Effect of anions in commercial phosphoric acid on the extraction of uranium by DEHPA /TOPO

Sadeddin Kherfan / *Gassan* Shadood / *Yahia* Koudsi

Abstract

Extraction of uranium from commercial phosphoric acid by DEHPA/TOPO process is a well-developed process on the commercial and pilot plant scale. Commercial phosphoric acid contains certain anions such as Cl^-, F^- and SO_4^{2-} in varying concentrations. The presence of such anions could have a negative effect on the extraction process.

This paper investigated the effect of Cl^-, F^- and SO_4^{2-} anions present in commercial wet phosphoric acid on the uranium extraction process. The effect of adding SiO_2 which complexes with F^- and other anions was also studied. The results obtained showed that these anions formed complexes with UO_2^{2+} and therefore had a negative influence on the extraction of uranium from laboratory and commercial phosphoric acids. This effect was strong in the case of F^- followed by SO_4^{2-} and much less for Cl^-. Addition of SiO_2 was found to negate the effect of F^- and other anions and to exert a positive effect on uranium extraction.

Keywords

Extraction · uranium · DEHPA/TOPO · anions · phosphoric acid

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1 Introduction

Uranium is extracted from phosphoric acid by the di-(2-ethylhexyl)phosphoric acid / trioctylphosphine oxide (DEHPA / TOPO) process developed by Hurst at Oak Ridge National laboratory [1–3]. The extraction efficiency is influenced by many factors. The presence of certain anions in wet phosphoric acid originating from the phosphate rocks or added during manufacturing such as Cl^-, F^- and SO_4^{2-} influences the efficiency of this extraction process. F^- is present in commercial phosphoric acid in the range of 2-4 wt%. This concentration is high and F^- exerts a strong influence on the extraction process and its efficiency. The fluoride concentration in the commercial Syrian phosphoric acid is relatively high averaging 1.8 wt%.

SO_4^{2-} is present in the acid since digestion of phosphate rocks to produce phosphoric acid by the wet method involves adding an excessive amount of concentrated sulfuric acid. Syrian commercial phosphoric acid produced by the wet method in the General Fertilizer Company GFC at Homs plant contains 1-4 wt % of SO_4^{2-}. It also contains Cl^- anion, which comes from the phosphate rocks. The concentration of Cl^- in phosphate rocks varies from 0.01 – 0.4 wt% while its concentration in the Syrian commercial acid is around 0.125 wt%.

Most studies on the extraction of uranium from phosphoric acid concentrated so far on the effect of operating factors such as concentration of the acid, temperature of extraction, concentration of solvent, effect of diluents, oxidation–reduction of acid, etc. [4]. Khorfan [5, 6] studied the influence of cations present in commercial phosphoric acid on the extraction of uranium by DEHPA/TOPO in kerosene. He concluded that the presence of Ca^{2+}, Al^{3+} and Mg^{2+} cations has a positive influence on the extraction of UO_2^{2+} from phosphoric acid by DEHPA/TOPO. This effect was found to be stronger in the pure acid due to the presence of F^- and SO_4^{2-} in the commercial acid. Murthy [7] found that when the fluoride content of two commercial acids were reduced to 2 g/L by addition of NaCl the distribution ratio of uranium for both acids by octylphenyl phosphoric acid (OPAP) was better. He mentioned however that the explanation was not clearly understood. Long [8] stated qualitatively that F^- had a negative effect on the extraction of uranium from phospho-

ric acid by octyl pyrophosphoric acid (OPPA) solvent. Arnold [9] found that both F^- and SO_4^{2-} had a negative effect on the extraction of uranium from phosphoric acid by OPAP solvent but the effect of F^- was much stronger. Ezahr [11] studied the influence of F^-, SO_4^{2-} and P_2O_5 on the extraction of uranium from laboratory grade and three different Moroccan commercial phosphoric acids. His results showed that uranium extraction was greatly reduced by an increase in the concentration of P_2O_5 and also by an increase in F^- up to 1 wt%. However he found that SO_4^{2-} exerted no influence up to 4 wt%. The effect of F^- on stripping uranium from DEHPA /TOPO solvent was studied by several workers and was found to have a positive effect [6,10]. Alibrahim studied the extraction of uranium(VI) from nitric acid medium by 20% tri butyl phosphate (TBP) / dodecane. The effects of the nature of the diluent and nitric acid concentration on uranium distribution ratio (D) were investigated in this study. The experimental results showed that (D) using different diluents increases in the order: chloroform, carbon tetrachloride, dodecane and n-hexane [13]. Abdulbake studied reduction of fluoride and sulfate ions contents in wet phosphoric acid from GFC company in Homs by liquid – liquid extraction with tertiary aliphatic amines. The effect of solvent concentration and temperature on the extraction was studied. The effect of diluents on the extraction yield and raffinate acid specifications were also studied [14]. Another study investigated stripping of uranium from 0.3 mol/L DEHPA/ 0.075 mol/L TOPO in kerosene by different ammonium carbonate solutions. The results obtained showed that ammonium carbonate prepared from direct reaction of ammonia and carbon dioxide gases had a high purity and gave the same stripping yield as the laboratory grade. The phase separation was slightly improved using a pure synthesized ammonium carbonate solution. The phase separation was found to be best at a concentration of 0.5 mol/L ammonium carbonate solution, a phase ratio A/O of 1/1 and a temperature of 50 ^{0}C. It was possible to obtain > 99% yield of uranium by operating 2 stripping stages counter-currently under these conditions [15].

In this paper the influence of Cl^-, F^-, SO_4^{2-} anions and P_2O_5 on uranium extraction by DEHPA/TOPO from a laboratory and a commercial Syrian phosphoric acid was studied. The effect of SiO_2 addition on neutralizing the effect of F^- was also investigated.

2 Experimental

Syrian commercial phosphoric acid produced by the wet method at Homs plant was treated from solids and organics. The specifications of this acid were determined and listed in Table 1. Pure phosphoric acid with a concentration of 3.80 mol/L H_3PO_4 was prepared and uranium was added in the form of pure uranyl nitrate $UO_2(NO_3)_2.6H_2O$ so that uranium concentration was 58 mg/L. Extraction was carried out with a solvent of 0.5 mol DEHPA/0.125 mol TOPO in 1 liter of kerosene. The aqueous /organic phase ratio A/O was kept at 2/1. The temperature was controlled at 25 °C. The time of mixing was fixed at 5 min-

Tab. 1. Characteristics of pretreated commercial wet phosphoric acid

H_3PO_4	3.94 mol/L
Density	1.28 kg/L
U	60 mg/L
EMF	400 mv
Solids	85 mg/L
Fe^{3+}	1300 mg/L
Ca^{2+}	850 mg/L
Mg^{2+}	5000 mg/L
Al^{3+}	760 mg/L
F^-	1.8 w/w
Cl^-	0.125 w/w
SO_4^{2-}	2 % w/w

utes which was enough to reach equilibrium and that of settling at 20 minutes, which was enough to have good phase separation. Fluoride was added in the form of NaF salt to the commercial and laboratory phosphoric acids. Sulfate anion was added in the form of sulfuric acid and the concentration was calculated on the SO_3 wt% basis. Chloride anion was added to the commercial and pure phosphoric acids in the form of NaCl salt. To investigate the effect of silica certain quantities of SiO_2 were added to the acid. The concentration of uranium in the aqueous phase was determined by the thiocyanate method using UV spectroscopy [12]. The concentration of uranium in the organic phase was calculated by material balance. The distribution ratio (D) of the uranium between the organic and aqueous phases was calculated according to the equation:

$$D = \frac{\text{Concentration of uranium in the organic phase}}{\text{Concentration of uranium in the aqueous phase}}$$

3 Results and discussions

3.1 Effect of fluoride anion F^-
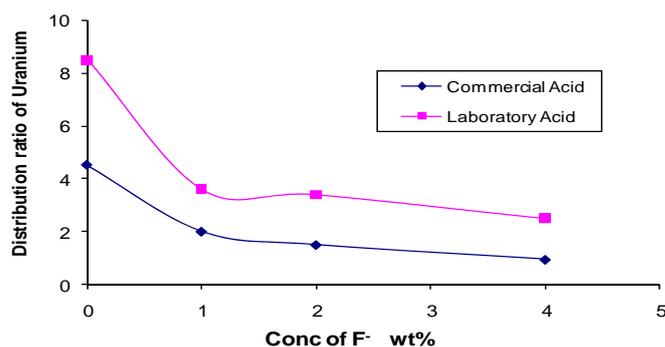
Fig. 1. Effect of fluoride anion F^- on distribution ratio of uranium

The results obtained on the effect of fluoride anion on the extraction of uranium from commercial and laboratory phosphoric acids were shown in Fig. 1. The results indicated that fluoride anion F^- had a strong negative influence on the extraction of uranium from phosphoric acid. This was represented by the decrease in distribution ratio (D) with the increase in the fluoride concentration. The decrease was rapid up to 2 wt% F^- (which is the concentration of F^- in commercial Syrian phosphoric acid)

and more gradual after that concentration. The value of (D) decreased by a factor of 2-3 times for an increase in F^- from 0 to 2 wt%. This influence was quite as expected and reported in the literature [7–9] since F^- complexes UO_2^{2+} according to the reaction:

$$UO_2^{2+} + 2F^- \Longrightarrow UO_2F_2 \qquad (1)$$

This reaction competes with the ion-exchange reaction by DEHPA solvent $(HX)_2$:

$$UO_2^{2+} + (HX_2) \Longrightarrow UO_2X_2 + 2H^+ \qquad (2)$$

3.2 Effect of silica addition

It is well-known in phosphoric acid industry that SiO_2 complexes with F^- and thus negates its influence. This fact was sometimes used in phosphoric acid industry to neutralize F^- and therefore to inhibit its corrosive effect. This can be represented by the following reaction:

$$6HF + SiO_2 \Longrightarrow H_2SiF_6 + 2H_2O \qquad (3)$$
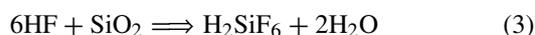
This reaction competes strongly with reaction (1) causing a shift in the ion exchange reaction (2) to the right. To test the effect of adding silica on F^-, commercial and pure phosphoric acids containing 4 wt% F^- were prepared. SiO_2 was added in the range of $0-3$ wt%. The results obtained were plotted in Fig. 2 which illustrated the influence of SiO_2 addition on uranium extraction. The distribution ratio (D) obtained increased steadily for both acids with the increase of SiO_2 added. At a concentration of 2.5 wt% SiO_2, (D) reached the original value with no fluoride F^- present. At values of $SiO_2 > 2.5$ wt%, (D) continued to increase steadily which indicated that SiO_2 did not only negate the influence of F^- but negated also the influence of other anions which complexes with UO_2^{2+} and that Si^{4+} had a positive influence of its own on the extraction of uranium which could be attributed to the salting out effect.
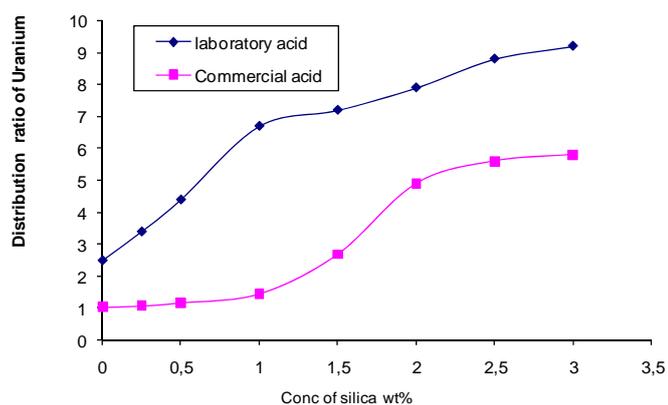
Fig. 2. Effect of silica SiO_2 on distribution ratio of uranium

3.3 Effect of sulfate anion SO_4^{2-}

The second most important anion present in commercial phosphoric acid produced by the wet method is SO_4^{2-}. This anion comes from adding concentrated H_2SO_4 to digest the phosphate rocks. The concentration of SO_4^{2-} in commercial Syrian

phosphoric acid is in the range of 0.75- 4 wt% SO_3. The results were represented in Fig. 3 which is a plot of (D) versus concentration of SO_4^{2-} calculated on SO_3 basis. The results obtained showed that SO_4^{2-} had a negative effect on the extraction of uranium from phosphoric acid but this effect was less marked than that of F^-. SO_4^{2-} complexes also with UO_2^{2+} according to this reaction:

$$UO_2^{2+} + SO_4^{2-} \Longrightarrow UO_2SO_4 \qquad (4)$$
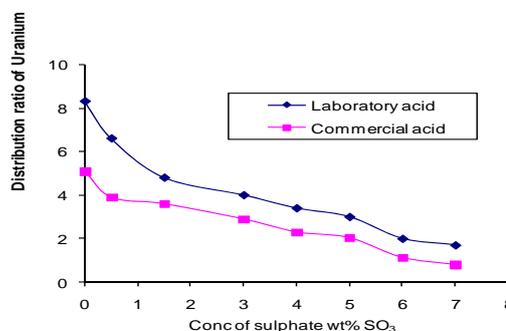
Fig. 3. Effect of sulfate anion SO_4^{2-} on distribution ratio of uranium D

For SO_4^{2-} in the range of 0.75 - 4 wt% which is the usual range found in commercial phosphoric acid, (D) decreased by 30-100%. The same applied for extraction from commercial phosphoric acid.

3.4 Effect of chloride anion Cl^-

The effect of Cl^- on the distribution ratio (D) in both commercial and pure phosphoric acids was investigated by adding Cl^- in the form of NaCl. The results obtained were plotted in Fig. 4 which showed that Cl^- had a negative effect on extraction but this effect was much smaller than F^- or SO_4^{2-} especially considering the difference in concentrations of these anions in commercial phosphoric acid.
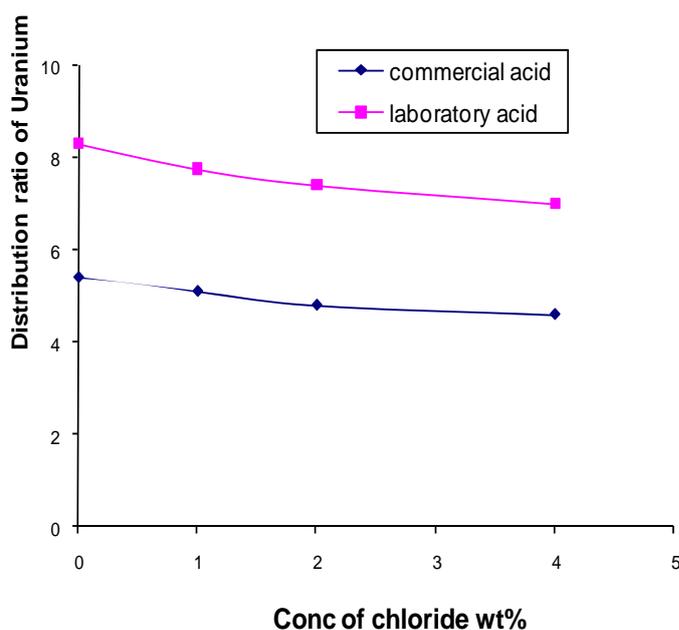
Fig. 4. Effect of chloride anion Cl^- on distribution ratio of uranium
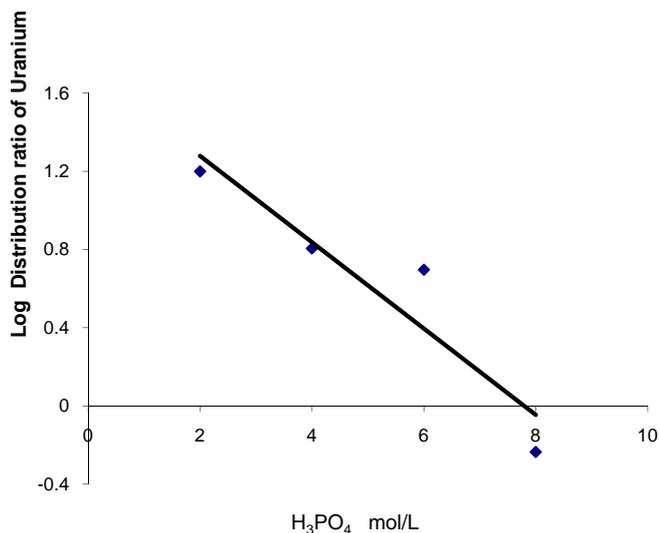
Fig. 5. Effect of concentration of phosphoric acid on distribution ratio of uranium

3.5 Effect of PO_4^{3-}

The influence of PO_4^{3-} was investigated using a laboratory acid containing 2-8 H_3PO_4 mol/L. The results were plotted in Fig. 5 where Log D was plotted versus concentration of PO_4^{3-}. The results showed that an increase in PO_4^{3-} greatly reduced the distribution ratio D. This illustrates that the concentration of P_2O_5 is a major variable affecting the extraction of uranium by the ion-exchange reaction represented in Eq. (2).

3.6 Effect of pH

The same conclusion was arrived at when plotting Log D versus pH of the phosphoric acid solution in the range pH 1 - 7. It is clear from the results illustrated in Fig. 6 that an increase in pH led to an increase in the distribution ratio D. The relationship between Log D and pH was a linear one.
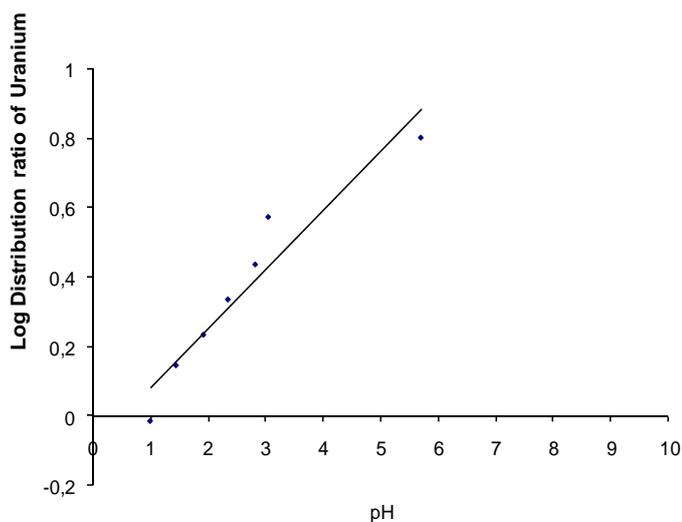
Fig. 6. Effect of pH on distribution ratio of uranium

4 Conclusions

The results obtained showed that extraction of uranium from phosphoric acid by DEHPA/TOPO was influenced by the presence of anion impurities such as F^-, SO_4^{2-} and Cl^-. The strongest influence was due to F^- followed by SO_4^{2-} and very little for Cl^-. The increase in the concentration of PO_4^{3-} also negatively affected extraction of uranium. The distribution ratios were in all cases higher for laboratory acid than for commercial acid as might be expected. Silica complexes the fluoride anion and thus had a positive effect on uranium extraction.

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