



Uranium Recovery From the Concentrated Phosphoric Acid Prepared by the Hemi-Hydrate Process

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ملخص

أمكن إذابة اليورانيوم من خام فوسفات السباعية خلال تحضير حامض الفوسفوريك المركز بطريقة الهيمي هيدرات وذلك باستخدام 10 كيلو جرام كلورات بوتاسيوم/ طن خام فوسفات. وفي العمل الحالي أمكن استخلاص حوالي 90% من اليورانيوم من الحامض المركز باستخدام خليط من مذيب ثنائي إيثيل هكسيل حامض الفوسفوريك (0,75 جزيئي) مع مذيب ثلاثي أوكتيل هكسيل أكسيد الفوسفين (1, 0 جزيئي)، كما تم استرجاع اليورانيوم من الوسط العضوي باستخدام محلول 10 جزيئي حامض فوسفوريك والذي أمكن ترسيب ركاز اليورانيوم منه مباشرة باستخدام فلوريد الأمونيوم في وجود الأسيتون.

Abstract

It has been proved that the uranium dissolution from El-Sebaiya phosphate ore is possible by using 10 kg of $KClO_4$ during the preparation of high strength phosphoric acid using the hemihydrate process.

In the present work, effective extraction of uranium (about 90%) from the high strength phosphoric acid using a new synergistic solvent mixture of 0.75M D2EHPA/0.1 M TOHPO has been succeeded. Stripping of uranium from the organic phase was possible by 10 M phosphoric acid while the direct precipitation of uranium concentrate from the latter was feasible by using NH_4F in presence of acetone.

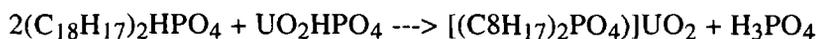
Introduction:

Uranium dissolution during the acidulation process of phosphate rocks depends primarily upon the nature of the produced phosphate material. If the latter is in the form of mono calcium phosphate $\text{Ca}(\text{H}_2\text{PO}_4)_2$ about 1/3 of the uranium content of Egyptian phosphate will be transferred to the phosphate product after dissolution. However, if the product is the phosphoric acid (30% P_2O_5), almost all of the uranium content will be transferred to the phosphoric acid. On the other hand, if the phosphoric acid is produced by the hemihydrate process (50% P_2O_5), uranium could be dissolved, however, it would be most probably associated with the calcium sulfate by-product. It is practically possible to keep uranium in the concentrated phosphoric acid during the acidulation process by using an oxidant (1).

In fact, uranium could be recovered from the wet process phosphoric acid using many methods, namely solvent extraction, ion exchange, solvent impregnated resins, precipitation, and more recently the liquid membrane process.

Indeed, three organic solvents have been industrially applied for uranium recovery from 30% wet process phosphoric acid. This includes octyl pyrophosphoric acid (OPPA), di (2-ethyl hexyl) phosphoric acid (D2EHPA) with tri-octyl phosphine oxide (TOPO), as synergistic mixture as well as octyl phenyl acid phosphate (OPAP) (mono and di).

Di (2-ethyl hexyl) phosphoric acid (D2EHPA) is now considered as the most versatile of all the extractants commercially available today (5). It has been used at the phosphoric acid plants in Huelva, Spain, Natron, Westing House and Prayon, however the latter is the only one still working. This is due to its chemical stability, good extraction kinetics, good loading and stripping characteristics beside its low solubility in the aqueous phase and ability for extraction of many metals, and finally its commercial production. The chemistry of D2EHPA solvent extraction is considered to occur as indicated by the following equation:-



Indeed, D2EHPA can be mixed with many other organic solvents, however tri-octyl phosphine oxide (TOPO) is the best. The mixture of D2EHPA and TOPO is stable and exhibits a remarkable synergistic effect. Since it extracts uranium in the hexavalent state, uranium is generally stripped from the solvent by ammonium carbonate solution,

then precipitated as ammonium uranyl tricarbonate (AUC). In practice, the recovery of uranium from wet process phosphoric acid (30% P_2O_5) is firstly performed after dissolving D2EHPA/TOPO in an organic diluent such as n- dodecane and Amsco oderless 450. The uranium extraction is essentially conducted in two cycles, and extraction is performed under oxidizing conditions (emf=350mv). In the first cycle, the D2EHPA/TOPO ratio is 4:1 while in the second cycle it is 2.5:1. In the former cycle, uranium is reductively stripped from the organic extractant with concentrated H_3PO_4 strip solution containing ferrous iron as a reducing agent. However, in the second extraction cycle, uranium is stripped from the organic phase with an ammonium carbonate solution and precipitated as (AUC) (3).

The other alternative for uranium precipitation is to be precipitated as uranyl peroxide.

Recovery of uranium, vanadium, yttrium and rare earths from phosphoric acid by precipitation method was studied by Weterings and Janssen (4). By applying the precipitation method using NH_4F (0.06 kg/kg P_2O_5), uranium can be precipitated from both low and high concentrated phosphoric acids after the addition of a dispersing agent such as acetone (0.6 kg/kg P_2O_5). Variation of all the interesting parameters such as uranium valency, phosphoric acid concentration, type as well as quantity of both the dispersion and the precipitation agents have been also studied on a laboratory scale.

Experimental :

As previously mentioned, it is very difficult to extract uranium from the concentrated phosphoric acid by the known organic solvents. A successful contact has been made with Merck Co. Germany, to get some organic solvents that might prove effective in uranium extraction from concentrated phosphoric acid. A derivative of Tri-octyl-phosphine oxide (TOPO) which is tri-octyl-hexylphosphine oxide (TOHPO) was supplied to be tested as a mixture with di-2ethyl hexyl phosphoric acid (D2EHPA).

Uranium extraction experiments by D2EHPA/TOHPO were thus performed at room temperature by contacting a volume of concentrated green phosphoric acid assaying 90 ppm uranium (25ml) with a volume of D2EHPA/TOHPO mixture in a small glass bottle (100 ml) which is shaken by a thermostated mechanical shaker (400 r.p.m.) for a certain

time (5 minutes) . A trial to predict the number of counter current stages required for the studied uranium extraction system was accomplished by the use of the McCabe-Thiele diagram (5).

On the other hand, from preliminary experiments, it was found that the stripping process from the loaded D2EHPA/ TOHPO organic phase (assaying 143ppm uranium) by a relatively concentrated phosphoric acid can be successfully achieved at room temperature when applying an aqueous: organic ratio of 1:5 for 10 minutes contacting time . So, only the effect of the phosphoric acid molarity will be investigated in this study.

In order to study the feasibility of direct uranium precipitation from the prepared concentrated phosphoric acid, the procedure of Weterings et al (4), was tried. The uranium content in 100 gm of the high strength phosphoric acid (~ 52.7% P_2O_5) was reduced from U^{6+} to U^{4+} by mixing with 0.15 gm of iron powder for 15 min., at ambient temperature. At the end of the agitation time 3 l .2 gm acetone was added as a dispersion agent to the phosphoric acid followed by the addition of 3.162 gm NH_4F as precipitating agent. The mixing was continued for two extra minutes. Then, the precipitate containing U was filtered washed with water and acetone and analysed for its uranium content.

Results and Discussion :

Preliminary tests have proven that uranium recovery from the hemihydrate phosphoric acid is feasible using D2EHPA/TOHPO solvent mixture, so it was necessary to study in detail the different factors controlling such a process. First of all the potentiality of each organic solvent to recover uranium from the phosphoric acid was separately investigated.

I. Results of 50% P_2O_5 phosphoric acid pretreatment:

Acid pretreatment aims at overcome two essential problems; namely the presence of solids and organic matter in the acid which greatly affect the efficiency of the solvent extraction process. Accordingly, experiments conducted in this work include the following series:

i-Determination of the cooling temperature convenient for the solvent extraction process of the prepared phosphoric acid. In this respect, it was decided to cool the acid received from the hemihydrate

process to about 25-30 C in order to achieve additional solids precipitation from the phosphoric acid as well as to minimize possible diluent evaporation from the organic phase.

ii. Purification of the concentrated phosphoric acid by activated carbon columns to overcome the organic matter problem. This step was performed using a glass column of 2 cm diameter and 30 cm height packed with activated carbon. From the results of the preliminary experiments, it was possible to attain the conditions necessary to obtain sufficiently a pure concentrated phosphoric acid as well as to obtain the so-called green acid which has a low affinity for curde forming problems. These conditions involve the application of granular activated carbon (mesh size Imm) with an acid flow rate of ml/min to achieve the best retention time. Uranium adsorption by this type activated carbon was negligible (6) .

iii. Complete oxidation of the tetravalent uranium to the hexavalent state which is very important to the D2EHPA/ TOHPO organic solvent systems. Although the hemihydrate phosphoric acid process was performed under oxidizing conditions, it was found necessary to add 0.075 gm H_2O_2 (34%) to 1 kg of the green phosphoric acid to be sure that all uranium content is in the hexavalent state as well as to oxidize any remaining organic matter.

II. Results of uranium recovery from high strength phosphoric acid.

1- The extraction of uranium from the prepared hemihydrate phosphoric acid solution assaying 90ppm U, has been investigated at room temperature, while the D2EHPA concentration was varied from 0.01 M to 1.5 M for a contact time of 5 min, and an aqueous / organic ratio of 1/1 . The obtained results are presented in fig, (1). These results show that the best D2EHPA concentration obtained was 0.75M where a reasonable distribution coefficient was achieved (2.2). However, the efficiency of D2EHPA for uranium recovery from phosphoric acid is decreased above 0.75 M. From this result, It is concluded that D2EHPA alone is not sufficient to extract uranium efficiently from the hemihydrate phosphoric acid (7).

2- The effect of initial TOHPO concentration on uranium recovery were performed by shaking the hemihydrate phosphoric acid with TOHPO having concentration ranging from 0.06 M to 1.2M in an

aqueous / organic ratio of 1/1 for 5 minutes at room temperature (25 C). The obtained results are presented in fig. (2). These results indicate that the distribution coefficient increases with increasing TOHPO concentration up to 0.6M where a maximum distribution coefficient of only 2.6 was obtained. By further increasing of TOHPO concentration the distribution coefficient decreases. Thus TOHPO is also non efficient by itself to extract uranium from the hemihydrate phosphoric acid (7).

3- The effect of synergistic mixture from D2EH: PA/TOHPO on uranium recovery were performed by shaking the hemi-hydrate phosphoric acid with D2EHPA (0.75M) and different concentrations from TOHPO at aqueous /organic ratio of 1/1 for 5 mins. shaking time at room temperature. The obtained results are presented in fig.(3). These results indicate that the distribution coefficient increases with increasing TOHPO concentration up to 0.1 M. By further increasing TOHPO concentrations ,distribution coefficient decreases. Thus, the more efficient synergism is D2EHPA/TOHPO with concentrations 0.75M/O. 1M respectively.

4- The extraction of uranium from the hemihydrate phosphoric acid, at different temperatures, was investigated. The extraction experiments were carried out by contacting the hemihydrate phosphoric acid with a D2EHPA/TOHPO mixture (0.75/ 0.1M respectively) in kerosene for 5 minutes while the O/A ratio was fixed at 1/1 but the temperature was varied between 20 and 45°C. The results are presented in fig,(4). From the obtained data, it can be noticed that uranium recovery from the concentrated hemihydrate phosphoric acid (52% P₂O₅) can be performed in the range from 25-30°C. It is worthy to mention there in that the uranium recovery from the dihydrate phosphoric acid (~ 30% P₂O₅) is performed by two cycle of extraction. In the 1st cycle the temperature of the dihydrate phosphoric acid should cooled to 35°C which is higher than that used for the one cycle uranium extraction from the hemihydrate phosphoric acid.

5 - The effect of contact time on uranium extraction from the hemihydrate phosphoric acid has been investigated using D2EHPA / TOHPO mixture (0.75/ 0.1 M respectively)in kerosene at O/A ratio of 1/1 at 25°C while the contact time ranged from 30 sec to 5.0 minutes. The results are presented in fig (5) .From these results, it is found that the optimum contact time for loading uranium on the D2EHPA / TOHPO organic solvent mixture was 3 minutes.

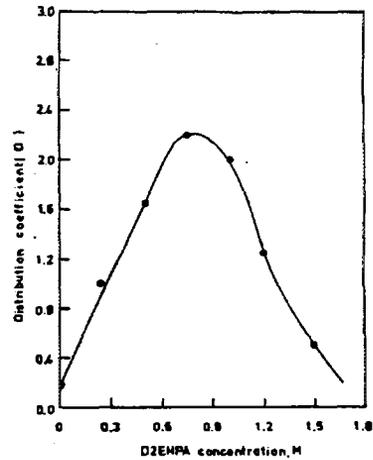


Figure 1 : Effect of initial D2EHPA concn. on the recovery of U from the hemihydrate phosphoric acid.

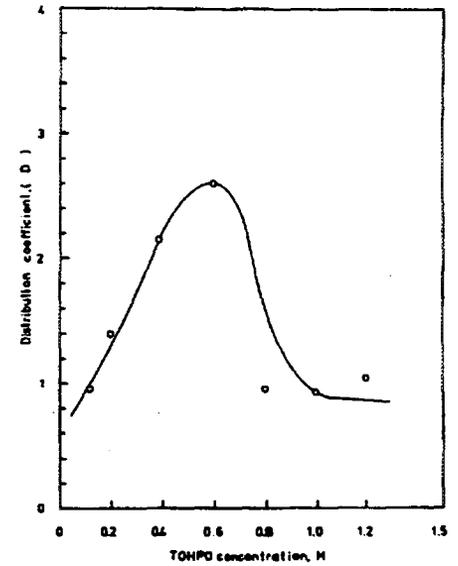


Figure 2 : Effect of initial TOHPO concentration on the recovery of U from the hemihydrate phosphoric acid.

6- Diluents do significantly affect both uranium extraction and phase separation characteristics. Accordingly, different diluents have been studied such as kerosene, benzene, n-hexane, xylene and diethyl ether. The used experimental conditions involved a D2EHPA/ TOHPO ratio of 0.75 M/0.1 M, respectively, O/A phases ratio of 1/1, a contact time of 3 minutes while the temperature was fixed at 25 C. From the obtained results represented in table (1), it is found that ordinary kerosene with a relatively high number of aliphatic carbons is much more convenient than aromatic diluents for uranium extraction from the study concentrated phosphoric acid ($D= 7.6$).

7- The effect of the aqueous / organic phase ratio on uranium recovery from the study concentrated phosphoric acid was investigated at an A/O ratio varying from 0.5 up to 5. All experiments were performed using D2EHPA/TOHPO (0.75M/0.1M, respectively) in kerosene for a contact time of 3 minutes at 25°C. From the obtained results, it is clear that by increasing the A/O ratio above 2/1 (which gives a distribution coefficient of 8) uranium extraction coefficient was decreased.

8- On the other hand the obtained data were used to construct the Mc- Cabe. Thiele diagram. From fig . (6), it can be concluded that in a continuous extraction system, four extraction stages are sufficient to recover 97.3% of the uranium content from the concentrated phosphoric acid. This diagram has been constructed using an operating line of a slope of 3.5. Accordingly 7, an A/O ratio of 3.5 would realize the mentioned extraction efficiency using the previously determined conditions. From all obtained results of studying the extraction relevant factors, it is clear that uranium recovery from high concentrated phosphoric acid (52.6% P_2O_5) is feasible after proper acid pretreatment and oxidation of uranium to its hexavalent state. Thus uranium recovery can be achieved in 4 counter current stages using 0.75 M D2EHPA/0.1 M TOHPO mixture in kerosene as a diluent in a 3.5:1 of aqueous-organic ratio and a contact time 3 minutes at 25C

9- The effect of phosphoric acid concentration as a suitable stripping solution on re-extraction of the reduced uranium from the loaded organic phase the previously mentioned experimental conditions with the addition of 0.15 gm ferrous iron /l was briefly investigated. The obtained data are presented in fig. (7) where it is quite clear that the stripping coefficient is primarily dependent on H_3PO_4 concentration.

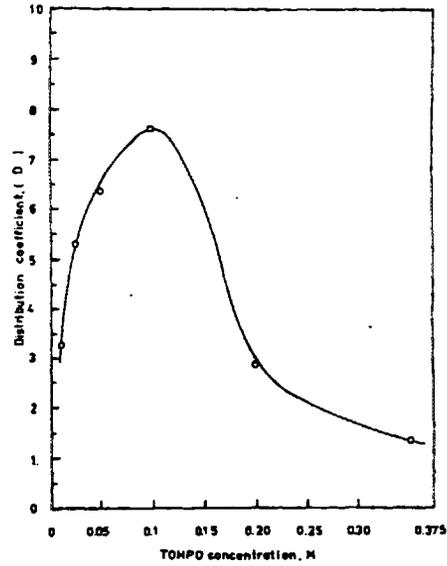


Figure 3 : Effect of synergistic mixture (0.75 D2EHPA -TOHPO) on uranium recovery from the hemihydrate phosphoric acid.

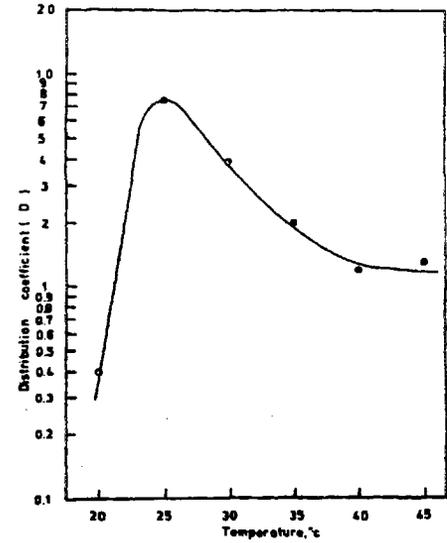


Figure 4 : Effect of temperature on uranium recovery from the hemihydrate phosphoric acid.

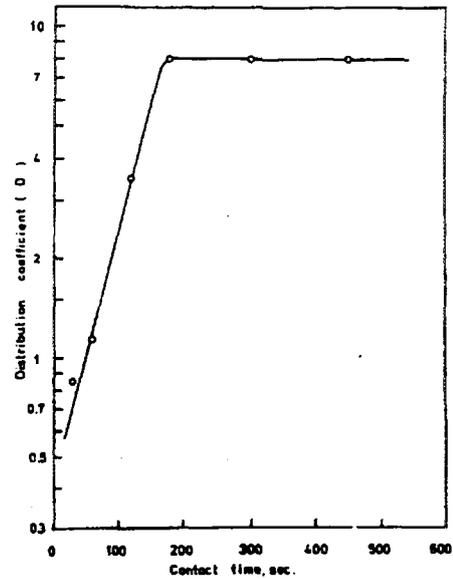


Figure 5 : Effect of contact time on uranium recovery from the hemihydrate phosphoric acid.

Table (1) : Effect of diluent on uranium recovery from the hemihydrate phosphoric acid.

| Diluent | U conc. , ppm | | Distribution Coeff., D. |
|----------------|---------------|------|-------------------------|
| | aq. | org. | |
| Benzene | 76.0 | 14.0 | 0.184 |
| Kerosene | 10.5 | 79.5 | 7.57 |
| Exylene | 80.0 | 10.0 | 0.125 |
| n-hexane | 50.0 | 40.0 | 0.80 |
| Di-ethyl ether | 58.0 | 34.0 | 0.61 |

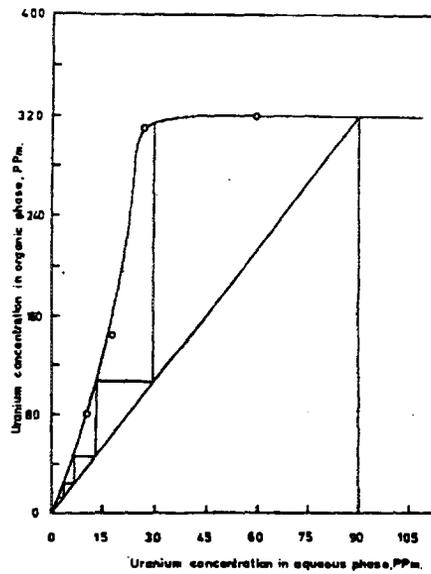


Figure 6 : McCabe-Thiele diagram of uranium extraction from the hemihydrate phosphoric acid.

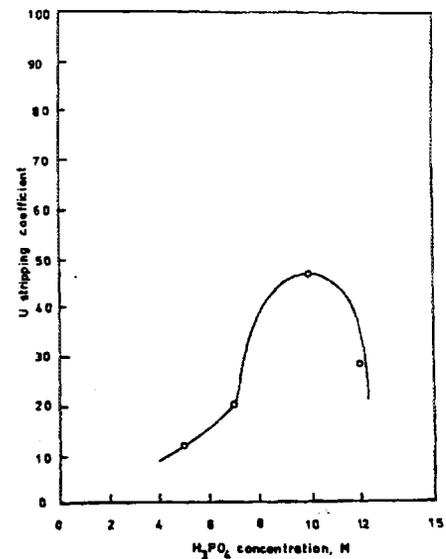


Figure 7 : Effect of phosphoric acid concentration on uranium stripping from loaded organic.

Thus, the uranium stripping was found to be very efficient when the phosphoric acid concentration attained 10 M which agrees with that found by Hurst (5).

III. Results of uranium precipitation from hemihydrate phosphoric acid:

Uranium has been precipitated from the obtained phosphoric acid strip solution assaying 1300 ppm by NH_4F (Weterings) (4) at ambient temperature. According to this author, X-ray diffraction analysis showed the presence of much (Al, Fe) $\text{NH}_4\text{HF}_2\text{PO}_4$ (S- Akyama) and churovite ($\text{Ca}_4\text{SO}_4\text{AlF}_6\text{SiF}_6\text{OH}\cdot 12\text{H}_2\text{O}$) and smaller quantities of $(\text{NH}_4)_2\text{SiF}_6$, $(\text{NH}_4)_2\text{SiF}_6\text{NH}_4\text{F}$, MgSiF_6 and $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ in the precipitate beside amorphous CaF_2 . It is clear also that the fluoride which was specially added, is precipitated along with the other substances. In this study the obtained precipitate weighed about 10 grams (100 g/kg hemihydrate phosphoric acid) while the uranium content assayed 0.585%. This result means that by applying Weterings precipitation method, it was possible to recover about 84.4% of the uranium in the strip solution which is very close to that obtained by this author. In an attempt to improve the process economics additional investigation should be performed on the recovery of the yttrium and REE. The latter can be recovered as > 90% and 80% respectively (Weterings) (4).

Summing up,

- 1- The possible application of one uranium extraction cycle instead of two cycles reported for the dihydrate phosphoric acid.
- 2- The direct precipitation of uranium from the strip phosphoric acid solution leads to 84.4% recovery of the uranium content.
- 3- The direct uranium precipitate can further be refined to obtain REE, V, and Y as by products which would add more benefits to the direct precipitation method.

Conclusion :

From the obtained data, it was possible to show that 97.3% of the uranium content of the ore was rendered soluble in the concentrated phosphoric acid prepared by the hemihydrate process. In addition, it was possible to extract about 90% of the uranium content in the concentrated phosphoric acid using the solvent mixture of D2EHPA-

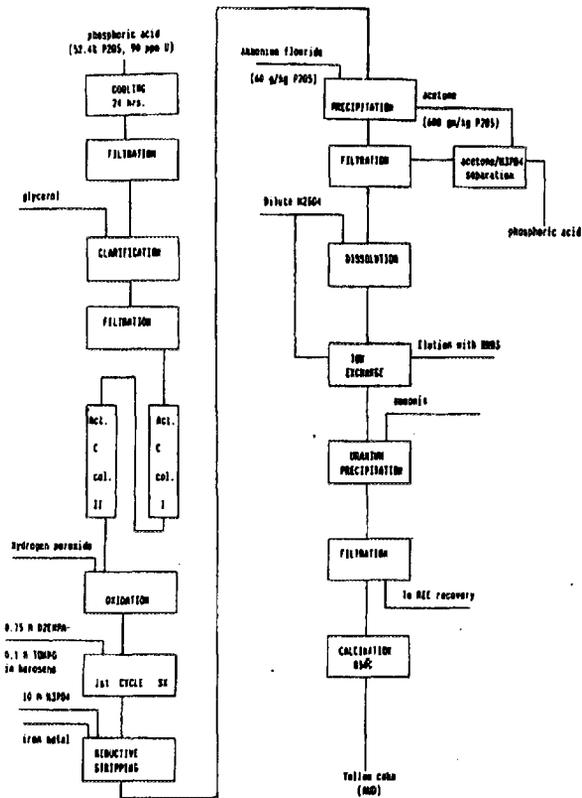


Fig. (8) : Proposed flowsheets for uranium recovery from concentrated phosphoric acid produced by the hemihydrate process by solvent extraction.

TOHPO as a new synergistic mixture in kerosene .The relevant factors indicate that uranium extraction increased with increasing solvent concentration up to 0.75 M D2EHPA- 0. 1 TOHPO at 25°C using three minutes contact time and an A/O ratio of 3.5/1.

Uranium has been stripped in this study by contacting the loaded organic phase with 10 molar phosphoric acid as an aqueous solution. This was followed by direct precipitation of uranium using NH₄F and adding acetone as a dispersing medium. The obtained data showed that the obtained precipitant contained 84.4% of the uranium content in the phosphoric acid. The obtained low grade uranium precipitate can furthermore be refined by solvent extraction or ion exchange to obtain conventional uranium concentrates (yellow cake) beside REE, V and Y as by- products; a matter which would add to the recovery of direct precipitation process.

On the other hand, the obtained data was utilized to construct a proposed Flowsheet (fig. 8) for uranium recovery from the phosphate ore using the hime hydrate process

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