

Separation of uranium and iron from aluminum sulfate leach solutions by solvent extraction

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Batch shake out tests on uranium and iron separation from sulfate leach liquor of Gibbsite ore by solvent extraction using long chain amines, preferably tertiary amines and di-2-ethyl hexyl phosphoric acid (D2EHPA) as extractants were investigated. Separation of uranium and iron can be increased to a higher value by manipulating process variables such as extractant type and concentration, leach liquor acidity, mixing time and speed of mixing. The largest influence on uranium and iron separation is observed for the leach liquor acidity. Variation of the extractant concentration was also investigated. The separation of uranium and iron was found to be strongly dependent on the extractant concentration. As a result, uranium and iron can be effectively separated from aluminum sulfate leaching solutions at the high pH value. Aluminum is not co-extracted with uranium and iron by two extraction systems.

تمت دراسة فصل اليورانيوم و الحديد من محاليل الإذابة الكبريتية لخام الجبسييت بواسطة طريقة الإستخلاص العضوى باستخدام الأمينات الثلاثية وكذلك ثنائى -2- إيثيل هيكسيل حامض الفوسفوريك المذاب فى الكيروسين كوسطى إستخلاص. يمكن زيادة كفاءة الإستخلاص لهذين العنصرين وذلك بدراسة المتغيرات التالية: نوع و تركيز وسط الإستخلاص ، حامضية محاليل الإذابة، وكذلك زمن و سرعة الخلط. تبين من النتائج التأثير الكبير لحامضية محاليل الإذابة على عملية فصل اليورانيوم و الحديد من محاليل كبريتات الألومنيوم. وجد أيضا أن عملية فصل اليورانيوم و الحديد من محاليل كبريتات الألومنيوم تعتمد إعتقادا كبيرا على تركيز وسط الإستخلاص. من هذه الدراسة يتبين أنه يمكن فصل كلا من اليورانيوم و الحديد من محاليل الإذابة الكبريتية لخام الجبسييت المتواجد فى جنوب غرب سيناء- مصر بكفاءة عالية.

Key words: Separation, iron, Uranium, Aluminum, D2EHPA, Tertiary amines.

1. Introduction

Most of the recent research and development work in extractive metallurgy reflects the need to treat low-grade feedstock or secondary materials in an environmentally acceptable manner. Noteworthy example within the area of hydrometallurgy include direct leaching processes by mineral acids such as sulfuric, hydrochloric and nitric acid.

Gibbsite is an aluminum-tri-hydrate mineral found in Um Karasi, southwestern Sinai, Egypt contains 47.54% alumina, 16.63% silica, 2.77% iron oxides and 350 ppm uranium. Due to the high content of silica, sulfuric acid is used to dissolve the valuable metals, e.g. aluminum and uranium, from this Gibbsite ore materials [1].

The US Bureau of Mines has published detailed experimental data on the gas induced crystallization technique [2-8]. However, these data refer to experiments carried out using iron free liquors, since their flow sheet

incorporates an iron removal step by solvent extraction, prior to aluminum precipitation stage. Efficient methods for iron removal from sulfuric acid solutions are often necessary for the recovery of a quality metal product. Solvent extraction has long been studied for iron removal from sulfate solutions.

The US Bureau of Mines is currently removing iron from hydrochloric acid leaching solution of clays by solvent extraction. Extraction is accomplished using 15% Alamine 336 in kerosene containing 10% isodecanol in 6 stages of mixer settlers [9]. J. Chen and others [10] developed four types of mixed solvent systems for iron removal from sulfate solutions. The extraction of iron (III) from sulfuric, hydrochloric and nitric acid by D2EHPA was studied by T. Sato and others [11]. Separation of uranium from ferric iron sulfate solutions was achieved by applying D2EHPA-tri-octyl phosphine oxide (TOPO) synergistic mixture [12].

The present work deals with the separation of iron as an impurity and recovery of uranium from Gibbsite leaching solutions as a secondary source. This was accomplished by applying two extraction systems of tertiary amines such as Tri-N-Octyl Amine (TNOA), Tri-Iso Octyl amine (TIOA) and Tri Dodecyl Amine (TDA) and D2EHPA.

2. Experimental

Aqueous aluminum sulfate solution was prepared by the leaching of Gibbsite ore, southwestern Sinai, Egypt by 4 M sulfuric acid solution at a temperature of 90°C for 4 hours mixing time and 600 rpm mixing speed using a magnetic stirrer [1]. This was followed by solid - liquid separation and pH adjustment. This solution was used as a stock solution for the extraction experiments.

Extractants used were of AR grade and were applied as received without further purification. Three tertiary amines TNOA, TIOA and TDA were tested in the extraction experiments. Pre-equilibration of amines was performed by contacting the amine solution for 10 minutes with a sulfuric acid of a concentration equal to that of the amine to ensure complete salt formation. The amine was dissolved to a certain concentration in kerosene. D2EHPA (Sigma Co.) of analytical grade was used as extractant in the second extraction system and diluted with kerosene to the selected concentrations (0.01 to 0.4 M). An electrical liquid shaker was used to mix the aqueous and organic phases in round bottom flask. The experiments were performed by mixing equal volumes of the aqueous and organic phases for 5 minutes at room temperature. After phase separation, the aqueous phase was analyzed for uranium, iron and aluminum content.

Uranium and aluminum were analyzed spectrophotometrically using Arsenazo III and Alizarine red as indicators, respectively. Iron was analyzed by atomic absorption spectrophotometer.

3. Results and discussions

3.1. Separation of uranium and iron with tertiary amines

3.1.1. Effect of type and concentration of the tertiary amine

The influence of type and concentration of a tertiary amines on the extraction of uranium and iron from aluminum sulfate leach solutions were investigated and plotted in figs. 1, 2, and 3. These figures show that the extraction efficiency of uranium reaches 46% at 0.2M TNOA and 0.06 M TDA while reach 47.2% at 0.06M TIOA concentration. The highest iron extraction % was observed with 0.2M TIOA. It is observed from figs. 1,2 and 3 that the uranium extraction efficiency firstly increased by increasing the amine concentration and then decreased. This may be attributed to the increase in organic phase viscosity with the increasing of amine concentration. Aluminum was extracted in negligible quantities with the tertiary amines. This lowest percentages of aluminum extraction is attributed to the fact that the aluminum ion in aqueous solutions almost entirely exists as the hex aqua ion $Al(H_2O)_6^{+3}$, this hydration sphere causes the slow ion exchange. As the result, the extraction of iron (III) is the reverse of that of aluminum [13,14].

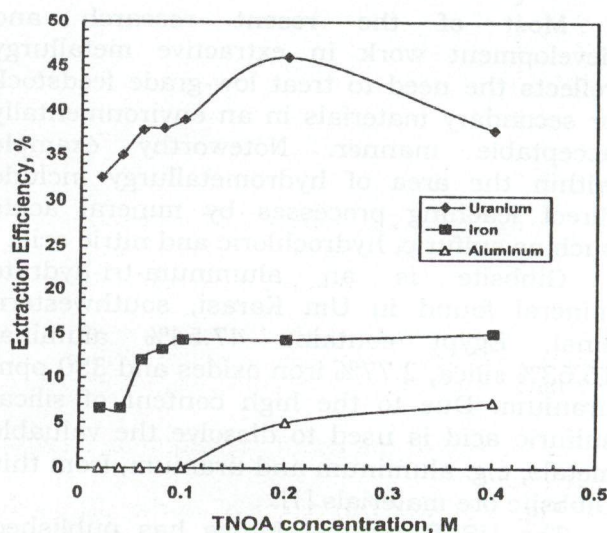


Fig.1. Effect of TNOA concentration on separation of uranium and iron from aluminum sulfate solution: pH=0.8, time = 5 min., speed = 300 rpm, aq./org. = 1/1.

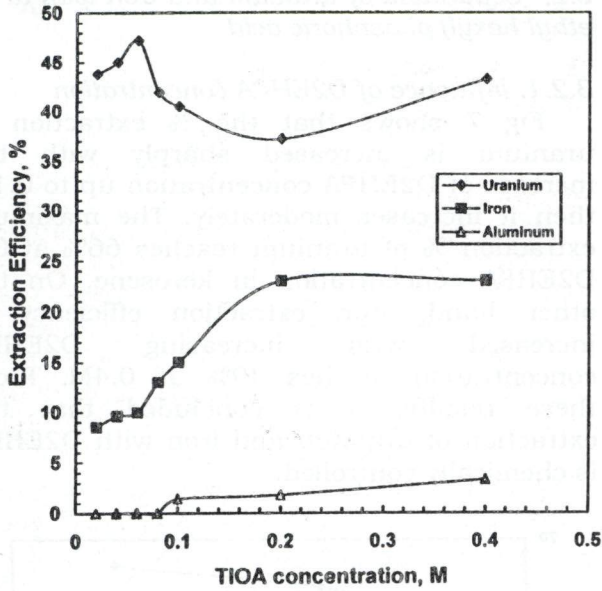


Fig. 2. Effect of TIOA concentration on separation of uranium and iron from aluminum sulfate solutions: pH = 0.8, time = 5 min., speed = 300 rpm., aq./org. = 1/1.

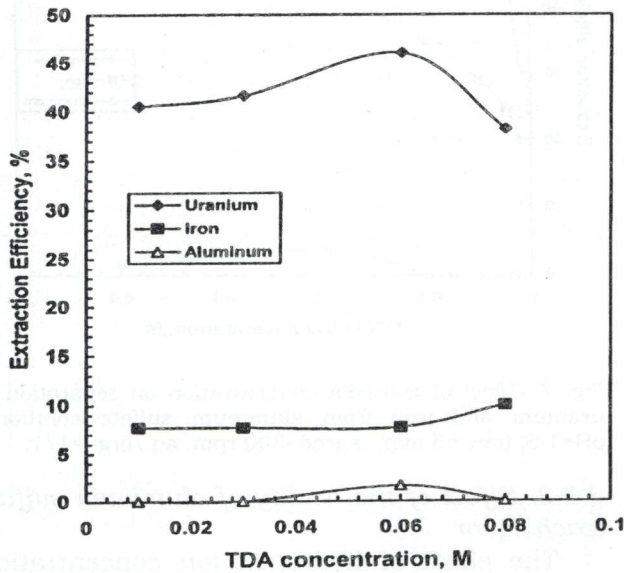


Fig. 3. Effect of TDA concentration on separation of uranium and iron from aluminum sulfate solutions: pH = 0.8, time = 5 min., speed = 300 rpm., aq./org. = 1/1.

3.1.2. Effect of the acidity of aluminum sulfate leach liquor

Fig. 4 shows the effect of initial pH of the aqueous phase on the extraction efficiency of uranium and iron with 0.1M TNOA. From this figure, it is observed that the uranium and iron extraction efficiency increased as the pH

increased. This was attributed to the cation exchange reaction that occurs at higher pH values in which hydrogen is liberated but at lower pH values the extraction occurs as a solvating reaction.

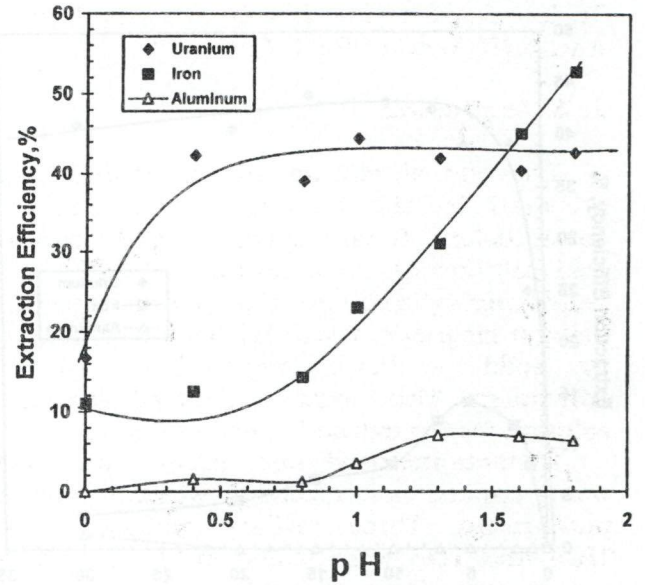


Fig. 4. Effect of the acidity of aluminum sulfate solution on separation of uranium and iron from aluminum sulfate solutions with 0.1 M TNOA: pH=0.8, tim=5min., speed=300 rpm, aq./org. =1/1.

3.1.3. Effect of mixing time on the separation of uranium and iron from aluminum sulfate leach liquor

The percentage of uranium, iron and aluminum extraction from aluminum sulfate leach liquor as a function of time was investigated and results are presented in fig. 5. From this figure, it is showed that the uranium extraction is higher than that of iron. It is observed that the initial rate of extraction of uranium is higher than the rate of iron extraction.

3.1.4. Effect of mixing speed on the separation of uranium and iron from aluminum sulfate leach liquor

Fig 6 shows the influence of mixing speed on percent extraction of uranium and iron (III) from aluminum sulfate solutions. The higher mixing speed gave the higher extraction efficiency of uranium. Iron extraction reaches 14.3% at 300rpm mixing speed. From this figure, it is clear that uranium extraction is

diffusion controlled but the extraction of iron is chemically controlled. The extraction of aluminum is slightly increased at higher mixing speeds. This is due to the slow rate of hex aqua aluminum ion present in the aqueous solutions.

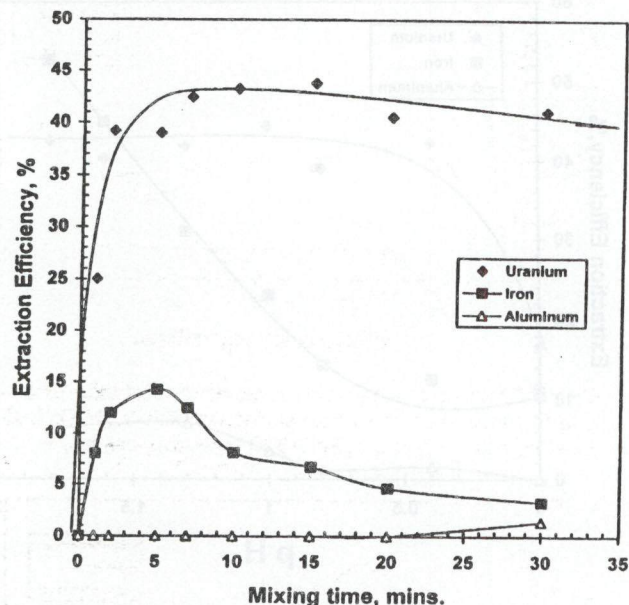


Fig. 5. Effect of mixing time on separation of uranium and iron from aluminum sulfate solutions with 0.1M TNOA: pH=0.8, time =5 min., speed=300 rpm, aq./org.=1/1.

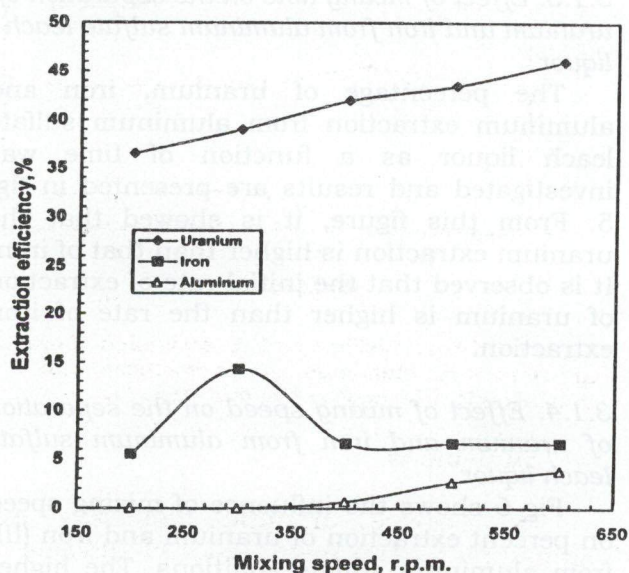


Fig. 6. Effect of mixing speed on separation of uranium and iron from aluminum sulfate solutions with 0.1M TNOA: pH=0.8, time=5min., aq./1/1.

3.2. Separation of uranium and iron with di (2-ethyl hexyl) phosphoric acid

3.2.1. Influence of D2EHPA concentration

Fig 7 shows that the % extraction of uranium is increased sharply with the increase of D2EHPA concentration up to 0.1M then it increases moderately. The maximum extraction % of uranium reaches 66% at 0.4 D2EHPA concentration in kerosene. On the other hand, iron extraction efficiency is increased with increasing D2EHPA concentration reaches 49% at 0.4M. From these results, it is concluded that the extraction of uranium and iron with D2EHPA is chemically controlled.

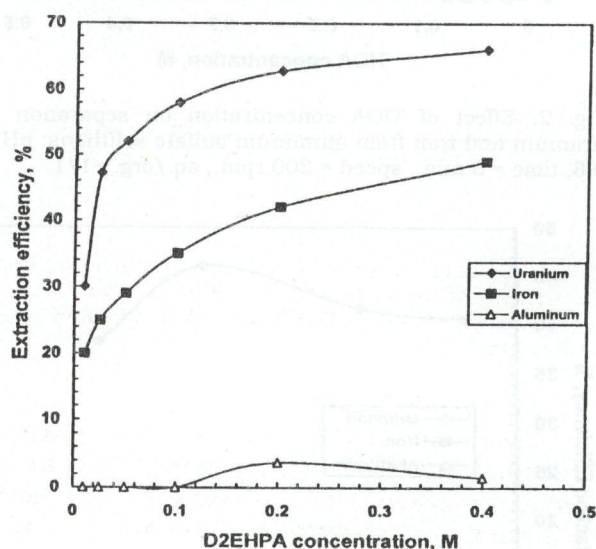


Fig. 7. Effect of D2EHPA concentration on separation of uranium and iron from aluminum sulfate solutions: pH=1.5, time =5 min., speed=300 rpm, aq./org. =1/1.

3.2.2. Effect of the acidity of aluminum sulfate leach liquor

The effect of hydrogen ion concentration on the extraction of uranium and iron from aluminum sulfate leach liquor is investigated. The results are illustrated in fig. 8. From this figure, it is observed that the uranium extraction efficiency is increased with the increase in pH of the aqueous phase whereas the iron extraction efficiency is decreased. On the contrary to iron, aluminum extraction efficiency increased as the pH increased reached 16.2% at pH 1.8. From these results, it is concluded that in the presence of Al and

U ions, the Fe (III) extraction efficiency with D2EHPA from sulfate solutions decreased with decreasing the acidity of the aqueous phase.

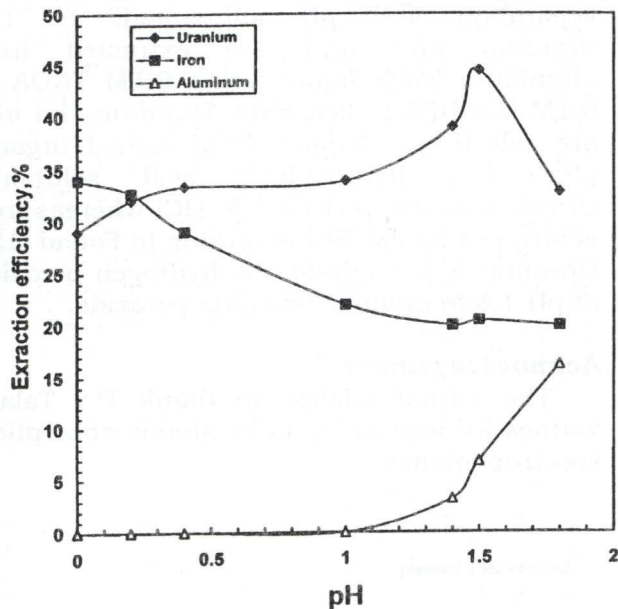


Fig. 8. Effect of the acidity of aluminum sulfate solution of separation of uranium and iron from aluminum sulfate solutions with 0.1M D2EHPA: pH=1.5, time 5 min., speed = 300 rpm, aq./org. =1/1.

3.2.3. Effect of mixing time

Fig 9 shows that the uranium extracted with 0.1M D2EHPA is increased as the mixing time increased. The maximum extraction efficiency for uranium is ~73% after 12 mins. and 21% for iron after 8 mins. From fig. 9, it is observed that the higher rate of extraction was attained for uranium but iron is extracted with slow rate. The great effect of mixing time on uranium and iron separation from aluminum sulfate leach liquor was attained.

3.2.4. Effect of mixing speed

The effect of mixing speed on uranium and iron extraction with 0.1M D2EHPA solution is illustrated in fig.10. From this figure, it is observed that uranium extraction is increased with increasing mixing speed up to 300rpm and then decreased. The iron extraction efficiency is slightly affected by mixing time, whereas the aluminum extraction efficiency was increased slightly with increasing mixing speed.

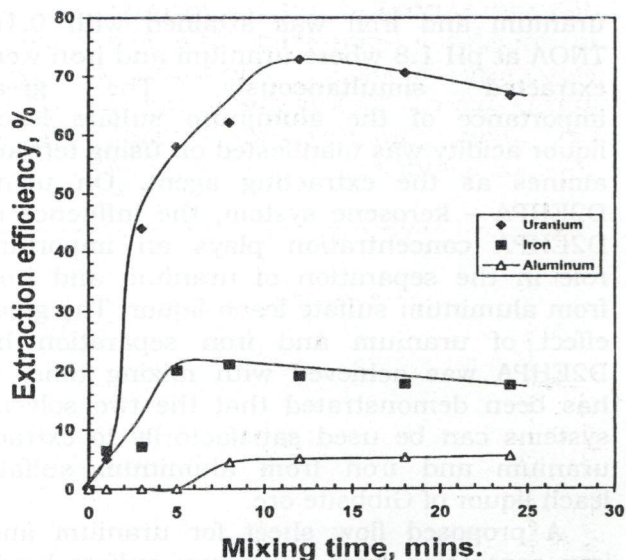


Fig. 9. Effect of mixing time on separation of uranium and iron from aluminum sulfate solutions with 0.1M D2EHPA: pH=1.5, time=5 min., speed=300 rpm, aq./org.=1/1

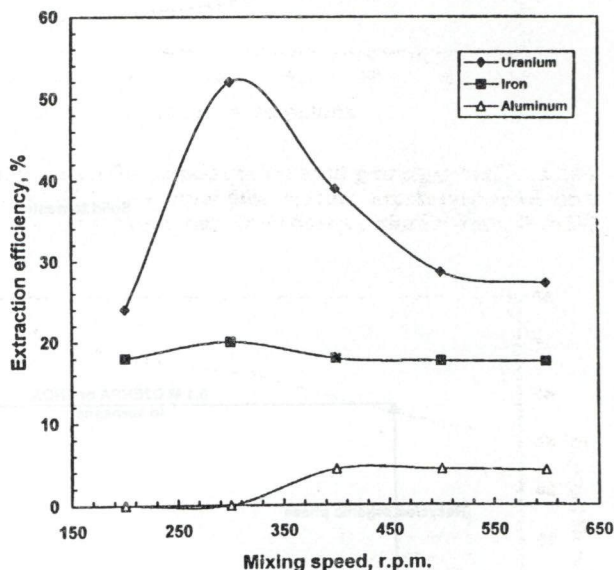


Fig. 10. Effect of mixing speed on separation of uranium and iron from aluminum sulfate solutions with 0.1M D2EHPA: pH=1.5, time=5 min., aq./org.=1/1.

4. Conclusions

To separate uranium and iron from aluminum sulfate leach liquor of Gibbsite ore by solvent extraction, two solvent systems, consisting of tertiary amines (TNOA, TIOA and TDA) and D2EHPA in kerosene, were examined. It was found that the separation of

uranium and iron was attained with 0.1M TNOA at pH 1.8 where uranium and iron were extracted simultaneously. The great importance of the aluminum sulfate leach liquor acidity was manifested on using tertiary amines as the extracting agent. On using D2EHPA – kerosene system, the influence of D2EHPA concentration plays an important role in the separation of uranium and iron from aluminum sulfate leach liquor. The great effect of uranium and iron separation by D2EHPA was achieved with mixing time. It has been demonstrated that the two solvent systems can be used satisfactorily to extract uranium and iron from aluminum sulfate leach liquor of Gibbsite ore.

A proposed flow sheet for uranium and iron separation from aluminum sulfate leach liquor of southwestern Sinai, Egypt gibbsite ore is shown in fig. 11. Leaching of Gibbsite

ore is applied by 4 M sulfuric acid at 90°C and liquid/solid ratio of 20 for 4 hrs mixing time [1]. This lead to complete dissolution of aluminum and uranium. After solid/liquid separation and pH adjustment to 1.5, uranium and iron are extracted from aluminum leach liquor using 0.1M TNOA or 0.1M D2EHPA in kerosene. Uranium and iron are selectively stripped from loaded organic phase by hydrochloric acid solutions. Uranium is stripped by 8 M HCl whereas iron is stripped by 2M HCl according to Fouad [15]. Uranium is precipitated by hydrogen peroxide at pH 1.8 to produce uranium peroxide.

Acknowledgement

The author wishes to thank Dr. Talaat Younes for iron analysis by atomic absorption spectrophotometer.

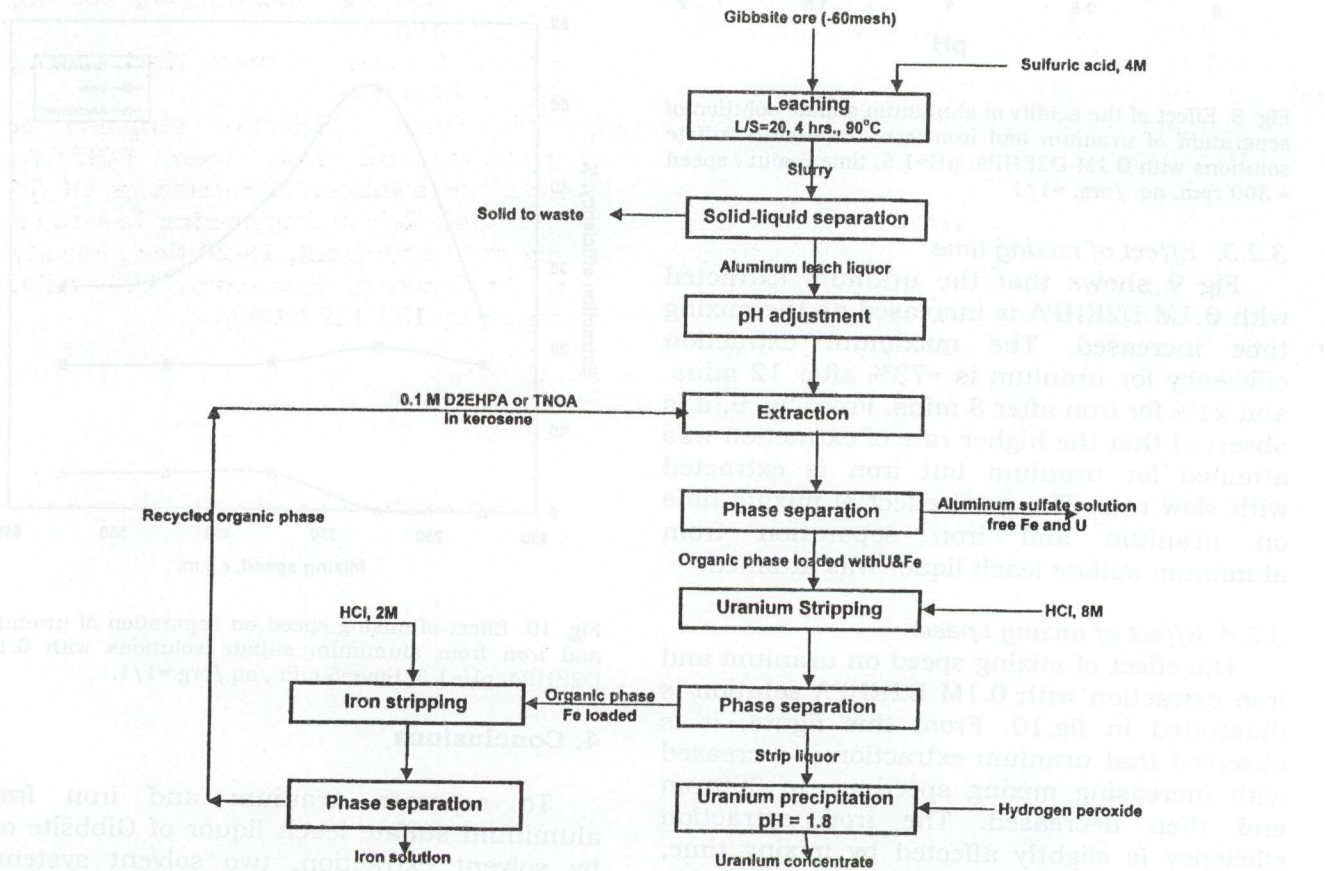


Fig. 11. Proposed flow sheet for separation of uranium and iron from gibbsite ore material, South Western Sinai, Egypt.

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Received July 11, 2001

Accepted September 9, 2001

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