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Uranium Production as a Byproduct from Yarimca Phosphoric Acid Plant (Turkey)

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Abstract

This paper deals with uranium production from the phosphoric acid products of Yarımca Fertilizer Plant. After examination of the phosphate rocks consumed in this plant and the acid products, solvent extraction tests were conducted to determine the effects of acid concentration, solvent concentration in kerosene, contact time and acid/solvent ratio on the recoveries of uranium. 98 % of total uranium in acid was recovered in the organic phase by applying 5 stage extraction. Following the extraction tests, acidic and basic stripping were applied to organic phase and uranium was precipitated as yellow cake from the stripping solutions. In the stripping tests mainly aqueous/organic phase ratio and stripping time were investigated using HCl and Na_2CO_3 as stripping agents. Na_2CO_3 provided higher uranium recoveries both at the short time and low ratio of the stripping solution. Yellow cakes were produced containing 13-18.4 %U_3O_8 from acidic and 30-46.4 % U_3O_8 from basic stripping solutions.

INTRODUCTION

Uranium recovered from wet process phosphoric acid accounts for about 5 % of current world production. About 2000 tons per year uranium is produced as by products from the several phosphoric acid plants located in the U.S.A., U.K., Canada, and Spain [1, 2].

Yarımca phosphoric acid plant, which is subjected to this study, consist of phosphoric acid, super-phosphate and triple super-phosphate units. Phosphoric acids with 28 and 50 % P_2O_5 contents are produced in this plant with the annual capacity of 150.000 tons, on the basis of the acid containing 50 % P_2O_5.

In this paper, the properties of the raw materials, which are fed to Yarımca phosphoric acid plant, were investigated as well as the phosphoric acid products. Extraction tests were conducted to estimate the best extraction conditions. After applying 5 stage extraction under the optimum conditions, the stripping tests were conducted and uranium was recovered as yellow cake after precipitation.

MATERIALS AND METHOD

The properties of phosphate rocks from Morocco, Senegal and Togo were fed to Yarımca phosphoric acid plant during this investigation, are shown in table 1.

From the phosphate rocks, the dilute and concentrated phosphoric acid were produced in the plant. The properties of these products can be seen at Table 2. Concentrated and dilute phosphoric acids contain, 142-260 and 68-120 mg/l U_3O_8, respectively, with the highest value in the acid produced from Morocco phosphate rocks. Uranium recoveries of the phosphoric acids were calculated as 80-95 % metal, after uranium analysis of tailings, which contain not more than 6 ppm U_3O_8.

Table 1: Properties of the Phosphate Rocks

Element	Morocco	Senegal	Togo
U_3O_8 ppm	136	85	95
P_2O_5 %	33.01	36.72	36.75
CaO %	53.53	52.40	50.12
SiO_2 %	1.09	2.80	2.20
Al_2O_3 %	0.36	1.04	1.02
Fe_2O_3 %	0.22	0.19	1.05
MgO %	0.49	0.13	0.13
K_2O %	0.05	0.01	0.04
Na_2O %	0.18	0.04	0.30
F %	3.30	3.35	3.50
Cl %	0.08	0.05	0.15
SO_3 %	1.85	0.32	0.57
Loss of Ignition	6.90	2.91	4.12

Table 2: Properties of the Phosphoric Acids

Analysis	Morocco		Togo		Senegal	
	Dilute	Conc.	Dilute	Conc.	Dilute	Conc.
U_3O_8 mg/l	120.0	260.0	68.0	142.0	100.0	215.0
P_2O_5 g/l	332.5	850.4	329.4	808.3	337.8	755.8
MgO g/l	4.4	10.8	0.7	1.5	0.8	1.9
K_2O g/l	0.3	0.4	0.6	0.8	0.3	0.3
Na_2O g/l	1.5	2.3	1.4	1.9	1.0	0.2
CaO g/l	0.2	---	1.2	---	0.4	0.2
SO_3 g/l	24.9	47.9	18.6	34.1	12.9	18.4
Fe g/l	1.8	4.4	6.1	9.3	5.4	11.6
Cl g/l	Trace	Trace	Trace	Trace	Trace	Trace
F g/l	13.2	25.60	12.5	20.8	11.83	19.70
Color	Green	D. Green	Brown	D.Brown	Green	D. Green
P_2O_5 %	26.2	53.2	26.1	50.5	26.6	47.8
Sp. Gr.	1.27	1.60	1.26	1.60	1.27	1.58

EXPERIMENTS

Solvent Extraction

Solvent extraction tests were applied to dilute and concentrated phosphoric acids containing 120 and 260 mg/l U_3O_8, respectively. Organic solvent were chosen as octyl pyro-phosphoric acid (OPPA) diluted in kerosene [3]. After determination of the oxidation potentials of acids [4], which were sufficient for the extraction studies, experiments were conducted to investigate the optimum conditions relating to the OPPA concentrations in kerosene, phosphoric acid concentrations, OPPA/acid contact time and the ratio of OPPA and acid. At the end of these extraction tests, 5 stage extraction was applied to dilute phosphoric acid under the optimum conditions [5, 8, 11].

Experimental Procedures

A 240 ml separation funnel was used in the extraction tests with a glass stirrer in it. Octyl pyro-phosphoric acid was prepared in the laboratory by mixing octyl alcohol and phosphor penta-oxide [9]. This organic solvent was diluted in kerosene (1-7 percent) before using in the extraction tests. Experiments were conducted at room temperature according to the results of the previous tests [6, 10].

OPPA Concentration in Kerosene

In the first series of experiments; OPPA concentration in kerosene was changed between 1 and 6. Experiments were conducted under the constant conditions of 1/1 OPPA/acid ratio and two minute contact time for dilute and concentrated acids. The effect of OPPA concentration to extraction recoveries of uranium are shown in Figure 1.

Extraction recoveries increase linearly until 4 % in both acids with higher values for the dilute one. Recoveries are 50 and 75 percent, respectively, at the point of 4 % OPPA in kerosene for concentrated and dilute acids.

Effect of Phosphoric Acid Concentration

Experiments were conducted to determine the proper acid concentration for uranium extraction from the phosphoric acids. In these experiments, the constant conditions were OPPA concentration in kerosene (2 %), OPPA/acid ratio (1/1) and the contact time (2 mins.). As in Figure 2, uranium can be recovered much better in dilute acid than the concentrated one with the highest value of 90 % uranium at 10 % of acid concentration.

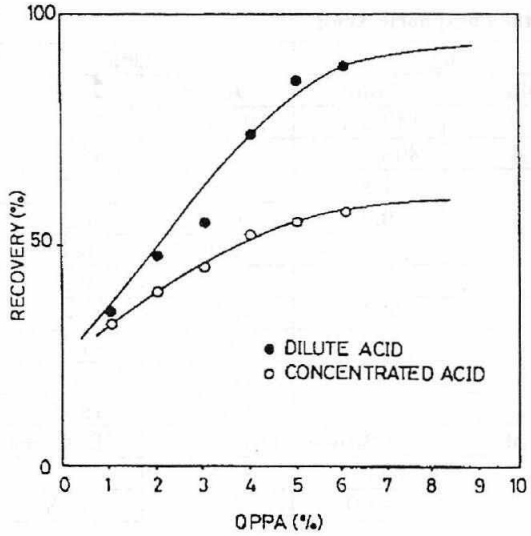

Fig. 1: Effect of the OPPA Concentration on the Uranium Recovery

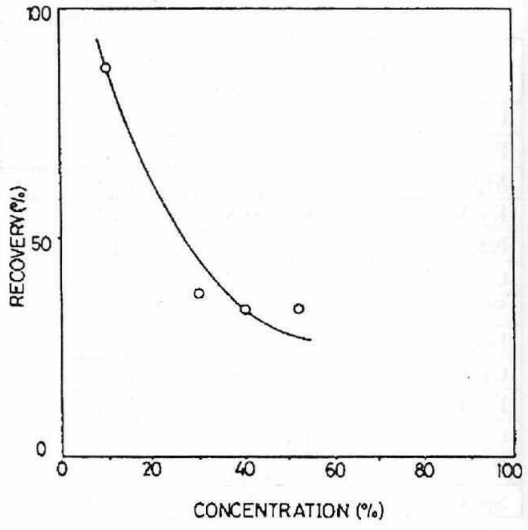

Fig. 2: Effect of the Phosphoric Acid Concentration on the Uranium Recovery

Effect of Contact Time

The contact time between the extractant and the aqueous solution was investigated for dilute and concentrated phosphoric acids. In this series of experiments, the time was changed between ½ and 10 minutes using two % OPPA in kerosene and 1/1 OPPA/acid ratio. The recoveries of uranium extraction remained the same after the first minute (see Figure 3), with the values of 50 % in dilute acid and 40 % in the concentrated one.

Effect of OPPA/Acid Ratio

In the last series of extraction tests, the effect of OPPA/acid ratio were investigated between the values of 1/16 and 1/1. During this group of experiments, OPPA concentration and contact time were constant as 2 % and one minute, respectively. As in Figure 4, the extraction recoveries slightly increases (between 30 and 40 percent) in concentrated acid with the increasing of the OPPA/acid ratio, although these values have changed between nearly 10 and 50 % for dilute acid.

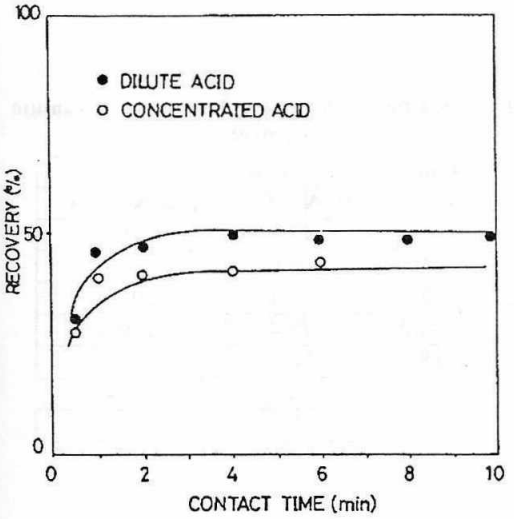

Fig. 3: Effect of Contact Time on the Uranium Recovery

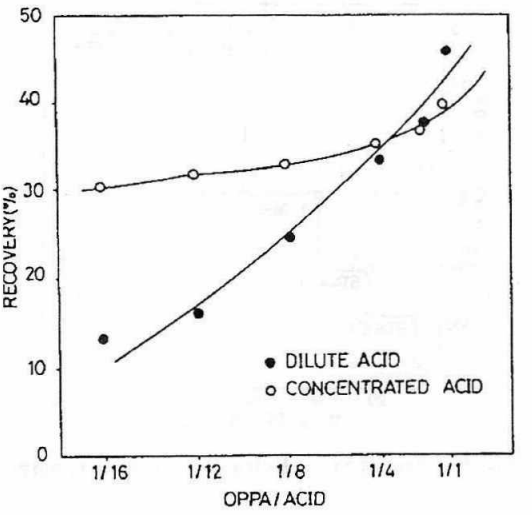

Fig. 4: Effect of the OPPA/Acid Ratio on the Uranium Recovery

Extraction Tests

Five stage extraction was applied to dilute phosphoric acid in order to recover the most of uranium in the organic phase. Experiment was conducted under the following conditions:

OPPA Concentration	:	5 % in kerosene
Contact Time	:	1 minute
OPPA/Acid Ratio	:	1/4
Stage Number	:	5 (fresh extractant was added in each stage)

The diagram for 5 stage extraction can be seen in Figure 5. Uranium recovery in the organic phase is only 46 % after the first stage. This value can be raised to 67, 81, 94 and 98 % by applying 4 more stages using fresh organic solution at each stage. As a result, after five stages of extraction, only 2 % of uranium can be left in the dilute phosphoric acid.

Stripping and Precipitation of Uranium

Strong acids and bases are recommended [7] to strip uranium from the alkyl pyro-phosphoric acid type solvent. In this study, hydrochloric acid and sodium carbonate are chosen as stripping agents depending on the results of the previous study [9]. Stripping tests with 10 N HCl solution were conducted after oxidation of U^{+4} to U^{+6} by 4 g/l sodium chlorate. In the case of sodium carbonate, no oxidation agents were used for this purpose. The stripping time, stripping solution/OPPA ratio were investigated in the experimental study and stage stripping was applied with both reagents under the optimum conditions. At the end of this study, uranium was recovered as yellow cake from the aqueous solutions.

Effect of Stripping Time

The stripping time was changed between 0.5-60 minutes in the experiments with both 10 N HCl and 1 M Na_2CO_3 solutions under the conditions of 2 % OPPA in kerosene containing 0.5 g/l U3O8 and the ratio of 1/1 between stripping agent and OPPA. As in Table 3, two minutes of stripping time is sufficient for Na_2CO_3 solution but more than 30 minutes are necessary for appreciable uranium recovery with HCl solution.

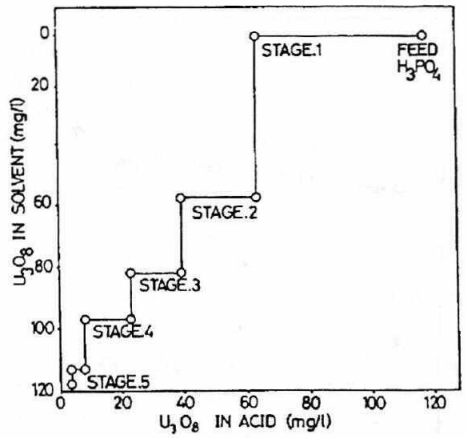

Fig. 5: Effect of Stage Extraction on the Uranium Recovery

Table 3: Effect of Stripping Time on the Uranium Recovery

Time mm	U Recovery %	
	10 N HCl	1 M Na_2CO_3
0.5	45.3	98.0
1.0	65.0	99.2
2.0	71.1	100.0
8.0	75.4	100.0
15.0	78.4	---
30.0	88.2	---
60.0	99.0	---

Effect of Stripping Agent/OPPA Ratio

Under the same conditions of the previous experiments the ratio of aqueous and organic phase was changed by applying 2 minutes of the stripping time. Table 4 presents stripping recoveries of uranium depending on the acid/OPPA and carbonate/OPPA ratios. Although a small amount of aqueous solution is sufficient in basic stripping, acidic stripping requires almost equal amounts of organic and stripping solutions.

Table 4: Effect of the Aqueous and Organic Solution Ratio on Stripping of Uranium

Ratio Aqueous/OPPA	U Recovery %	
	10 N HCl	1 M Na_2CO_3
1/1	71.1	99.2
1/2	45.8	98.3
1/4	13.0	96.1
1/8	---	93.2
1/10	---	92.4

Stage Stripping Tests

Stage stripping tests were performed with 1/2 and 1/4 acid/OPPA ratios and 1/10 carbonate/OPPA ratio under the previous conditions.

Table 5: Effect of Stage Stripping on the Uranium Recovery

Stage No	U Recovery %		
	Acid/ OPPA 1/2	Acid/ OPPA 1/4	Carbonate/ OPPA 1/10
1	45.8	23.0	92.4
2	72.9	44.9	99.5
3	89.6	68.3	100.0
4	99.0	80.7	---
5	---	93.7	---
6	---	98.4	---
7	---	99.7	---

It can be seen at Table 5 that 4 stage stripping for 1/2 ratio and 7 stage for 1/4 ratio is necessary when HCl is used as stripping agent. In the case of Na_2CO_3, two stage stripping is sufficient for more than 99 % of uranium recovery.

Production and Properties of Yellow Cake

Uranium was precipitated from acidic solution by neutralization with ammonia. After filtration and drying at 105°C, the yellow cakes containing 13-18.4 % U_3O_8 were produced with 99.5 % recovery from the acidic solutions containing 2 and 3 g/l U_3O_8.

In the case of Na_2CO_3 solutions, at first pH value was dropped to 3 with sulphuric acid. Following this treatment uranium was precipitated again by neutralization of this acidic solution with ammonia. Yellow cakes containing 30-46.5 % U_3O_8 were produced with the recoveries of 99-97.8 % depending on the concentrations of stripping solutions which were changed between 7.2 and 20 g/l.

CONCLUSIONS

- The imported phosphate rocks consumed in Yarımca Phosphoric Acid Plant contain 85-136 ppm U_3O_8.
- 80-95 % of uranium in these rocks can be recovered in the acid phase after phosphoric acid manufacturing.
- Dilute and concentrated phosphoric acids are produced at Yarımca Phosphoric Acid Plant, containing 26-27 % and 48-53 % P_2O_5 respectively. Uranium values of these acids are 70-120 mg/l U_3O_8 in the dilute and 140-260 mg/l U_3O_8 in the concentrated one.
- Dilute phosphoric acids are most suitable for the solvent extraction process with octyl pyro-phosphoric acid as extractant.
- The best conditions for extraction were found as 5 % solvent in kerosene, 1/4 organic/aqueous ratio and under this condition, 98 % of uranium can be extracted after 5 stage extraction.
- Stripping of uranium from organic phase with HCl requires high concentration of acid (10 N), high aqueous/organic ratio (1/1-1/4) and long stripping time. Four stage stripping for 1/2 ratio and 7 stage stripping for 1/4 ratio are necessary for high uranium recovery.
- Sodium carbonate as stripping agent provides appreciable results at short stripping time and low aqueous/organic ratio (1/8-1/10) when its concentration in water is 1 M
- Yellow cakes containing 13-18.4 % U_3O_8 are produced from acidic solutions after neutralization with ammonia. In the case of basic solutions 30-46.5 % U_3O_8 in yellow cakes were obtained depending on the concentration of the stripping solutions.

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