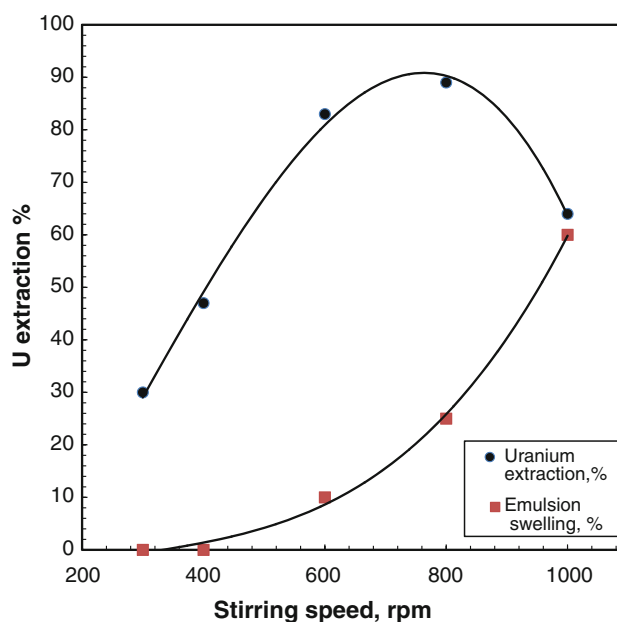


Fig. 11 Effect of contact time on uranium extraction at 600 and 800 rpm mixing speed using 40 % P_2O_5 with 1 % ascorbic acid as internal phase

have a high stability under high shear rates applied on the emulsion globules.

ELM extraction of uranium by D2EHPA/TOPO from Abu Zaabal commercial phosphoric acid

After purification, clarification and adjustment of the composition of Abu Zaabal commercial green acid (28 % P_2O_5 and 63 ppm U), it was found necessary to evaluate

the applicability of the studied emulsion liquid membrane technique upon it. For this purpose, two series of experiments have been performed using the optimum conditions previously determined. These involved the synergistic mixture of 4 % D2EHPA and 1 % TOPO encapsulating phosphoric acid (40 % P_2O_5). However, in the first experimental series of 300 ppm Fe added to the internal phase, 1 % Span 80 was used in the ELM preparation and the stirring time was fixed at 10 min. In the second series of experiment of 1 % ascorbic acid added to the internal phase, 3 % Span 80 was used in the ELM preparation and the stirring time was fixed at only 5 min. In both series of experiments, the emulsion was formed at 5,000 rpm mixing speed for 30 min and the feed acid was oxidized by adding H_2O_2 till an e.m.f. of 575 mV.

The obtained results of both permeation experiments are plotted in Figs. 12 and 13. From these figures, it was clearly evident that the extraction efficiency of uranium using ascorbic acid as an additive is both higher and faster than in case of using iron addition. Thus, at 800 rpm which was found quite convenient, 54 % of uranium was extracted after 5 min when using ascorbic acid and which was only 34 % after 10 min in case of using iron. In this regard, the comparable uranium ELM extraction efficiency at the same conditions from the synthetic uraniferous phosphoric acid using 1 % ascorbic acid in the internal phase has been much higher; viz, 93 %. Similarly, in case of the comparable uranium extraction efficiency at the same condition from the synthetic uraniferous phosphoric

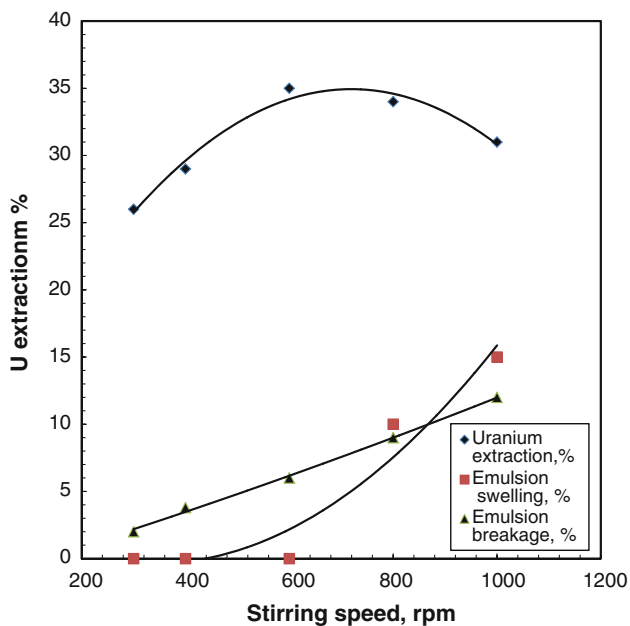


Fig. 12 Effect of stirring speed upon uranium extraction from the Abu Zaabal green phosphoric acid using 40 % P_2O_5 phosphoric acid associated with 1 % ascorbic acid besides 3 % Span 80 in the emulsion

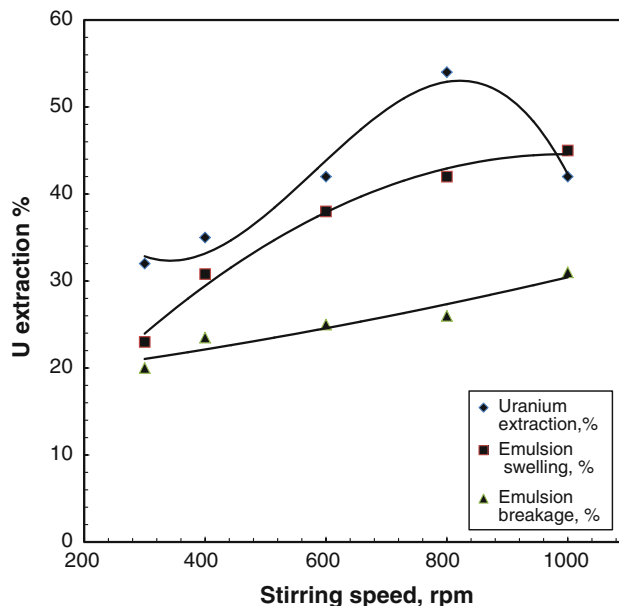


Fig. 13 Effect of stirring speed upon uranium extraction from the Abu Zaabal green phosphoric acid using 40 % P_2O_5 phosphoric acid associated with 300 ppm Fe besides 1 % Span 80 in the emulsion

acid using 300 ppm Fe in the internal phase has been much higher; viz, 85 %.

However, investigation of the swelling data revealed that the swelling % of the emulsion containing iron is much less than when ascorbic acid is used where it reached up to 42 % at 800 rpm as compared to only 10 % in case of the former. In the mean time, from the emulsion breakage curves, Figs. 12 and 13, it was indicated that breakage percent of the emulsion containing 300 ppm iron achieved only 9 % at 800 rpm as compared to the emulsion containing 1 % ascorbic acid which has attained up to 26 %. Summing up, it has to be mentioned that the characteristics of uranium extraction from Abu Zaabal acid by ELM are quite different from those in case of synthetic acid. This is actually due to the presence of several elemental impurities besides presence of excess sulfuric acid (4 %) and possible HF equivalent to a F^- % of 0.12.

Conclusions

As previously mentioned, the present work is concerned with studying the potentiality of applying ELM technique for U recovery from locally produced Abu Zaabal phosphoric acid, Egypt using D2EHPA/TOPO system. The extraction of uranium is found to be better when using an iron or ascorbic acid as a reductant in the stripping phase. Presence of 300 ppm Fe in the internal solution increased greatly the extraction efficiency of uranium where it attained about 85 % after 10 min. From the foregoing

results, it can be concluded that ascorbic acid is indeed a good additive for the H_3PO_4 acid internal solution (40 % P_2O_5) where it has proved to be capable of converting the extracted hexavalent uranium to its non-transferable tetra-valent state. It was clearly evident that the extraction efficiency of uranium using ascorbic acid as an additive is both higher and faster than in case of using iron addition. When applying the extraction system on Abu Zaabal phosphoric acid, uranium extraction efficiency reached 54 % using the D2EHPA/TOPO system together with 1 % ascorbic acid added to the internal phosphoric acid (40 % P_2O_5) and 1 % Span 80 at 800 ppm. On the other hand the extraction efficiency reached 34 % by the addition of 300 ppm iron to the internal phase.

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