



Nuclear Materials Authority
P.O.Box 530 Maadi, Cairo, Egypt

ISSN 2314-5609
Nuclear Sciences Scientific Journal
6, 171-180
2017
<http://www.ssnma.com>

IRON SCRUBBING FROM D₂EHPA AND TOPO MIXTURE DURING SECOND CYCLE OF URANIUM EXTRACTION FROM PHOSPHORIC ACID USING OXALIC ACID

MOHAMED H. TAHA

Nuclear Materials Authority, P.O. Box 530, El Maddi, Cairo, Egypt

ABSTRACT

The iron scrubbing from organic mixture, 0.03 M D₂EHPA & 0.075 M TOPO was carried out using oxalic acid solution. The influence of various factors affecting the scrubbing process as shaking time, oxalic acid concentration, scrubbing temperature and aqueous/organic phase ratio has been studied in terms of the maximum iron scrubbing efficiency and the minimum uranium scrubbing efficiency. The obtained results have been mathematical treated in order to model the iron scrubbing process. The logarithm of the apparent scrubbing equilibrium constant K was calculated and found to equal -1.55 ± 0.09 . The iron scrubbing process shown the endothermic character and the thermodynamics parameters (ΔH , ΔG and ΔS) were 20.17 KJ/mol, 8.84 KJ/mol and 38.02 J/mol K respectively. By applying the optimum conditions for iron scrubbing process, it is found that one stage is sufficient for scrubbing about 96.0 % of the total iron in loaded organic phase. The iron concentration in the precipitated yellow cake was within the permissible limits of the yellow cake international standard.

INTRODUCTION

Phosphoric acid, H₃PO₄, is second only to sulfuric acid in volume produced in the world. About 80% of the rock phosphate is being used as raw material for the manufacturing of phosphate fertilizers whereas the remaining 20% rock phosphate is being utilized for the production of detergents, metal surface treatment reagents, chemicals for food industry, and phosphorus compounds (European Fertilizer Manufacturers Association, 2000). During the treatment of rock phosphate with sulfuric acid, about 80 – 90 % U₃O₈ of the total uranium content present in the rock matrix is solubilized (Guzman et al., 1995).

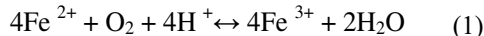
Although several methods such as ion-exchange (Beltrami et al., 2012), solvent impregnated materials (Aly et al., 2013), membrane separation (El-Hazek and El-Sayed, 2003),

and precipitation (Mousa et al., 2013) have been investigated, Solvent extraction alone has been found to be a successful process for industrial recovery of uranium from commercial phosphoric acid. On the pilot plant scale, three solvent extraction systems are of commercial interest for uranium recovery from wet process phosphoric acid assaying about 28– 30 % P₂O₅ and produced by the dihydrate process. Two of these are based on the extraction of U(IV) by octylpyrophosphoric acid (OPPA) (Khorfan, 1993) or mono (MOPAP) plus dioctylphenyl acid phosphate (DOPAP) (Ali et al., 2002) and the third is based on the extraction of U(VI) by a mixture of di(2-ethylhexyl) phosphoric acid (D₂EHPA) plus trioctylphosphine oxide (TOPO) (Beltrami et al., 2012; Khleifia et al., 2013; Ali et al., 2012). This process has proved greatly successful and several plants were constructed in different

countries since 1976 (Hurst, 1977).

Based on D₂EHPA/TOPO process, uranium is recovered from wet phosphoric acid in two cycles; first cycle: this cycle contains two stages, at the first stage; uranium is extracted from the commercial acid in four counter current stages using organic solvent using D₂EHPA & TOPO mixture in kerosene. At the second stage, uranium is stripped from loaded organic phase in three counter current stages using 6.0 M pure phosphoric acid containing 10-20g iron powder as a reducing agent to convert uranium to less extractable tetravalent uranium. In the second cycle uranium is extracted from the concentrated acid by contacting it with D₂EHPA/TOPO solvent in kerosene in other four stages. The loaded solvent is then stripped by an alkaline solution. Ammonium carbonate solutions in different concentrations and pHs are usually used at a temperature of 50°C (Hurst, 1977).

During the stripping step in the first cycle, Fe (II) is oxidized to Fe (III) and remains in the resulting strip solution with uranium according to equation (1);



Therefore, it creates a problem due to hydroxide precipitation during subsequent carbonate stripping. This caused pollution of the yellow cake. The high concentration of Fe leads to precipitation of iron phosphates in the mixer-settler (Dahdouh et al., 1997; Stas et al., 2002).

When iron is extracted from acidic solution by solvation, its stripping from D₂EHPA phase is difficult even with concentrated H₂SO₄ acid. In view of the above difficulty, it is therefore desirable to examine the feasibility of using other reagents such as oxalic acid (Akhlaghi et al., 2010; Ambikadevi and Lalithambika, 2000). Removal of extracted Fe from the loaded organic phase, D₂EHPA & TBP, at various stages of scrubbing with 20 % sulfuric acid and 7.5 % (w/v) oxalic acid has been reported (Mishra et al., 2002; Singh

et al., 2006; Singh et al., 2013).

Although the extraction behavior of iron (III) from phosphoric acid medium by D₂EHPA & TOPO has been reported (Ocio and Elizalde, 2011; Meles and Prostenik, 1984), the information given about the parameters affecting the iron (III) scrubbing from loaded organic phase, D₂EHPA & TOPO, is limited. In addition, iron (III) scrubbing mechanism, during uranium recovery from phosphoric acid, has not yet been well understood.

Therefore this work aims to study the different factors affecting the maximum iron scrubbing and the minimum uranium from loaded organic mixture 0.3 M D₂EHPA + 0.075 M TOPO using oxalic acid prior to the stripping of the uranium with ammonium carbonate solutions in order to precipitate yellow cake with iron content in the permissible limits of the international standard. In addition, the obtained results will be mathematically treated to suggest an approximate model for the iron (III) scrubbing process and to calculate the thermodynamic parameters of the scrubbing process.

EXPERIMENTAL

Reagent and Solution

All reagents used were of analytical reagent grade except D₂EHPA and TOPO manufactured by Aldrich AG which were of a commercial grade and used without purification. Kerosene was obtained from Misr petrol. Ltd., Egypt. Iron (III) solution was prepared from analytical grade ammonium iron (III) sulfate. Crystalline uranyl nitrate hexahydrate was an AR product of Fluka, Switzerland. It is used for the preparation of all uranium solutions. Oxalic acid solution (Laboratory grade) was prepared by dissolving the required amount in desired volume of water. Iron and Uranium concentrations were determined by ICP-MS. A synthetic ortho phosphoric acid solution prepared from AR

ortho phosphoric acid 85 % P₂O₅ supplied from Merck, Germany. Concentration of AR ortho phosphoric acid used is 35 % P₂O₅ and uranium and iron concentrations are 7 g/ L and 15 g/ L respectively. This phosphoric acid represents the loaded feed phosphoric acid in the second cycle of uranium extraction from phosphoric acid according to Hurst, 1977 (Hurst, 1977).

Synthetic loaded organic phase of 0.3 M D₂EHPA+ 0.075 M TOPO was prepared separately by contacting with the synthetic prepared ortho phosphoric acid in four stages at phase ratio (R_{org/aq}) equal 1. The loaded extract (analyzing 12.2 g/L iron and 11 g/L uranium) was performing to the iron scrubbing study.

Procedure

The utilized loaded organic extract was composed of D₂EHPA-TOPO in kerosene. This phase was brought into contact with oxalic acid solution. The scrubbing experiments were based on high dispersion in a separating funnel by mechanical shaking. Unless otherwise stated, the two phases were brought into contact at a temperature of ≈ 25°C using organic to aqueous volume ratio (R_{org/aq}) equal 1. The concentrations of iron and uranium in the aqueous phase were determined as per the procedure described by Basset and Nagle, respectively (Basset et al.,1985; Nagle and Murthy, 1972). The results were evaluated in terms of the iron and uranium scrubbing efficiency and iron scrubbing distribution coefficient (SD), given by the relation;

$$\text{Uranium scrubbing efficiency, \%} = \frac{\text{Concentration of uranium in aqueous phase}}{\text{Total uranium concentration}} \times 100$$

$$\text{Iron scrubbing efficiency, \%} = \frac{\text{Concentration of iron in aqueous phase}}{\text{Total iron concentration}} \times 100$$

$$\text{Iron } S_D = \frac{\text{Concentration of iron in aqueous phase}}{\text{Concentration of iron in organic phase}} \times \frac{\text{Volume of organic phase}}{\text{Volume of aqueous phase}}$$

RESULTS AND DISCUSSIONS

The following is a discussion for the results obtained from the iron scrubbing from

loaded organic solvent D₂EHPA & TOPO mixture using oxalic acid during the uranium extraction from phosphoric acid. The different factors affecting the scrubbing process were studied in terms of high efficiency for iron scrubbing with minimum uranium. Here, the effects of shaking time, oxalic acid concentration, Aqueous/organic (R_{aq/org}) phase ratio and scrubbing temperature, on the iron scrubbing process have been investigated. The obtained results were mathematically treated to model the scrubbing reaction and to calculate the thermodynamic parameters.

Effect of Shaking Time

To study the effect of shaking time for the iron and uranium scrubbing from 0.3 M D₂EHPA & 0.075 M TOPO mixture loaded by 12.2 g/l iron and 11 g/l uranium, several experiments were carried at different times ranges from 1.0 to 60.0 min using 0.6 M oxalic acid, aqueous/ organic phase ratio (R_{aq/org}) equal 1 at 25 ± 1°C temperature. The experimental results are given on Fig. (1) as a relation between scrubbing efficiency % and Time. From the Figure it is clear that, as the shaking time increases from 1.0 to 15.0 min, the scrubbing efficiency % increased from

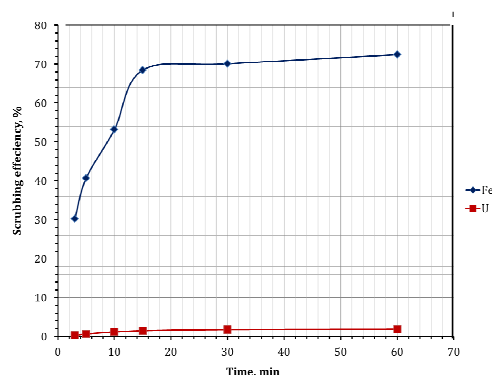


Fig.1 :Effect of time on iron and uranium scrubbing efficiency % from 0.3 M D₂EHPA & 0.075 M TOPO mixture using 0.8 M oxalic acid with fixed phase ratio (R_{aq/org}) equal 1 at 25 ± 1°C temperature

30.3 to 68.5 % for iron and from 0.3 to 1.9 for uranium. Further increase in time than 15 min has slight effect on both of iron and uranium scrubbing efficiency, which means that the scrubbing process tended to equilibrium. Therefore, 15 min represents the preferred time to maximize iron scrubbing from 0.3 M D₂EHPA and 0.075 M TOPO mixture.

Effect of Oxalic Acid Concentration

The effect of oxalic acid concentration ranging from 0.2 to 0.8 M on the scrubbing of iron and uranium from organic phase, 0.3 M D₂EHPA & 0.075 M TOPO, was investigated using aqueous/ organic phase ratio ($R_{aq/org}$) equal 1 at a temperature of 25 ± 1 °C. The results were plotted on Fig. (2) as a relation between scrubbing efficiency % and oxalic acid concentration. The obtained results indicate that, as the oxalic acid concentration increases from 0.2 to 0.8 M the scrubbing efficiency increased from 17.4 to 73.4 % for iron and from 0.4 to 1.6 % for uranium. Therefore, 0.8 M oxalic acid is the choice acid concentration used for the other experiments of the iron scrubbing from organic mixture, 0.3 M D₂EHPA & 0.075 M TOPO.

Effect of Aqueous/Organic Phase Ratio

The effect of aqueous/ organic ($R_{aq/org}$) phase ratio ranging from 0.5/ 1 to 4/ 1 on the scrubbing of iron and from organic mixture, 0.3 M D₂EHPA & 0.075 M TOPO, loaded by 12.2 g/ L iron and 11 g/l uranium was studied using 0.8 M oxalic acid at 25 ± 1 °C temperature and shaking time is 15 min. The results shown on Fig. (3) as a relation between scrubbing efficiency % and aqueous/ organic ($R_{aq/org}$) phase ratio clear that, iron scrubbing efficiency increases from 47.9 to 89.6 % and uranium scrubbing efficiency increases from 0.6 to 1.9 % as aqueous/ organic phase ratio ($R_{aq/org}$) increases from 0.5 to 2. Further increase in ($R_{aq/org}$) phase ratio more than 2 has nearly no effect on both of iron and uranium scrubbing process. Aqueous/ organic phase ration was kept at ($R_{aq/org}$) equals 1 for

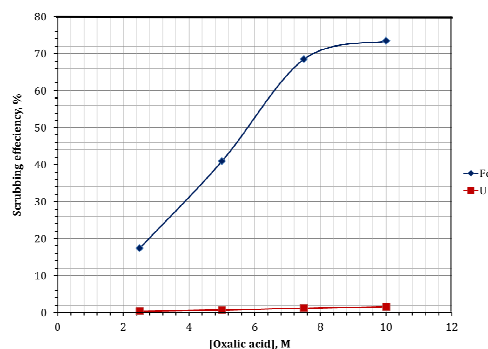


Fig.2 : Effect of oxalic acid concentration on iron and uranium scrubbing efficiency % from organic phase, 0.3 M D₂EHPA & 0.075 M TOPO, with fixed phase ratio ($R_{aq/org}$) equal 1 and shaking time is 15 min at 25 ± 1 °C temperature

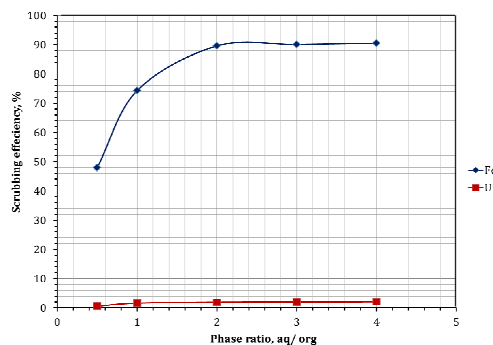


Fig.3: Effect of (aq/org) phase ratio on iron and uranium scrubbing efficiency % from 0.3 M D₂EHPA & 0.075 M TOPO mixture using 0.8 M oxalic acid with temperature 25 ± 1 °C and shaking time is 15 min

economic aspects.

Effect of Temperature

To study the effect of temperature on iron and uranium scrubbing from 0.3 M D₂EHPA & 0.075 M TOPO mixture loaded by 12.2 g/ l iron and 11 g/l uranium by 0.8 M oxalic acid several experiments were carried out at different temperature from 25 to 50 ± 1 °C. The other parameters were fixed at 15 min shaking

time and aqueous/organic phase ratio ($R_{aq/org}$) equal 1. The experimental results are given on Fig. (4) as a relation between scrubbing efficiency % and temperature. From the Figure it is obtained that, as the temperature increases from 20 to 50 °C, the iron scrubbing efficiency increases from 73.5 to 84.1 while the uranium scrubbing efficiency slightly increased from 1.6 to 1.8 %. This behavior indicates that the scrubbing of iron from 0.3 M D₂EHPA & 0.075 M TOPO mixture using oxalic acid is an endothermic process. Room temperature considered the preferred temperature for the further work.

Iron Scrubbing Isotherm

To develop a process for counter-current iron scrubbing from organic mixture, 0.3 M D₂EHPA & 0.075 M TOPO, loaded by 12.2 g/l iron and 11 g/l uranium the number of stages for scrubbing process should be evaluated. In this investigation, the isotherm of iron scrubbing from organic phase, 0.3 M D₂EHPA & 0.075 M TOPO was studied by applying the following preferred conditions for iron scrubbing from organic phase, 0.3 M D₂EHPA & 0.075 M TOPO; 0.8 M oxalic acid, room temperature, shaking time of 15.0

min and aqueous/ organic phase ratio ($R_{aq/org}$) equal 1. These preferred conditions represent the high efficiency for iron scrubbing (\approx 75 %) with minimum uranium efficiency less than 2 %.

The results are given on Fig. (5) as a relation between concentration of iron in aqueous and organic phases. From the obtained results, it is found that two stages are sufficient for scrubbing about 96.0 % of the total iron in loaded organic phase, 0.3 M D₂EHPA & 0.075 M TOPO, at phase ratio ($R_{aq/org}$) equal 1. This result disagrees with the data obtained from the stripping of iron (III) from organic phase: 1.5 M D₂EHPA + 0.2 M TBP using 7.5 % (w/v) oxalic acid where four stages are required for about 99 % stripping of iron (III) (Singh et al., 2006).

From the loaded organic phase, uranium was stripped and the strip solution was filtered to remove traces of iron precipitate. Finally, uranium is precipitated from the filtered strip medium by using H₂O₂ followed by neutralization using sulfuric acid with pH maintained in the range of 3-4 to thereby precipitate the uranium (Singh et al., 2003). The iron concentration in the precipitated yellow uranium peroxide (UO₄·xH₂O) was in the per-

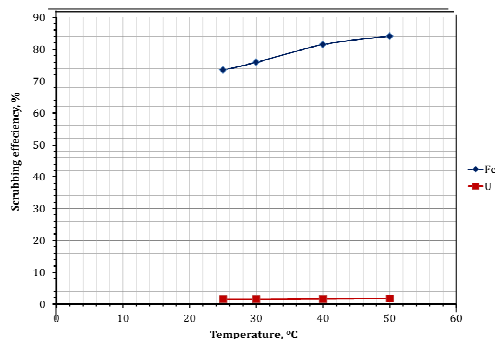


Fig.4: Effect of temperature on iron and uranium scrubbing efficiency % from organic phase, 0.3 M D₂EHPA & 0.075 M TOPO, loaded by 12.2 g/L iron using 0.8 M oxalic acid with fixed phase ratio ($R_{aq/org}$) equal 1 and shaking time is 15 min.

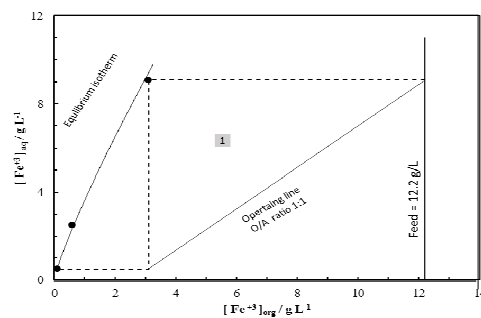


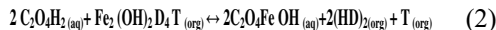
Fig.5: The Mac-Cab Thiele diagram for iron scrubbing from organic phase, 0.3 M D₂EHPA & 0.075 M TOPO, loaded by 12.2 g/l iron and 11 g/l uranium using 0.8 M oxalic acid, and at room temperature, shaking time of 15 min, phase ratio ($R_{aq/org}$) equal 1

missible limits of the international standard yellow cake (Elshafeea et al., 2014).

Proposed Chemical Equilibrium

This part aims to study iron scrubbing mechanism from loaded organic phase, 0.3 M D₂EHPA & 0.075 M TOPO, using oxalic acid and propos a chemical equilibrium for the iron scrubbing process. The main equilibrium involved is based on the different iron species in D₂EHPA & TOPO mixture. In a critical review on iron thermodynamic and species in the organic phase during the uranium extraction from phosphoric acid, it is found that, Iron forms different complexes with D₂EHPA, (HD)₂, such as Fe(OH)D₂(HD)₂ and Fe(HD)₂₃ (Singh et al., 2003; Singh et al., 2013; Shuquian Chen, 1989). In addition, it is found that, during the uranium extraction, one molecule of TOPO or TBP involved in the extracted species of iron in the organic phase when the extraction was performed with the mixtures of D₂EHPA & TOPO or D₂EHPA & TBP. Therefore, extracted species may be as [Fe₂(OH)₂D₄TOPO] (org).

Based on the results obtained from the effect of oxalic acid concentration on the scrubbing of iron (III) Figure 2, an average positive slope of 2 obtained from the plot between log oxalic acid concentration and log iron scrubbing distribution coefficient (log S_D) Fig. (6) which indicated that 2 moles of the oxalic acid shared in the iron (III) scrubbing process. Based on the average positive slope of 2 for the scrubbing dependence on oxalic acid concentration Fig. (6) and the expectable scrubbed iron species [Fe₂(OH)₂D₄TOPO] the following equilibrium can be proposed.



Where (HD)₂ is D₂EHPA and T is TOPO. From equation (2), the apparent scrubbing equilibrium constant K was calculated by the relation;

$$K = \frac{[C_2O_4FeOH]_{(aq)}^2 [(HD)_2]_{(org)}^2 [T]_{(org)}}{[Fe_2(OH)_2D_4T]_{(org)} [C_2O_4H_2]_{(aq)}^2} \quad (3)$$

Since $S_D = \frac{[C_2O_4FeOH]_{(aq)}^2}{[Fe_2(OH)_2D_4T]_{(org)}}$

then $K = S_D [(HD)_2]_{(org)}^2 [T]_{(org)} / [C_2O_4H_2]_{(aq)}^2$

Taking logarithm for both sides

$$\log K = \log S_D + 2 \log [(HD)_2] + \log [T] - 2 \log [C_2O_4H_2] \quad (4)$$

Based on equation 4, the logarithm of the apparent scrubbing equilibrium constant K was calculated from all the experimental results and found to equal -1.55 ± 0.09 . This value was used to calculate the corresponding distribution ratio as shown in Table 1.

From the Table it is clear that, there is a slight deviation in the value of log S_D within the experimental error for high oxalic acid

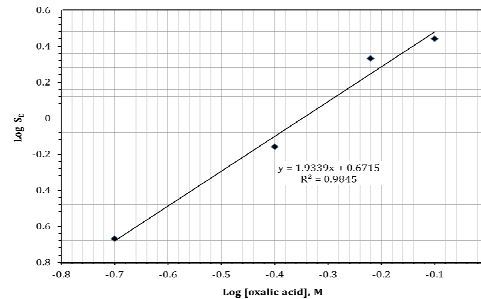


Fig.6: The relation between log oxalic acid concentration and log S_D based on the data obtained from Fig. 2

Table 1: Average K and calculated corresponding distribution ratio based on proposed scrubbing equilibrium for iron scrubbing from organic phase, 0.3 M D₂EHPA & 0.075 M TOPO, using 0.8 M oxalic acid

Log [C ₂ O ₄ H ₂], M	Log S _D (exp.)*	Log K	Log S _D (cal.)**
-0.70	-0.67	-1.44	-0.78
-0.40	-0.16	-1.53	-0.18
-0.22	0.33	-1.62	0.18
-0.10	0.44	-1.63	0.42

Log K = -1.55 ± 0.09

* Experimental distribution ratio; ** Calculated based on the value of K obtained

concentration, 0.8 M. Therefore, this can justify our proposed scrubbing equilibrium in high oxalic acid concentration.

Thermodynamic Parameters

Chemical thermodynamics can be used to ascertain the feasibility of a given chemical reaction. It permits quantitative calculation of the state of equilibrium of a system. Conversely, the concepts of chemical equilibrium can be used to find out conditions for making a desired reaction feasible. In this concern, the thermodynamic parameters of iron scrubbing from organic phase, 0.3 M D₂EHPA & 0.075 M TOPO were calculated based on the data obtained on Fig. (4).

The enthalpy changes associated with iron scrubbing from D₂EHPA & TOPO mixture using 0.8 M oxalic acid can be calculating using Van't Hoff equation (Srinivasan et al., 1997).

$$\text{Log } S_D = \frac{-\Delta H}{2.303 R} \cdot \frac{1}{T} + C \quad (5)$$

where R is the universal gas constant, and C is a constant.

The plot of log iron scrubbing distribution coefficient (log S_D) against (1/ T) yields a straight line equation with slope equal to -ΔH. Figure (7) shows the plot of log S_D against

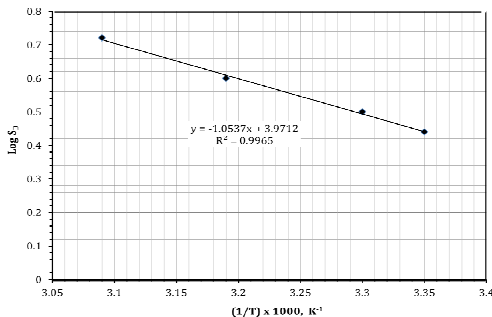


Fig.7: Relation between log S_D and 1/T for iron scrubbing from,0.3 M D₂EHPA & 0.075 M TOPO mixture, using 0.8 M oxalic acid with fixed phase ratio (R_{aq/org}) equal 1 and shaking time is 15 min

(1/ T). From this Figure, an enthalpy change of 20.17 KJ/mol was obtained in the given range of temperature, which indicates that the scrubbing is an endothermic process.

The magnitude and sign of the enthalpy change (ΔH) associated with the scrubbing process will consist of (1) enthalpy change for dehydration (ΔH_d) which can be expected to be positive because energy is required to break the ion–water and water–water bonding of the hydrated metal ions, and (2) enthalpy change for complexing (ΔH_c) which will make ΔH more negative due to the formation of metal complex (Masterton et al., 2012). The positive ΔH value obtained for the scrubbing of iron (III) indicates that dehydration seems to be more significant than complexation in the scrubbing system.

This result disagrees with the data obtained from the stripping of iron from organic phase: 1.5 M D₂EHPA+0.2 M TBP using oxalic acid, where the change in enthalpy for the stripping process has been evaluated and the ΔH value has been found to be - 123.69 kJ/ mole (Singh et al., 2013) this may be as a result of the difference in the organic phase composition and concentration.

The Gibbs free energy change, ΔG of the iron scrubbing process was also calculated based on the logarithmic value of the proposed chemical equilibrium Log K at 25± 1°C according to the Equation (6):

$$-\Delta G = 2.303 RT \log K \quad (6)$$

Also, the entropy change, ΔS was obtained from ΔG and ΔH with the Equation (7):

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

The thermodynamic parameters of the iron scrubbing from D₂EHPA & TOPO mixture using oxalic acid were given in Table 2.

The positive values of ΔG indicated that the iron scrubbing process is a non-spontaneous reaction. The positive value of ΔS cleared the increase in the system.

Table 2 : Thermodynamic parameters for iron scrubbing from D₂EHPA & TOPO mixture using 0.8 M oxalic acid

ΔH (KJ/ mol)	ΔG (KJ/ mol)	ΔS (J/ mol K)
20.17	8.84	38.02

CONCLUSION

Iron scrubbing from organic mixture 0.3 M D₂EHPA & 0.075 M TOPO using oxalic acid during second cycle uranium extraction from phosphoric acid has been achieved. According to the maximum iron scrubbing efficiency and the minimum uranium scrubbing efficiency, the preferred scrubbing conditions were shaking time 15 min, oxalic acid concentration 0.8 M, temperature at 25 °C, aqueous/ organic phase ratio equal 1. Based on the preferred conditions, one stage is sufficient for scrubbing about 96.0 % of the total iron and the iron concentration in the precipitated yellow cake was within the permissible limits of the yellow cake international standard. The thermodynamics analysis for the iron scrubbing results showed that the endothermic behavior of the process and the thermodynamics parameters (ΔH , ΔG and ΔS) were 20.17 KJ/mol, 8.84 KJ/mol and 38.02 J/mol K respectively. Logarithm of the apparent scrubbing equilibrium constant K was calculated and found to equal -1.55 ± 0.09 .

REFERENCES

- Akhlaghi, M.; Rashchi, F.; and Vahidi, E., 2010. Stripping of Fe(III) from D2EHPA Using Different Reagents. Inter.Mineral Proc. Congress, XXV(IMPC), Brisbane,Australia, 255-262.
- Ali, A.M.I.; Daoud, J.A.; Zeid, M.M., and Aly, H. F., 2002. Counter-current extraction process for recovery of U (IV) from phosphoric acid using octylphenyl acid phosphate (OPAP) extractant. J. Radioanalytical and Nuclear Chemistry, 254 (2), 263–269.
- Ali, H.F.; Ali, M.M.; Taha, M.H., and Abdel-Magied, A.F., 2012. Uranium Extraction Mechanism from Analytical Grade Phosphoric Acid Using D₂EHPA and Synergistic D2EHPA-TOPO Mixture. Inter. J. Nuclear Energy Science and Engineering, 2 (2), 57-61.
- Aly, M.M.; Mousa, M.A.; Taha, M.H.; Kandil, K.M., and El-Zoghby, A.A., 2013. Kinetics and Thermodynamics of Uranium Adsorption from Commercial Di-hydrate Phosphoric Acid Using D₂EHPA-Impregnated Charcoal. Arab J. Nuclear Science and Applications, 46 (5), 29-37.
- Ambikadevi, V.R., and Lalithambika, M., 2000. Effect of organic acids on ferric iron removal from iron-stained kaolinite. Appl. Clay Sci., 16, 133–145.
- Basset, J.; Denney, R.C.; Jeffery, G.H., and Mendham, J., 1985. Vogel's Text Book of Quantitative Inorganic Analysis. ELBS Publication, London, 742p.
- Beltrami, D.; Chagnes, A.; Haddad, M.; Laureano, H.; Mokhtari, H.; Courtaud, B.; Juge, S., and Cote, G., 2012a. Development of new cationic exchangers for the recovery of uranium (VI) from wet phosphoric acid. Sep. Sci. Technol., LSST-2012-5962.R2.
- Beltrami, D.; Chagnes, A.; Mokhtari, H.; Courtaud, B., and Cote, G., 2012. Modeling of the extraction of uranium (VI) from concentrated phosphoric acid by synergistic mixtures of bis-(2-ethylhexyl)-phosphoric acid and tri-n-octylphosphine oxide. Hydrometallurgy, 129-130, 118-125.
- Dahdouh, A.; Shlewit, H.; Khorfan, S., and Koudsi Y., 1997. Study of factors affecting uranium stripping from DEHMA/TOPO solvent by factorial design. J. Radioanalytical and Nuclear Chemistry, 221 (1-2), 183-187.
- El-Hazek, N.T., and El- Sayed, M.S., 2003. Direct uranium extraction from dihydrate and hemidihydrate wet process phosphoric acids by liquid emulsion membrane. J. Radioanalytical and Nuclear Chemistry, 257 (2), 347-352.

- Elshafeea, H.Y.A.; Etemad, E., and Adam, K.S., 2014. Precipitation and purification of uranium from rock phosphate. *J. Radioanalytical and Nuclear Chemistry*, 299 (1), 815-818.
- European Fertilizer Manufacturers Association, (EFMA), 2000. Booklet No. 4 of 8 Production of phosphoric acid. Belgium.
- Guzman, E.T.R.; Rios, M.S.; Garcia, J.L.I., and Roqil, E.O., 1995. Uranium in phosphate rock and derivatives. *J. Radioanalytical and Nuclear Chemistry*, 189 (2), 301-306.
- Hurst, F.J., 1977. Recovery of uranium from wet-process phosphoric acid by solvent extraction. *Trans. Soc. Min. Eng. AIME*, 262, 240-248.
- Khorfan, S., 1993. Study of the stability of octylpyrophosphoric acid (OPPA) solvent in the extraction of uranium from phosphoric acid. *Chemical Engineering and Processing: Process Intensification*, 32 (5), 273 - 276.
- Khleifia, N.; Hannachi, A., and Abbes, N., 2013. Studies of Uranium Recovery from Tunisian Wet Process Phosphoric Acid. *Inter. J. Innovation and Applied Studies*, 3 (4), 1066-1071.
- Masterton, W.L.; Hurley, C.N., and Neth, E., 2012. *Chemistry: Principles and Reactions*, 7th Edition. ISBN-13: 9781111427108.
- Meles, S., and Prostenik, M.V., 1984. Solvent extraction of Fe (III) by di-(2-ethyl hexyl) phosphoric acid from phosphoric acid solutions. *Polyhedron*, 5, 615.
- Mishra, S.L.; Giriyaiker, A.B.; Vijayalakshmi, R.; Iyer, N.S.; Koteker, M.K.; Anitha, M., and Singh, H., 2002. Uranium Extraction from Phosphoric Acid Process Streams by Synergistic Organophosphorous Solvents. In: *Solvent Extraction* (Mishra, V.N.; Das, S.C.; Srinivasa Rao, K., Eds). Proc. Inter. Symposium, Allied Publishers Pvt. Ltd.: New Delhi, India, 393p.
- Mousa, M.A.; Gado, H.S.; Abd-El Fattah, M.M. G.; Madi, A.E.; Taha, M.H., and Roshdy, O. E., 2013. Removal of Uranium from Crude Phosphoric Acid by Precipitation Technique. *Arab J. Nuclear Science and Applications*, 46 (5), 38-47.
- Nagle, R.A., and Murthy, T.K.S., 1972. Spectrophotometric Determination of Uranium in Commercial Wet Process Phosphoric Acid and Phosphate Rock Using Thiocyanate, Report BARC-638, AEC, India.
- Ocio, A., and Elizalde, M.P., 2011. Iron (III) Extraction from Phosphoric Acid Solutions by Cyanex 301. *Solvent Extraction and Ion Exchange*, 29, 337-362.
- Shuqiu, Y., and Chen, J., 1989. Stripping of Fe (III) extracted by d-2-ethylhexyl phosphoric acid from sulfate solutions with sulfuric acid. *Hydrometallurgy*, 22, 267.
- Singh, D.K.; Mishra, S.L., and Singh, H., 2006. Stripping of Iron(III) from the D₂EHPA + TBP Extract Produced during Uranium Recovery from Phosphoric Acid by Oxalic Acid. *Hydrometallurgy*, 81, 214-218.
- Singh, D.K.; Yadav, K.K., and Singh, H., 2013. Extraction and Stripping Behavior of Iron (III) from Phosphoric Acid Medium by D₂EHPA Alone and Its Mixtures with TBP/TOPO, *Separation Science and Technology*, 48 (10), 1556-1564.
- Singh, H.; Mishra, S.L.; Vijayalakshmi, R.; Giriyaiker, A.B., and Gupta, C.K., 2003. Solvent extraction process for recovery of uranium from phosphoric acid (25-55% P₂O₅). US.Patent, 6, 645, 453 B2.
- Srinivasan, T.G.; Rao, P.R.V., and Sood D.D., 1997. The Effect of Temperature on the Extraction of U (VI) from Nitric Acid by Tri-n-Amyl Phosphate, *Solvent Extraction and Ion Exchange*. 15, 15-31.
- Stas, J.; Dahdouh, A.; Shlewit, H., and Khorfan, S., 2002. Statistical study of factors affecting the co-extraction of uranium and iron in the second cycle of extraction with DEHPA/TOPO in kerosene. *Hydrometallurgy*, 65, 23-30.

إزالة الحديد من خليط المذيبات العضوية (ثنائي-2- إيثيل هكسيل حمض الفوسفوريك & ثلاثي أوكثيل أوكسيد الفوسفين) المحملة -أثناء المرحلة الثانية لعملية إستخلاص اليورانيوم من حمض الفوسفوريك-
بإستخدام حمض الأوكساليك

محمد حلمي طه

تم إزالة الحديد من خليط المذيبات العضوية (٠,٣ عياري ثنائي-٢ إيثيل هكسيل حمض الفوسفوريك و ٠,٠٧٥ عياري ثلاثي أوكثيل أوكسيد الفوسفين) بإستخدام حمض الأوكساليك. لقد تم دراسة تأثير العوامل المختلفة علي عملية إزالة الحديد بهدف الوصول الي اعلي نسبة لإزالة الحديد مع أقل نسبة إزالة لليورانيوم. ولقد وجد ان التفاعل ماص للحرارة وتم حساب معاملات الديناميكا الحرارية للتفاعل. وايضا تم عمل معالجة رياضية للنتائج التي تم التوصل اليها بهدف إفتراض نموذج لعملية إزالة الحديد. تم حساب لوغاريتم ثابت الاتزان الافتراضي لعملية إزالة الحديد ووجد انه يساوي $-1,55 \pm 0,09$. وتطبيق الظروف المفضلة لعملية إزالة الحديد وجد انه يمكن إزالة ٩٦,٠ % من كمية الحديد الموجود بخليط المذيبات العضوية علي مرحلتين. ولقد وجد أن نسبة الحديد في العجينة الصفراء الناتجة متوافقة مع المعايير العالمية للعجينة الصفراء.