

Separation of uranium from its sulfate leach liquor rich in iron

Elsayed Ali Fouad

Basic Sciences Department, Benha Higher Institute of Technology, Benha, Egypt

Due to the fact that uranium and ferric iron are co-extracted by D2EHPA (Di-2-ethyl hexyl phosphoric acid), different trials were investigated to overcome this difficulty. These trials involved the use of masking and reducing agents as well as the application of Di-2-ethyl hexyl phosphoric acid-Tri octyl phosphine oxide (D2EHPA/ TOPO) as a synergism. The obtained data revealed that the separation of uranium from ferric iron sulfate leach liquor of G.Gattar ore material is not satisfactory by using tartaric acid, oxalic acid, DTPA (Di ethylene tri amine penta acetic acid) and NaF as a masking agents or ascorbic acid as a reducing agent. On the contrary, the addition of these agents increased the extraction of ferric iron with great pronounce acceleration effect. This can be referred to the salting out effect. However, when using ascorbic acid as a reducing agent, the iron extraction efficiency was decreased with no simultaneous effect upon uranium extraction efficiency. On the other hand, the investigation of the D2EHPA/TOPO synergism revealed that successful separation of uranium from ferric iron was achieved by increasing TOPO concentration. The uranium extraction reached completion when using 0.1 M D2EHPA and 0.05 M TOPO, at a contact time of 10 minutes. In the meantime the ferric iron extraction efficiency reached as low as 10%.

نظرا لصعوبة فصل اليورانيوم عن الحديد بطريقة الاستخلاص بالمذيبات العضوية حيث أنهما يستخلصان معا. فقد أجريت دراسة عملية لمحاولة فصل اليورانيوم من محاليل الإذابة الغنية بالحديد وذلك بإضافة مواد عضوية مثل حمض الطرطريك و حمض الأكساليك و ثنائي الإيثيلين ثلاثي الأمين ثنائي حمض الأسيتيك و أخرى غير عضوية مثل فلوريد الصوديوم. هذه المواد تكون متراكبات مع الحديد وبالتالي تقل نسبة استخلاصه. إلا أن هذه المواد عملت على زيادة نسبة استخلاص الحديد. وبالتالي فقد تم إضافة حمض الأسكوربيك إلى محاليل الإذابة كعامل مختزل و كذلك تكوين خليط من المذيب العضوي المستخدم ثنائي-2- إيثيل هكسيل حمض الفوسفوريك مع ثلاثي أكتيل أكسيد الفوسفين. وقد بينت نتائج هذه الدراسة إمكانية فصل اليورانيوم من محاليل الإذابة الكبريتية الغنية بالحديد بنسبة تصل إلى 10%.

Keywords: Separation, Extraction, Uranium, Iron, D2EHPA.

1. Introduction

The recovery of metals from clarified leach solutions by solvent extraction or ion exchange has been practiced for many years. Uranium has been recovered from filtered and clarified liquors containing from about 10 ppm to several grams per liter by both ion exchange and solvent extraction techniques. As the demands for higher purity products and the need for processing lower-grade ores increase, processing costs for different routes will be a determining factor in any planned expansion of a mill be or in the design of a new operation. Solvent extraction will be considered under these circumstances. Purification generally plays an important role in hydrometallurgy, since it is very difficult to exclude impurities by selective leaching [1].

Sulfuric acid is the most common reagent used for the leaching and dissolution of uranium ore materials. The presence of such impurities is undesirable because they lower the quality of the precipitated yellow cake produced from such leach liquor. The most important impurity is iron. Ferrous and ferric ions are the most common chemical species existing in a leach solution, and the removal of these ions from the leach solutions is an important objective from an industrial point of view. Efficient methods for iron removal from uranium leach liquors are, therefore, often necessary for the recovery of a quality metal product. Apart from various precipitation methods, which all have some disadvantages in common, solvent extraction, which can give very effective separations, has not been widely used for iron removal from process streams,

largely because the additional capital and operating costs are difficult to recover for a low value. Solvent extraction has long been studied for removing iron [2]. The problems associated with the solvent systems for iron separation from sulfate solutions are usually the slow rates of extraction, the occurrence of precipitates in the extraction equipment and, in particular, difficulties in stripping the iron from the organic phase. Special methods have been developed to improve the stripping operation, such as reductive stripping and hydrolytic stripping. These methods still suffer from a number of problems and probably can only be used under unique conditions [3].

Previous investigations on the synergistic extraction of iron in sulfate solutions by a mixture of tertiary amine and 2-ethyl hexyl 2-ethyl hexyl phosphonic acid (HEHEHP) have dealt with the synergistic effect of tertiary amine with HEHEHP [4]. Similar results were later reported by Hirato et al. [5] using a synergistic mixture of Di-2-ethyl hexyl-phosphoric acid (D2EHPA) and tri butyl phosphate (TBP) as the organic phase. They found that this mixture is effective in the stripping of iron (III), and that less concentrated acid solution is required as a stripping agent.

Also, several mixed solvent systems for iron removal were developed by Chen, J. and others [6]. The extraction and stripping for some of the mixed solvent systems have the common feature that iron extracted into the organic phase can be stripped with dilute sulfuric acid. M. Hideto, and others. [7] studied the mechanism of iron (III) extraction with D2EHPA in homogenous system. They found that the extraction and stripping rates were limited by the formation and the dissociation of Fe(III)-D2EHPA complex at the interface.

As an alternative to the above processes, the effect of masking and reducing agents on the rate of iron and uranium extraction by D2EHPA has been investigated. Also, the separation of uranium and iron in organic phase containing D2EHPA as an acidic extracting and TOPO as a neutral extractant are investigated.

2. Experimental

Due to the relatively high uranium content in the G.Gattar ore material - eastern desert, Egypt, it is necessary to adapt the iron separation from uranium leach solutions because some iron is co-extracted with uranium by using D2EHPA as an acidic extractant. Because of this opportunity, G.Gattar ore material (-60 mesh) was leached in 75g/l sulfuric acid solution at solid /liquid ratio of 1/1. The leach liquor was separated from undissolved solids by filtration. The concentration of uranium and iron in the leach liquor are 1073 and 1400 ppm respectively. Extraction tests were performed in beakers with magnetic agitation for 10 mins. Separation of the organic phase (D2EHPA-kerosene) and aqueous phase (leach liquor) was done in a separating funnels. Since, the G. Cattar leach liquor contain appreciable amounts of iron (1400 ppm), it was decided worth while to study their behavior during extraction of uranium by D2EHPA. So, it was essential to separate iron through the extraction of uranium by D2EHPA-Kerosene system. For this purpose, variable amounts of many masking or reducing agents such as oxalic acid, tartaric acid, citric acid, ascorbic acid, DTPA and sodium fluoride were then added to the aqueous phase. 10 milliliters of the leach liquor so prepared were agitated for 10 mins. At ambient temperature with 10 ml solvent. The mixture was then transferred in a separating funnel, allowed to settle, the two phases separated and then analyzed for U and Fe.

Tests were also conducted using TOPO with D2EHPA as a synergistic mixture. Aqueous samples were analyzed for uranium spectrophotometrically using Arsenazo III as a complexing agent and iron by atomic absorption spectrophoto, tometry. A material balance was calculated for each series.

3. Results and Discussion

3.1. Effect of D2EHPA concentration on the behavior of uranium and iron

Fig. 1 indicates the data obtained for U and Fe extraction by D2EHPA as an

extractant. From this fig, it is revealed that by increasing D2EHPA concentration there is a slight increase in U extraction. But for iron extraction, at concentration range from 0.05M to 0.35 slight increase was obtained but above this value, the Fe extracted reached 45% at D2EHPA concentration 0.5 M.

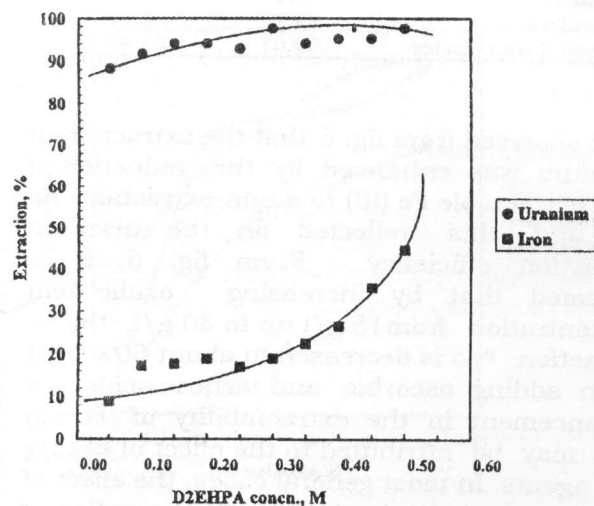


Fig. 1. Effect of D2EHPA concentration on the extraction of uranium and iron at p.H:1.1, mixing time: 0mins., A/O= 1/1.

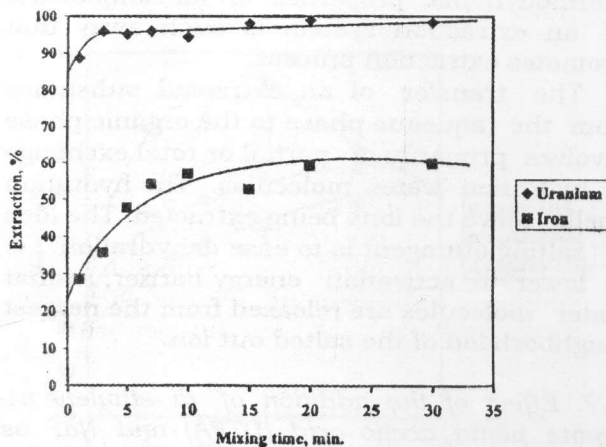


Fig. 2. Effect of mixing time on the extraction of uranium and iron at 0.3M D2EHPA concn., A/O: 1/1.

3.2. Effect of mixing time

The effect of mixing time on U and Fe extraction by D2EHPA is illustrated in fig. 2.

We noticed that the reaction between Fe and D2EHPA is slower than the U-D2EHPA reaction. This is observed from fig. 2. by increasing the mixing time from 1 min. to 10 min., gradual increase in the Fe extraction % was noticed, but the U extraction rate increased from 1 to 2 min. and become stable. It is concluded that the equilibrium between U-D2EHPA is faster than Fe-D2EHPA.

3.3. Effect of leach liquor acidity

It is observed from fig. 3. that the influence of pH on Fe extraction is great but for uranium a slight increase in the extraction rate was observed. The uranium extraction % increased from 95 to 98% at the pH change from 0.7 to 0.9 however the iron extraction increased from 40% to 90% when pH increased from 0.7 to 1.8. It is clear from this fig. that the percent extraction of iron in the organic phase increased with the pH increase. This suggests that low concentration of H_2SO_4 is not preferable for the separation of uranium and iron by solvent extraction when D2EHPA is used as an extraction agent.

3.4. Effect of type of diluent

The effect of different diluents on uranium and iron extraction from sulfate leach liquor of G.Gatter ore by using D2EHPA was reported in Table 1. From this table, it is observed that good separation was occurred by using kerosene as a diluent. Lowest separation factor was observed when carbon tetrachloride used. Xylene and diethyl ether have the same result. Similar results were attained when using the aromatic diluents toluene and benzene.

3.5. Construction of Mc-Cabe Thiele diagram for uranium extraction with D2EHPA from G.Gatter leach solution

By plotting the equilibrium concentration of U in the organic Phase with that of the aqueous phase. we construct the equilibrium line. The operating line was drawn from the point of intersection of the vertical feed concentration line at 1073 ppm with the

equilibrium line. It is clear from fig. 4, that three stages was sufficient for complete extraction of uranium by using 0.3 M D2EHPA-Kerosene system.

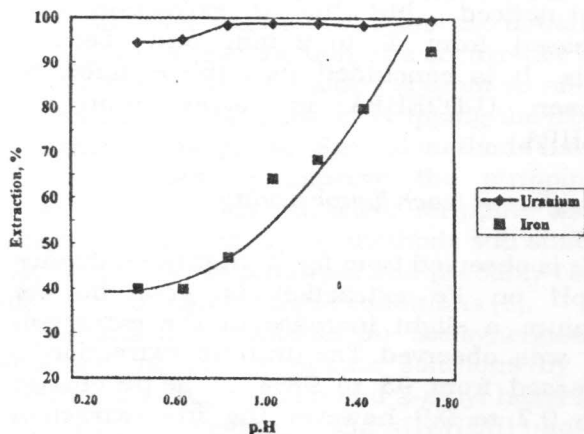


Fig. 3. Effect of leach liquor acidity on the extraction of uranium and iron at 0.3M D2EHPA, A/O: 1/1, mixing time: 10 mins.

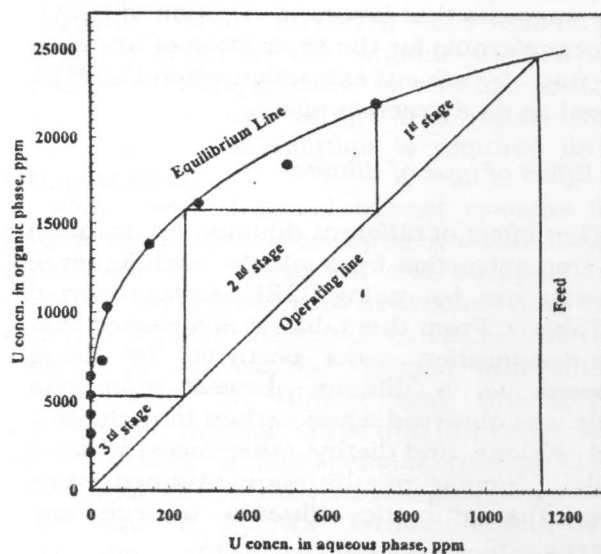


Fig. 4. McCabe Thiele diagram for uranium extraction from leach liquor of G.Gatter ore material by 0.3M D2EHPA-kerosene system.

3.6. Effect of masking or reducing agents on the separation of uranium and iron.

Figs 5 and 6 report the data on the effect of masking and reducing agents on the extraction rate of Fe and U.

Table 1
Effect of type of diluent on uranium and iron extraction at 0.3M D2EHPA, mixing time: 10 min, A/O: 1/1

Type of diluent	Extraction %	
	Uranium	Iron
Toluene	99.7	41.4
Xylene	99.6	25.7
Diethyl ether	93.8	22.86
Benzene	99.58	40
Kerosene	94.2	18.9
Chloroform	99.74	35.7
Carbon tetra chloride	99.67	51.43

It is observed from fig. 5 that the extraction of uranium was enhanced by the reduction of the extractable Fe (III) to a non-extractable Fe (II) and this reflected on the uranium extraction efficiency. From fig. 6, it is indicated that by increasing oxalic acid concentration from 15 g/l up to 30 g/l, the Fe extraction % is decreased to about 50%. But when adding ascorbic and tartaric acids, the enhancement in the extractability of Fe (III) ions may be attributed to the effect of salting out agents. In most general cases, the effect of salting out agent is due to the formation of compounds, which will pass into the organic phase to bind water and alter its thermodynamic properties. This change in the thermodynamic properties of all components of an extraction system is such away that promotes extraction process.

The transfer of an extracted substance from the aqueous phase to the organic phase involves primarily a partial or total exchange of hydration water molecules. The hydration shells leave the ions being extracted. The idea of salting out agent is to ease dehydration, i.e. to lower to activation energy barrier, so that water molecules are released from the nearest neighborhood of the salted out ion.

3.7. Effect of the addition of di-ethylene tri-amine penta acetic acid (DTPA) and NaF as masking agents

The effect of the addition of NaF and DTPA is indicated in figs. 7, 8. From fig. 7, it is observed that increasing the DTPA added hinders the extraction % of iron. This effect was attributed to the effect of DTPA to mask Fe (III) ions. On the other hand, there is no

effect on the extraction of uranium. Fig. 8 summa-ri-zed the effect of NaF added to the aqueous phase on the extraction behavior of U and Fe. No effect was observed on uranium extraction % but iron extraction was slightly increased with the addition of NaF. This may attributed to the salting out effect.

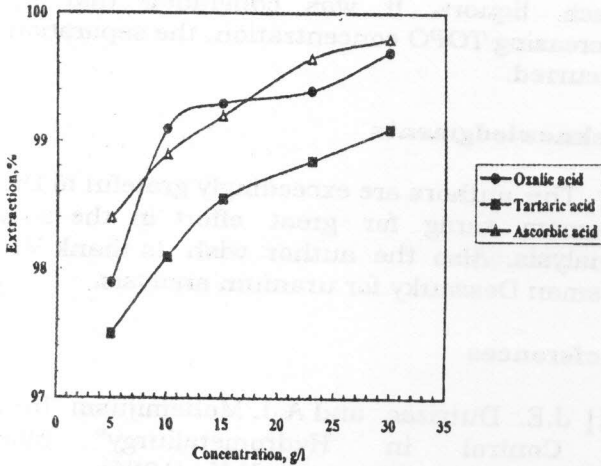


Fig. 5. Effect of the addition of organic acids as masking and reducing agents on uranium extraction at 0.3M D2EHPA, A/O: 1/1, mixing time: 10 min.

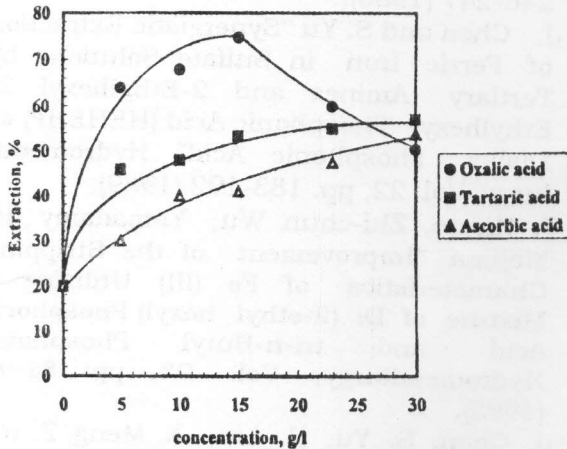


Fig. 6. Effect of the addition of organic acids as masking and reducing agents on iron extraction at 0.3M D2EHPA, A/O: 1/1, mixing time: 10 min.

3.8. Effect of the synergism of D2EHPA and TOPO

Neutral extractant (TOPO) was examined in a synergism with D2EHPA for the separation of Fe and U from sulfate leach liquor. Fig. 9 indicates the effect of the concentration of TOPO on the U and Fe extraction at two concentrations of D2EHPA (0.3M and 0.1M). As is clear in Fig. 9 the extraction of Fe can be reduced by neutral phosphorous extractant (TOPO) added to the D2EHPA. This might be called kinetic retardation effect. This results agree with the data obtained by Yu Jingfen and Ji Chen [9]. This might be due to the molecules of TOPO has interfacial activity and concentrate at the interface of all two phases. This means that the molecules of TOPO occupy interfacial area. So that effective interfacial area of molecules of reactants D2EHPA decreases. This leads to the decrease of the Fe (III) extraction rate.

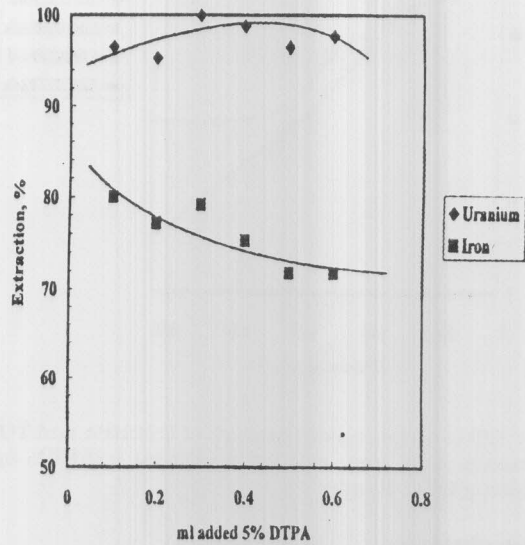


Fig. 7. Effect of the addition of DTPA on uranium and iron extraction at 0.3M D2EHPA, A/O: 1/1, mixing time: 10 min.

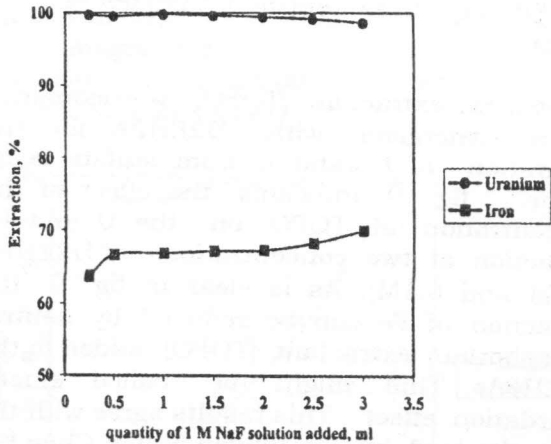


Fig. 8. Effect of the addition of NaF on uranium and iron extraction at 0.3M D2EHPA, A/O: 1/1, mixing time: 10 min.

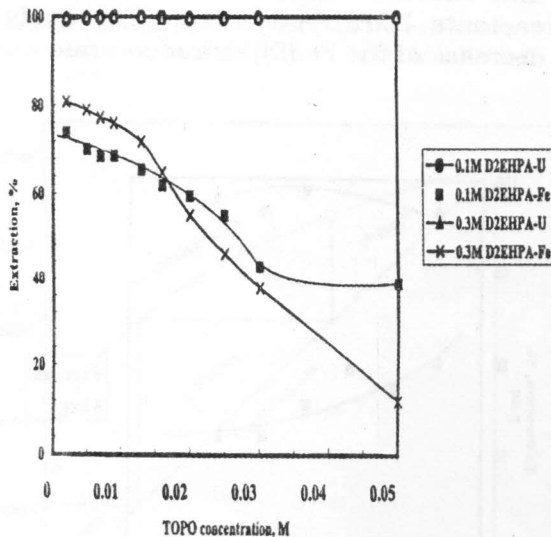


Fig. 9. Effect of synergistic mixture of D2EHPA and TOPO on uranium and iron extraction at 0.3M D2EHPA, A/O: 1/1, mixing time: 10 min.

4. Conclusions

To separate uranium from iron (III) with D2EHPA from sulfate leach liquor of G. Gatter ore material, the addition of masking agents such as tartaric, ascorbic acids, DTPA and NaF or reducing agents such as ascorbic acid were examined. It was found that by the addition of these agents, the extraction of iron (III) was increased and a pronounced

acceleration effect was attained. This was referred to a salting out effect. But when using oxalic acid as a masking agent the iron extraction efficiency was decreased at the same time the uranium extraction efficiency didn't affect. Another way for iron separation is by developing mixed solvent system consists of commercially available reagents D2EHPA and TOPO. They have used successfully to separate uranium from iron bearing sulfate leach liquors. It was concluded that by increasing TOPO concentration, the separation occurred.

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