Wet Process Phosphoric Acid Treatment by Hydrogen Peroxide

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Abstract

This work reports an experimental study on the increase of Electromotive Force (EMF) of Wet Process Phosphoric Acid (WPA) using hydrogen peroxide (H₂O₂) 30% wt. as oxidizing agent. This operation allows oxidizing many chemical species of WPA and is used as a preachment to metal extraction from the acid. The EMF was used as an indicator for the oxidation degree of chemical species contained in the acid. To ensure that relevant chemical species were at their highest valences, the oxidant was added until the uppermost EMF value was reached. The effects of WPA concentration and temperature were examined. The experimental results led to the determination of the best operating conditions of uranium oxidation in WPA produced from processing the Tunisian phosphate. For the WPA concentration range 25-35% wt. P₂O₅, the required H₂O₂ amount is independent of the acid concentration. The temperature increase reduces the contact time and the oxidizing agent specific consumption.

Keywords: Oxidation, Treatment, Hydrogen Peroxide, Phosphoric Acid, Electromotive Force

1. Introduction

The worldwide energy need is basically provided by coal, hydroelectric power, nuclear energy, oil and natural gas. Unfortunately, the perspectives of renewable energy having a significant share in the foreseeable future are very slim. In recent years, the growing worldwide energy demand associated with rising oil prices and reserves depletion are responsible for the rapid increase of nuclear energy demand. Despite the setback in the electronuclear energy, as a result of Fukishima disaster in 2011, all indications related to complex environmental as well as economical issues predict a significant increase in nuclear energy demand in the coming decades. That is justified by the increasing planned constructions of new electro-nuclear plants. The development of nuclear energy drove the growing interest of uranium extraction from non conventional resources such as: Phosphate rocks, sea water. Phosphate rocks, which are chemically processed for phosphoric acid and fertilizer production, are the most suitable alternative source for the uranium recovery. The uranium concentration in phosphate rocks changes from one deposit to another but, in general, it is within the range of 50 to 200 ppm (Ragheb & Khasawneh, 2010).

Tunisia, one of leading countries in phosphate production, transforms about 80% of phosphate rocks into phosphoric acid and fertilizer. The Tunisian processed phosphate contains uranium at a concentration level of 50 ppm. The Tunisian Wet Process Phosphoric Acid (WPA) is produced by a chemical reaction of the phosphate rock with sulphuric acid according to dihydrate process. In this process, typically 80% of uranium present in the raw material passes into the phosphoric acid in the form of U(IV) and U(VI) ions. When uranium is recovered from the WPA, this will allow increasing the profitability of phosphate transformation as well as improving fertilizers quality. This also will contribute to reduction of the negative environmental impact of
fertilizers use (Khleifia et al, 2013).

Several processes have been conceived for the recovery of uranium from WPA. The first industrial trials were based on solvent extraction (Hurst, 1972). Three commercial processes have been developed using the following extractants:

- Octylphenyl phosphoric acid (OPPA) (Hurst, 1983)
- Mixture of mono- and di-octylphenyl phosphoric acid (OPAP) (Hurst, 1974)
- Mixture of di(2-ethylhexyl) phosphoric acid (DEHPA) and trioctylphosphine oxide (TOPO) (Gasó & Moral, 1983)

The DEHPA-TOPO process has been the favoured because of its high efficiency and selectivity for the uranium extraction. In fact this extracting agent has a great affinity with uranium (VI), predominant uranium valency in WPA. The presence of small fraction of tetravalent uranium reduces the yield of the uranium recovery process. That is why this fraction should be transformed into the hexavalent form prior to the extraction operation. This is performed by oxidizing agents such as: NaClO₄, HNO₃ and H₂O₂ (Koudsi et al, 1995).

The overall extraction process includes several chemical and physicochemical steps in which oxidation is a key component. In the oxidation step, uranium (IV) is oxidized into U (VI) by an appropriate oxidizing agent. Hydrogen peroxide H₂O₂ is considered to be a particularly suitable oxidant that does not degrade the acidic properties. It will rapidly oxidize the uranium in the WPA (Koudsi et al, 1995). Uranium is oxidized by the hydrogen peroxide according to the following reactions:

\[ 2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \]

\[ 2Fe^{3+} + U^{4+} \rightarrow 2Fe^{2+} + U^{6+} \]

The research studies on the uranium oxidation in phosphoric acid solutions reported in the literature indicate that the oxidation depends on contact time and the oxidant amount. Experimental investigations on oxidation using 0.25 M Fe (III) solution as an oxidizing agent for treatment of 5 M synthetic phosphoric acid containing 6.3x10⁻³ M U (IV) at a temperature of 50 °C showed that the oxidation yield reached its maximum after 90 min (Daoud et al, 2002). Studies on oxidation of phosphoric acid at 25 °C and 29% wt. P₂O₅, using 30% wt. H₂O₂ showed that the oxidation required a period of 2 hours with a specific oxidant consumption of 1.8 g H₂O₂/kg P₂O₅ (Koudsi et al, 1995). The experimental results of Jordanian phosphoric acid oxidation showed that an Electromotive Force (EMF) of 450 mV was sufficient to oxidize almost all of the uranium (Khaled et al, 2002).

The available literature relative to uranium oxidation in WPA is scarce. Furthermore, most of the reported results are for synthetic phosphoric acid solutions. Several aspects need to be investigated. Indeed, the amount of oxidant and the oxidation contact time vary according to the WPA quality. Limited information is available on EMF evolution during the oxidation step. The objective of this work is to carry out an experimental study for the uranium oxidation in Tunisian WPA. The ultimate goal is to define the best operating conditions for the oxidation process.

2. Materials and Methods

In the experimental investigation, the uranium rich WPA was provided by the Tunisian Chemical Group. Before oxidation, the WPA was subject to a pre-treatment process that aimed to reduce the suspended solids and the organic matter contents of the acid. Typical analysis of key elements in the pre-treated WPA is given in Table 1.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Components Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>P₂O₅</td>
<td>25 wt.%</td>
</tr>
<tr>
<td>U (ppm)</td>
<td>37 ppm</td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>1500 ppm</td>
</tr>
<tr>
<td>Mg (ppm)</td>
<td>2900 ppm</td>
</tr>
<tr>
<td>Al (ppm)</td>
<td>1860 ppm</td>
</tr>
<tr>
<td>SO₄²⁻ (%)</td>
<td>0.91 wt.%</td>
</tr>
</tbody>
</table>

The oxidizing agent is the analytical grade hydrogen peroxide 30% wt. Experiments were conducted to investigate the kinetics of uranium (IV) oxidation in the Tunisian WPA. The aim was to unfold factors that affect the uranium oxidation. The parameters considered were the contact time, the temperature and the WPA concentration. The temperature range covered in this study was 25-60 °C, while the WPA concentration varied from 25-35% wt. P₂O₅. Oxidation experiments were carried out in an agitated covered beaker equipped with a temperature regulation system. The WPA was heated until the desired temperature is obtained, then regular injections of H₂O₂ with a microlitre syringe were performed. The evolution of the EMF of WPA determined at constant temperature of 25±2 °C with a potentiometer was followed as added hydrogen peroxide amount increased. Two electrodes were used, an Ag/AgCl reference electrode and a platinum electrode. These electrodes were immersed in a 200 ml cell containing the oxidized WPA. All along the investigation the measured value was recorded when the EMF reached a stable value within
a ±1 mV fluctuation. The electrodes were daily conditioned with an appropriate electrolyte system and checked before each measurement series.

3. Results and Discussion

The objective of this work was to determine the best operating conditions of uranium oxidation in WPA such as contact time, temperature, concentration of WPA and the required quantity of oxidizing agent. The oxidation was induced by regularly injecting 1 µL of 30% wt. hydrogen peroxide every minute.

3.1. Kinetics of Oxidation

The kinetics of uranium oxidation by peroxide hydrogen is illustrated in Figure 1. The oxidation was carried out at the operating conditions: T=60 °C and 24 % wt. P₂O₅. The initial EMF of the WPA was close to 400 mV. As the H₂O₂ was added, the EMF of the solution increased. This is demonstrated in Figure 1 where the EMF difference between the reached EMF value and the initial one (EMFₜ=0) evolution against time is presented. After approximately 10 min the EMF reached a plateau at 770 mV. Beyond this point any additional amount of H₂O₂ had no effect on the solution EMF. That is, all chemical species contained in the acid have reached their highest oxidation degree. This is also true for uranium that should be completely transformed in the uranium (VI) form. Therefore the H₂O₂ needed for total uranium oxidation is 0.16 mL/kg P₂O₅ for a WPA at 24% wt. P₂O₅ and the oxidation time is about 10 min.

![Figure 1. EMF Versus Contact Time (Temperature: 60 °C, WPA Concentration: 25% wt. P₂O₅)](image)

3.2. Effect of Temperature

The hydrogen peroxide required amount depends on the oxidation conditions which may vary with the origin of the WPA and with each process configuration. Temperature is one of the conditions which may affect considerably oxidation reactions and kinetics. In this study, the oxidation temperature was varied from 30-60 °C. The temperature effect on uranium oxidation is presented in Figure 2; where the EMF difference is presented as a function of the added H₂O₂ amount. The initial WPA EMF for the considered temperatures was 400±20 mV. It is clear that at low temperatures i.e. below 45 °C, there were two plateaus for the EMF. This suggests that the oxidation of all chemical species does not occur at the same EMF. For lower oxidation temperatures, the required H₂O₂ amount is slightly higher. At 60°C, all chemical species were oxidized simultaneously and only one EMF plateau is observed where the level of EMF was approximately 800 mV. One can concluded that increasing the temperature reduces the contact time and also the quantity of oxidizing agent required for oxidation process.

![Figure 2. EMF Difference Versus the Amount of Added H₂O₂ at Different Temperature](image)

3.3. Effect of Acid Concentration

The range of acid concentration used in this study was between 25-35% wt. P₂O₅. The effect of acid concentration on oxidation at 60 °C is shown in Figure 3; where the EMF difference is presented against the amount of added H₂O₂.

![Figure 3. EMF Difference Versus the Amount of Added H₂O₂ at Different Acid Concentration](image)

The initial WPA EMF for the covered concentration range
was about 400±20 mV. It is seen, that the EMF presents a similar behaviour, with one plateau, for all acid concentrations. However, in order to guarantee the uranium extraction operation, the amount of oxidizing agent added should be in excess of the stoichiometric amount involved in all oxidation reactions to account for the hydrogen peroxide consumption to oxidize organic matter and other metals. The results showed that no significant change in the WPA EMF difference for different acid concentrations. This means that the amount of H$_2$O$_2$ needed for uranium oxidation is independent of the acid concentration for the investigated concentration interval for the WPA despite the differences in concentration levels of the various species present in the acid.

3.4. Effect of Post Oxidation Rest Time

The oxidized WPA will undergo extraction operations, it is then very important to know how the post oxidation rest time will affect the EMF. This was investigated by letting the oxidized WPA to rest for a long period during which EMF was recorded. The used WPA had a concentration of 25% wt. P$_2$O$_5$ and was initially at 60 °C. No temperature regulation was performed. The results are plotted in Figure 4 in the form of EMF versus time in a semi-log scale. It was found that, after 75 min the EMF of oxidized acid started to significantly decrease. The decline of the EMF solution can be related to the occurrence of many complex reactions in the acid which could induce the reduction of a fraction of the uranium hexavalent form. This result shows that the time interval between the two successive operations of uranium oxidation and extraction is limited.

3.5. Effect of Temperature Decrease on Oxidized Acid EMF

The uranium extraction can be performed at a temperature different from that of the oxidation. It is then very important, to see how variation of acid temperature can affect the EMF. The oxidized WPA was initially at 60 °C. It was left to exchange heat with the ambiance and cool. The EMF was recorded monitored along the cooling process. Figure 5 shows the effect of temperature decrease on the EMF of the WPA after the oxidation operation. No significant change of acid EMF was observed when the temperature decreases from 60-30 °C. Therefore, during the WPA cooling, the oxidized chemical species in the acid will remain at their highest oxidation degree. The extraction of uranium can be performed at a temperature different from that of WPA oxidation.

4. Conclusion

The hydrogen peroxide 30% wt. H$_2$O$_2$ has been used in this study to oxidize the chemical species present in Tunisian WPA. Oxidation experiments were carried out to determine the effect of oxidation time, temperature, acid concentration and the amount of 30% wt. H$_2$O$_2$ needed for acid treatment. A study of oxidation was carried out by measuring the EMF of WPA as function of the quantity of oxidizing agent added at regular time intervals. Results showed that the temperature has a significant effect on contact time needed and also on amount of H$_2$O$_2$ required for oxidation. Furthermore, the effect of rest time and temperature on post oxidation was studied. The results showed that the time between the two successive operations of uranium oxidation and extraction should be limited.

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References


