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Studies of Uranium Recovery from Tunisian Wet Process Phosphoric Acid

Naima Khleifia[1], Ahmed Hannachi[1], and Noureddine Abbes[2]

[1]Chemical-Process Engineering Department,
National Engineering School of Gabes, University of Gabes,
Gabes, Tunisia

[2]Research Direction of Tunisian Chemical Group,
Gabes, Tunisia

ABSTRACT: The growing worldwide energy demand associated with several inter related complex environmental as well as economical issues are driving the increase of the share of uranium in energy mix. Subsequently, over the last few years, the interest for uranium extraction and recovery from unconventional resources has gained considerable importance. Phosphate rock has been the most suitable alternative source for the uranium recovery because of its uranium content. Solvent extraction has been found to be a successful process for uranium separation from phosphoric acid. The synergistic solvent mixture of Di-2-EthylHexyl Phosphoric Acid (DEHPA) and TriOctyl Phosphine Oxid (TOPO) diluted in kerosene has been the favored because of its high efficiency and selectivity for uranium extraction. In the present work, uranium extraction from Tunisian Wet Process Phosphoric Acid (WPA) using DEHPA in combination with synergistic reagent TOPO is presented. An experimental study was conducted in order to optimize the operating parameters affecting uranium recovery from phosphoric acid. The effect of temperature, solvent ratio, acid concentration and extractants concentrations were considered. The experiments were performed at a laboratory scale with batch extractions. Overall extraction yields are reported in this work. High uranium extraction yields exceeding 95% were obtained in all extraction steps but one where the yield was 92%. The overall recovery yield was 81%.

KEYWORDS: Uranium, industrial phosphoric acid, recovery, solvent extraction, yield.

1 INTRODUCTION

Nuclear power is expected to be an important part of the worldwide energy mix for the next 50 years. This in turn will make it necessary to develop alternatives and economically feasible technologies for the uranium production from sources other than uranium ore [1]. Many countries with limited energy resources, has invested substantial efforts in the study of uranium separation from non conventional resources such as coal, natural waters, including seawater and phosphate ores. These routes are technically feasible, economically attractive and potentially important because they may allow access to vast uranium resources [2].

Phosphate rocks have been the most suitable alternative source for uranium recovery. The concentration of uranium in phosphate rocks changes from one deposit to another, ranging from 50 to 200 ppm. It represents a significant potential source of uranium as large amounts of phosphate rock are processed [3]-[4]. Table 1, shows the uranium concentrations in phosphate rocks in various parts of the world.

Over the last few years, extensive studies on uranium recovery from wet-process phosphoric acid have been carried out. Various methods were used for uranium recovery from phosphoric acid. The most common are: solvent extraction, precipitation and ionic exchange [5]-[8]. Solvent extraction has been found to be the most successful process for industrial recovery of uranium from phosphoric acid [8]-[9].

Corresponding Author: Naima Khleifia (naima_khleifia@yahoo.fr)

Several solvent extraction processes have been developed [10]-[16]. Of the various extraction solvents reported in the literature, only three have a commercial interest:

- Octyl pyrophosphoric acid (OPPA)
- Octyl phenyl acid phosphate (OPAP)
- Synergistic solvent mixture of di-2-ethylhexyl phosphoric acid (DEHPA) and trioctyl phosphine oxide (TOPO).

While the first solvents are capable of extraction tetravalent uranium, the last extracts hexavalent uranium. Processes based on the latter are the most successful. Several plants adopting the DEHPA-TOPO solvent were constructed in many countries [17]-[19].

Exhaustive experimental studies were conducted in the literature on the uranium recovery from phosphoric acid employing different synergistic extractant mixtures. However, most reported studies were focused on uranium recovery from synthetic phosphoric acid solutions. Uranium extraction studies from real solutions are very scarce.

In the present paper, the uranium extraction process from Tunisian Wet Process Phosphoric Acid (WPA) using DEHPA in combination with synergistic reagent TOPO was considered. An experimental study has been carried out to optimize the main operating parameters affecting the uranium recovery from phosphoric acid. The considered variables are: temperature, solvent ratio, acid concentration and extractants concentrations. In this work, only extraction yields for each process extraction steps are reported.

Table 1. Uranium content of selected world phosphate rocks

Country	Uranium (ppm)
Tunisia	45 – 140
Algeria	25-100
Australia	80 – 92
Egypt	40 – 120
Jordan	46
Morocco	70 – 80
Saudia Arabia	25 – 185
Senegal	64 – 70
Syria	75
Tanzania	390
Togo	77 – 110
USA	41 – 200

2 URANIUM RESERVES IN TUNISIAN PHOSPHATE ORES

In Tunisia, the phosphate ores represent the most important source of uranium. They are extracted from four main locations in the Gafsa region in the southern part of the country: Metlaoui, Moulares, Redeyef and Mdhilla. Since the discovery of phosphate deposits in 1896, phosphate production is controlled and operated by Gafsa Phosphate Company (CPG). CPG currently processes annually an average of 8 million tons of commercial phosphates. Table 2 shows an average chemical composition and uranium content of the main exploited phosphate ores in Tunisia. The average uranium content in Gafsa basin phosphate ores is above 50 ppm. Phosphate reserves in these deposits are estimated to several hundreds of million tons. Consequently, the corresponding uranium amount in the phosphate reserves can be evaluated at 50 000 tons. Tunisia possesses other large phosphate deposits with reserves matching those of the Gafsa basin. They are located in Sraa-ouertane region in the north western part of Tunisia. Up to date, these reserves having an average uranium content of 100-140 ppm are not exploited.

Table 2. Typical chemical composition of the main exploited phosphate ores in Tunisia

Elément chimique	Metlaoui	Mdhilla	Moulares
P_2O_5 (%)	28,8	28,2	29,8
Fe (%)	0,18	0,10	0,18
Mg (%)	0,29	0,51	0,42
Al (%)	0,37	0,21	0,32
Cr (ppm)	115,0	84,0	139,0
Zn (ppm)	318,0	107,0	406,0
Cd (ppm)	37,0	20,0	50,0
Cu (ppm)	9,0	5,0	13,0
Ni (ppm)	12,0	7,0	23,0
Mn (ppm)	20,0	22,0	23,0
V (ppm)	32,0	31,0	53,0
U (ppm)	57,0	49,0	68,0

Nearly 80% of the extracted phosphate is processed into WPA and mineral fertilizers in the Tunisian Chemical Group (GCT). Tunisia is ranked among the top producers of phosphoric acid and fertilizers. Because of the huge quantities of processed phosphate ores in Tunisia, the corresponding uranium quantities are large. For instance, considering the presently processed phosphate quantities in GCT, the total amount of uranium at stake mounts to approximately 360 tons/year. This alone represents potentially a large resource of uranium when extracted economically as a by-product of the WPA production process.

In Tunisia, the WPA is produced by a chemical reaction of the phosphate rock with sulfuric acid according to the dihydrate process. This process involves the solubilization of most heavy metals and radionucleides contained in the raw material (Cd, U, Ni, Pb, Zn, Cr, Cu, etc.). A typical detailed analysis of Tunisian WPA is given in table 3.

Table 3. Typical analysis of Tunisian WPA

P_2O_5 (wt.%)	U (ppm)	Fe (ppm)	Mg (ppm)	Cd (ppm)	Al (ppm)	Cr (ppm)	V (ppm)	F (%)	SO_4^{2-} (%)
25	37	1500	2900	14	1860	160	38	0.82	0.91

3 MATERIALS AND METHODS

In order to economically obtain uranium from the WPA, recovery process should be investigated in detail. Therefore, experimental work has been conducted on a laboratory scale to select and optimize the operating parameters of each process step. To reach this aim, the experimental design method was used to study the effect of each parameter separately and their interactions. The main variables that can affect uranium recovery process were included: temperature, solvent ratio, phosphoric acid concentration, and extractants concentrations.

The WPA used in this study, of 25% wt. P_2O_5 content, was provided by the GCT. Its average chemical composition is shown in Table 3. Uranium extraction process flowsheet is shown in figure 1. The phosphoric acid has an initial ElectroMotive Force (EMF) of approximately 400 mV. Prior to extraction, the acid was treated with activated carbon for removal of soluble organic matter. The treated acid was oxidized with hydrogen peroxide till an adequately high EMF was obtained in order to convert all of uranium into the hexavalent state. The uranium rich pretreated phosphoric acid is extracted with DEHPA-TOPO system dissolved in kerosene. The extraction step is followed by a reductive stripping using phosphoric acid containing ferrous ions. In each of the previous operations, uranium gets concentrated in the main stream. The uranium content is further increased by performing a second extraction cycle. The uranium loaded acid, then feeds a second extraction step using the same solvent. Uranium is stripped from the organic solvent by an ammonium carbonate solution.

The DEHPA and TOPO used were of a purity exceeding 96%. The commercial grade kerosene was used as diluent after acid washing followed by alkaline solution neutralization and alkaline stripping with water. Extraction experiments were

carried out in covered beakers with a magnetic stirring and temperature control. The aqueous and organic phases were mixed and allowed to separate for 15 minutes. The uranium concentration in the aqueous phase was determined using a Jobain Yvon ICP 2000 spectrometer. The uranium content of the organic phase was calculated by mass balance.

4 RESULTS AND DISCUSSION

4.1 FIRST CYCLE OF URANIUM RECOVERY PROCESS

4.1.1 URANIUM OXIDATION

Hydrogen peroxide (H_2O_2) 30% wt. was employed as oxidizing agent in order to convert uranium into the hexavalent state. The electromotive force EMF was used as an indicator for the oxidation degree of uranium in the acid. To ensure that uranium was at its highest valence, the oxidant was added until the uppermost EMF value was reached. The effects of WPA concentration and temperature were examined to find the best operating conditions of this operation. Results showed that the temperature has a significant effect on contact time needed and subsequently on the hydrogen peroxide amount required for oxidation.

4.1.2 URANIUM EXTRACTION BY DEHPA-TOPO

The pretreated phosphoric acid with sufficient high EMF value is extracted with DEHPA-TOPO system. The study examined the effect of various factors on uranium extraction yield. Experiments were conducted at several levels of acid concentration, temperature, solvent rate and DEHPA-TOPO molar ratio according to a factorial design. The experimental domain was chosen in order to obtain the effect of each parameter on extraction performances. The results showed that the phosphoric acid concentration has a significant negative effect on the uranium extraction. However, the other parameters have slight effects on the extraction performance. The uranium extraction yield reached over 92% in the best operating conditions.

4.1.3 URANIUM REDUCTION

In the recovery process, uranium was stripped from the loaded DEHPA-TOPO solvent in the first cycle by reduced phosphoric acid. Iron was used as reducing agent. It was initially activated by sulfuric acid in order to enhance its reactivity and reduction capacity. The effect of the parameters affecting the reduction step was separately investigated. The operating parameters considered in the study were: contact time, temperature, phosphoric acid concentration and the amount of iron powder needed for the reduction. The electromotive force EMF was used as an indicator for the reduction degree of uranium.

The experimental study was intended to assess the best operating conditions for the reduction of U(Vl).The results showed that the reduction depends on the temperature, the iron acid initial content and the amount of added iron.

4.1.4 STRIPPING OF URANIUM FROM LOADED ORGANIC SOLVENT

The reduced acid was used to strip uranium from the organic extract exiting the extraction operation. The aim was to find the best operating conditions for the upper most uranium concentration in WPA. This study investigated the main operating parameters affecting the stripping operation. These were: phosphoric acid concentration, temperature and solvent rate. A factorial design was used. In the experimental study, results showed that uranium in the stripping acid could be 20 times, as much concentrated as the initial WPA.

4.2 SECOND CYCLE OF THE URANIUM RECOVERY PROCESS

4.2.1 URANIUM EXTRACTION

The uranium rich acid exiting the first cycle was diluted and oxidized before undergoing a second extraction with the same solvent. This operation was optimized following a similar procedure as for the first cycle. Results showed that the uranium extraction yield could reach 94%.

4.2.2 SOLVENT PURIFICATION

4.2.2.1 WASHING OF ORGANIC SOLVENT

The extract exiting the extraction step was then washed with distilled water. This treatment was intended to eliminate the traces of P_2O_5 in the extract. Washing experiments were conducted at several levels of washing rate. Results showed that the elimination rate of P_2O_5 increased with rising washing rate.

4.2.2.2 SEPARATION OF IRON FROM ORGANIC SOLVENT

Among the various impurities in the solvent, iron is one of the most detrimental to the quality of uranium oxide (U_3O_8). Often, iron is stripped using oxalic acid solutions. This stripping step was studied to find the best operating conditions: oxalic acid concentration and solvent rate. The experiments were conducted according to a factorial design. Under optimized operating parameters, 95% of iron can be stripped from organic solvent with uranium loss not exceeding 0.2%.

4.2.3 URANIUM STRIPPING BY AMMONIUM CARBONATE SOLUTION

The purified extract was then treated to extract uranium with an aqueous solution. The uranium stripping is mainly affected by the following factors: temperature, ammonium carbonate solution concentration and solvent rate. A factorial design was used to determine the best experimental operating conditions for the stripping operation. Results showed that all parameters had a significant effect on the extraction yield. At the best operating conditions, the average uranium extraction yield was 99%.

5 CONCLUSIONS

In this paper, an experimental work on uranium recovery process from the Tunisian WPA was reported. The DEHPA-TOPO dissolved in kerosene was used for uranium extraction step. The best operating conditions, for each uranium recovery process step, were selected according adequate experimental designs. Experiments were performed at a laboratory scale. In batch tests, under optimized operating conditions, a high uranium extraction yield was obtained. For three steps in the extraction process, out of four, the yields exceeded 95%. However, for the first extraction step, the yield was approximately 92%. The uranium rich solvent before exiting the second cycle was treated for purification purposes allowing to eliminate 95% of iron. The overall uranium extraction yield was 81%. The extraction yield could be further increased if continuous counter current extractions operations were performed.

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