Int. j.econ. & environ. geol. vol:1(2) 30-34

Uranium Extraction from Syrian Phosphate: A Case Study

J. STAS, I. OTHMAN* , M. ABBAS AND H. SHLEWIT

Syrian Atomic Energy Commission, P.O. Box 6091, Damascus – Syria*. atomic@aec.org.sy

---

Abstract. Uranium and trace elements were studied in few hundred samples from phosphatic formations in Syria. Uranium and trace elements were enriched in phosphorites facies compared to carbonate and siliceous facies. Uranium content of Syrian phosphorite by fission track method shows that uranium is related to the apatite mineral and organic matter. The concentration of uranium in phosphatic elements depends on the quality of these elements (grains, biogenic-elements). Further, uranium is relatively mobile during biomicritisation, coating and weathering. Investigation of uranium extraction from phosphoric acid produced at Homs plant (G.F.C) by using phosphate concentrate from Khneifiss and Charquieh mines, have been carried out in a micro pilot and pilot plant scales. The results show that the yield of uranium extraction from H_3PO_4 is more than 95%.

Introduction

Phosphate deposits occur in many areas in Syria-the palmyrides, the coast and Syrian desert (Fig. 1). These deposits belong to two stratigraphic periodes- the Senonian in the palmyrides and coastal area and the lower Eocene in the Syrian desert. The global reserves of phosphate were estimated to about 1 billion tons for all deposits (Atfeh, 1967).

Phosphate is exploited since 1970 in two sectors near the historic town of palmyra- Khneifiss and Charquieh in the central palmyrides. The annual production of phosphate is about 2 million tons/year. Most of the produced phosphate is exported and a small part is used in local fertilizer industry in the TSP plant at Homs. Like all sedimentary phosphate deposits, Syrian deposits are formed by hard and loose phosphorite levels (>18% P_2O_5) (Abbas and Othman, 1981; Abbas et al. 1985; Abbas et

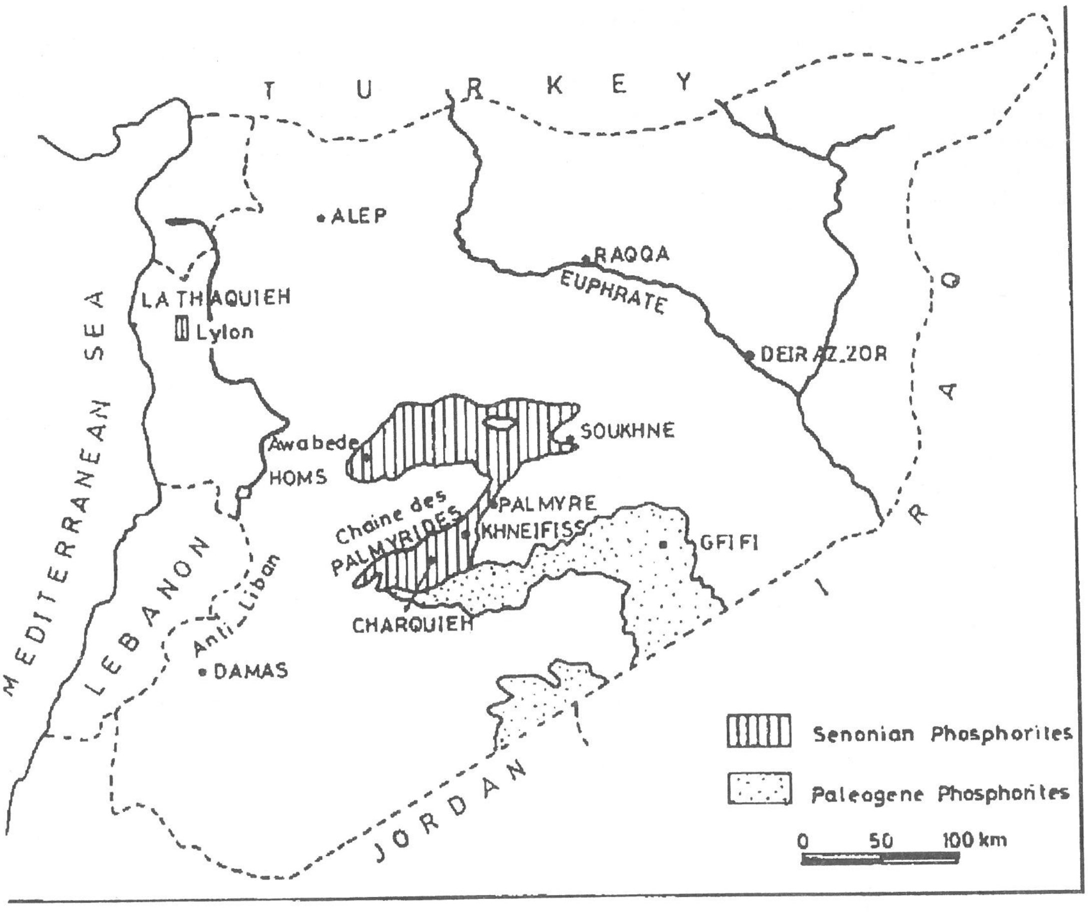


Fig. 1. Locations of Syrian phosphate deposits.

al., 1993 a, b) which alternate with carbonate levels, mostly calcareous and sometimes dolomitic or silicious levels. Carbonatic and silicious levels are more or less phosphatised (Fig 2).

Petrological study shows that phosphorites are granular i.e., composed of coated and non-coated grains and bioelements such as bones and teeth, etc. These elements are often cemented by a carbonate matrix. The successive diagenetic changes including recrystalization, silicification and weathering have affected the studied formations. Mineralogical study shows that the bulk rock mineralogical suite characterizes the slightly weathered series i.e., apatite, calcite, quartz, dolomite and glauconite only in the coastal area. Apatite is a slightly altered carbonate-flour-layer clay mineral (Abbas et al, 1985; Abbas et al., 1993 a, b).

A. Hard phosphorites: different phosphatic elements with coated grain (bone) in natural light-Khneifiss.

B. Same sample in (A) fission track study:
- Matrix free of uranium, n° 1.
- Uranium is always related to phosphatic grain.
- The coated grain, uranium in the nucleus (n° 2) is less than in the cortex (n° 3).

C. Uncoated phosphatic grain-pigmented at the cortex by organic matter-natural light-Morocco phosphorites.

D. The same sample in C-fission track study-The pigmented cortex is more rich in uranium (n° 1, 363 ppm) than non pigmented internal part of the grain (n° 2, 82 ppm).

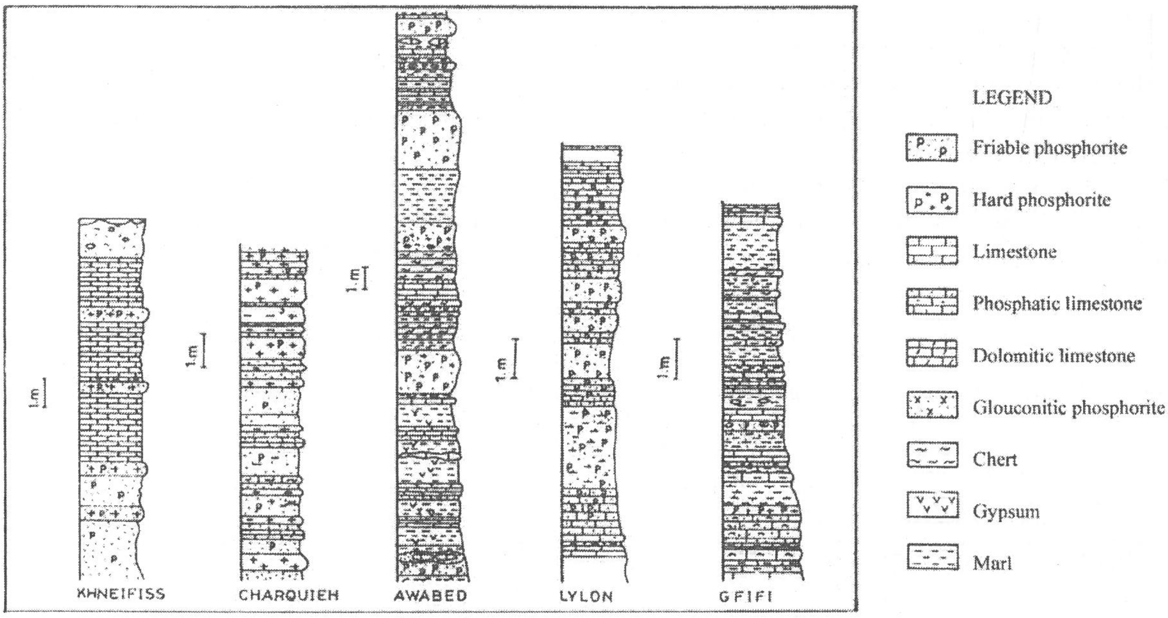


Fig. 2. Lithological features of Syrian phosphate deposits.

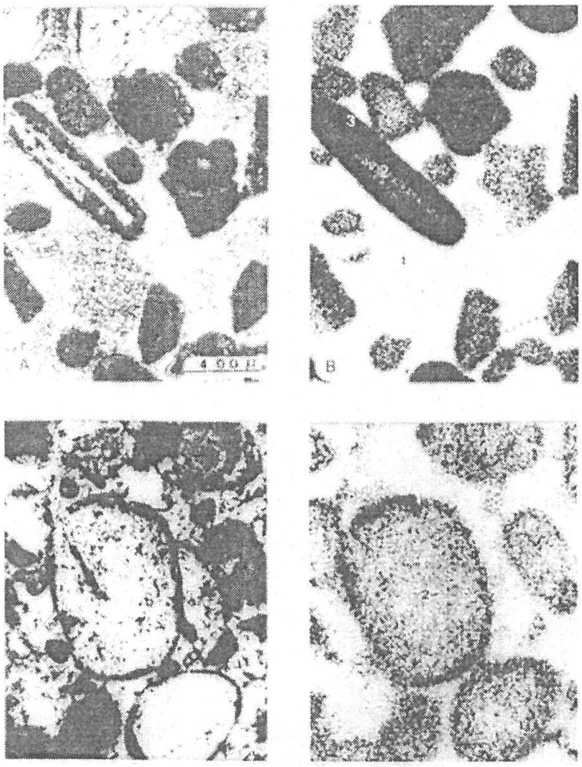


Fig. 3. Distribution of uranium in phosphorites by fission track method.

Uranium Geochemistry of Syrian Phosphate

The geological study of 34 elements including U in few hundred of phosphorite samples, shows that phosphorites are enriched in some trace elements, notably U, Y, Yb and La. Statistical treatment of geochemical data, specially by factor analysis, indicates that trace elements of phosphorites e.g., U, Yb. La, Sr, Cd, etc, which are accommodated in the apatite structure by substitution and adsorption, are mobilized and redistributed during weathering according to local conditions (Table 1) (Abbas, 1992; Abbas et al, 1993 a & b).

The geochemical study, particularly by fission tracks method applied to thin sections of phosphorites shows that uranium is disseminated in the apatitic bulk of phosphatic elements and in the matrix when it is phosphatic. Uranium concentration in phosphatic elements is mainly related to the following factors. 1- The organic matter. 2- The biomicritization. 3- The difference between cortex and nucleus of coated grains (Fig. 3). Uranium of phosphatic elements is relatively mobile and it is "displaced" during many primary or secondary espisodes such as biomicritization, coating and weathering. These indicate that part of uranium is not within the apatite lattice but probably adsorbed or simply trapped as in the case of organic matter. Weathering produce mobilization of uranium especially the part which is not in the apatite lattice. This mobilized uranium is trapped according to local conditions in phosphorites levels, in clay or in the form of phase of secondary mineralization containing few hundreds of ppm of uranium. The uranium concentration in the Syrian phosphorites is ranging from 55 to 101 ppm (Abbas, 1992; Abbas et al, 1993 a and b; Abbas, 1995 a and b).

Considering the above data and increasing demand for uranium as a nuclear fuel to produce electricity, uranium extraction study from phosphoric acid produced at Homs plant (General fertilizer Company) using phosphate concentrate from Khnefiss and Charquieh mines has been investigated in a micro pilot and pilot plant scale. Uranium is recovered in a two cycle process by a synergistic extractant combination of di-(2-ethy hexyl) phosphoric acid (DEHPA) and trioctylphosphine oxide (TOPO) in kerosene. In the first cycle 96% of uranium is extracted from the acid at 40°C by 0.5 M DEHPA+0.125M TOPO/kerosene, then uranium is stripped from the solvent by concentrated phosphoric acid containing ferrous ion. In order to reduce uranium from hexavalent to the less extractable tetravalent state, the strip solution is diluted, oxidized with hydrogen peroxide to convert all U(IV) and Fe(II) to the higher oxidation states U(VI) and Fe(III) and filtered. In the second cycle U(VI) is extracted with 0.3 extracted with 0.3 M DEHPA + 0.075 M TOPO/kerosene, the loaded solvent is scrubbed with

Table 1. Geochemical data of Syrian phosphorites compared to Negev phosphorites and the average of international phosphorites data.

Element	Charquieh 69 samples	Khneifiss 48 samples	Awabed 5 samples	Lylon 3 samples	Eocene 2 samples	Negev 185 samples	Int. Average Phosphorites Altschuler
SiO_2%	9.50	10.41	24.95	1.87	1.00	3.10	
Al_2O_3%	0.31	0.26	0.58	0.43	0.20	0.47	
MgO%	0.75	0.24	0.32	0.41	0.41	0.56	
CaO%	48.64	48.69	38.78	52.26	54.15	50.88	
Fe_2O_3%	0.21	0.14	0.13	1.17	0.10	0.35	
TiO_2%	0.05	0.03	0.05	0.07	0.03	-	
Na_2O%	0.37	0.39	0.53	0.46	0.63	-	
K_2O%	0.05	0.05	0.06	0.08	0.05	0.56	
P_2O_5%	25.37	28.60	20.98	22.03	19.66	25.71	
F%	3.00	3.36	2.16	2.35	2.18	3.05	
C%	-	-	1.68	4.85	4.47	0.70	
S%	-	-	0.34	0.43	1.51		
PF(1000)%	11.48	8.56	8.18	19.17	18.04	-	
Sr ppm	1456.02	1572.92	1968.75	14.58	19.70	2300.00	750.00
Ba ppm	267.46	521.92	618.00	33.40	1684.15	338.00	350.00
V ppm	72.49	125.38	47.20	53.80	219.50	155.00	100.00
Cr ppm	115.13	104.64	125.25	143.33	185.00	227.00	125.00
Ni ppm	16.98	23.44	31.85	30.90	32.10	89.00	53.00
Co ppm	8.80	8.36	7.85	5.00	7.05	5.00	7.00
Cu ppm	7.98	16.64	23.40	8.97	13.25	20.00	75.00
Mn ppm	-	-	9.83	21.30	16.55	-	-
Nb ppm	-	-	2.00	2.00	2.00	-	-
Zn ppm	114.24	122.94	172.75	36.23	59.20	521.00	195.00
Cd ppm	9.99	10.36	11.58	3.67	11.30	-	18.00
Sc ppm	1.35	2.70	4.88	4.77	5.35	-	11.00
Zr ppm	14.48	14.36	17.43	13.80	17.35	-	70.00
Y ppm	39.99	78.04	89.53	173.00	187.50	73.00	260.00
U ppm	59.47	100.79	75.15	65.34	55.08	111.00	120.00
La ppm	22.41	37.50	35.70	99.87	75.80	-	147.00
Ce ppm	26.90	44.46	22.33	53.80	43.25	-	104.00
Eu ppm	2.22	2.38	1.00	1.00	1.00	-	6.50
Yb ppm	1.72	3.92	5.25	8.77	10.60	-	14.00
Lu ppm	0.46	0.55	1.68	1.27	2.20	-	2.70

water and then stripped with ammonium carbonate solutions to produce ammonium uranyl tricarbonate (AUT).

Phosphoric Acid Characterization

Acid produced at the phosphoric acid plant in the (G.F.C) in Homs contains 1-4% of solid material (gypsum), with an average of 1.5% and contains some organic matter soluble and insoluble, the later is flocculated with gypsum. Table 2 shows the characteristics of the raw phosphoric acid from Homs plant. The above data in Table 1 show that phosphoric acid prodiced has the following advantages.

- Low P_2O_5%, which makes uranium extraction coefficient K_d higher.

Table 2. Characteristics of the raw phosphoric acid.

P_2O_5	SO_4^{2-}	F^-	Cl^-	Al_2O_3	Fe^{3+} (mg/L)	Fe^{2+} (mg/L)	CaO	SiO_2
23.8%	4.39%	1.64%	0.125%	0.11%	1289	111	0.92%	1.35%
MgO	U (mg/L)	S.S	μ (CP)	Temp (°C)	Emf (Mv)	D_{25} (g/cm^3)		
0.66%	53.7	1-4%	2.8	56.60	310	1.26		

- It is green acid poor in organic content.

Syrian phosphoric acid has the following disadvantage.

- High content of Cl^- and F^-, which can cause serious corrosion problems.

Phosphoric Acid Pre-treatment

Removal of Solids

As shown in Table 1, acid has 1 to 4% of solids. The gypsum solid can be completely removed by flocculation, settling in a clarifier and a brite column for residual gypsum removal. The flocculant used was N-100 (polyacrylamide).

Removal of Organic Matter

Tests have shown that the soluble organic matter in the green acid is low (optical density at 408 nm is about 0.2) and does not disturb the mass transfer and the separation of phases in the extraction process.

Solvent Extraction of Uranium

DEHPA-TOPO Method

Hurst and other workers at ORNL in the early seventies developed a process to extract uranium using DEHPA-TOPO in kerosene as a solvent in two extraction cycles. The process has been tested in many pilot plants and commercial units operated in Canada and United States. Fresh wet phosphoric acid from under the filter with 23-26% P_2O_5 is cooled from 60°C to 40°C for several objectives. It accelerates the precipitation of solids; it also increases the extraction coefficient. The uranium is oxidized by H_2O_2 to reach emf higher than 450 mv. The treated acid with less than 50 ppm solids and uranium in the hexavalent state U^{+6}, with minimum organic matter and at temperature of 40°C is conditioned and ready for solvent extraction.

Kinetic Tests

Several tests were carried out to establish the ideal time of mixing and the temperature was fixed at 40°C. Table 3 shows that increasing the mixing time more than 10 seconds did not give any improvement in the uranium extraction.

Table 3. Kinetic Tests.

Time (sec.)	K_d (distribution coefficient of U)
10	4.50
15	4.52
30	4.51
60	4.48
90	4.49

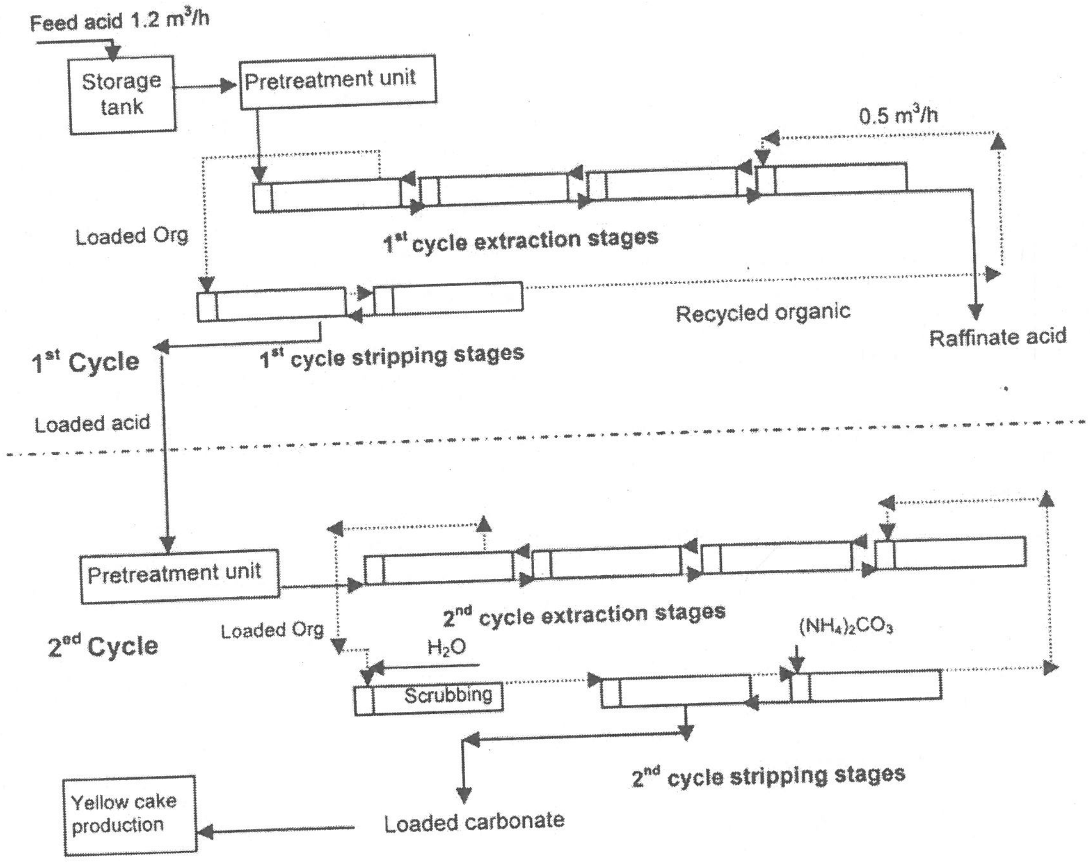
Continuous Solvent Extraction Test using Micro Pilot Plant

Results obtained from the extraction isotherm and the continuous extraction tests using micro pilot plant operated at a flow rate of 6 L/h of phosphoric acid and 3 L/h of DEHPA-TOPO in kerosene, showed that four extraction stages are enough to obtain a good extraction yield of uranium more that 95%. The flow rate of acid/solvent can be increased to 3 without any effect on efficiency and permits to increase uranium concentration in the loaded organic to more than 160 mg/L.

Continuous Solvent Extraction Tests using Pilot Plant

A pilot plant of mixer settler type has been constructed at the General Fertilizer company in Homs closed to the phosphoric acid plant since 1999 and operated to treat 1.2 m^3/h of the fresh phosphoric acid. DEHPA/TOPO method has been applied to extract uranium from the treated acid in two extraction cycles. Results obtained using the micro pilot plant were used. Very useful data have been obtained and used to prepare the prefeasibility study corresponding to a commercial unit, if any.

The following flow sheet demonstrates the two cycles of uranium extraction in the Pilot-Plant.



References

Atfeh, S. (1967) Ph.D. Thesis, University of London, King's College, 348p.

Abbas, M; Othman, I. (1981) Internal report, AEC, Damascus, Syria. 3p.

Abbas, M; Prevot, L; Lucas, J. (1985) *Sci. Geo. Mem.*, 77, pp. 35-39.

Abbas, M. (1992) *Int. Sym and Field Workshop on Phosphorites,* Assiut, Egypt, Feb. 22 to Mar 1.

Abbas, M; Mouty, M; Maleh, K; Lucas, J; Prevot, L. (1993 a), SAEC, G-FRSR, 75 Damscus.

Abbas, M; Mouty, M; Maleh, K; Lucas, J; Prevot, L. (1993 b) SAEC, G-FRSR, 74 Damscus.

Abbas, M. (1995 a) *Int. Sym and Field Workshop* IGCP 325. Abstract; Abbottabad, Pakistan, May 21-25.

Abbas, M. (1995 b) Arab Atomic Energy Agency. Cairo, Egypt.