(Ex SIAPE / SAEPA)

المجمع الكيميائي التونسي

GROUPE CHIMIQUE TUNISIEN

URANIUM EXTRACTION FROM TUNISIAN PHOSPHORIC ACID

VIENNE NOVEMBER 5, 2009

Presented by M. Chaker CHTARA Manager Scientific Research GCT

The area of Tunisia : 163 610 km²

Population : 10.2 million (2006)

The CPG currently operates seven open pits and one underground mine.

Annual production : 8 million tonnes of phosphate merchant placing Tunisia in the 5th among the world producers of phosphate.

After a long experience of exporting raw phosphate, Tunisia has turned towards the transformation and recovery of this mineral by the establishment of a loca industry to produce phosphoric acid and mineral fertilizers.

The GCT has four industrial parks located in SFAX, M'DHILLA (plants TSP), GABES (phosphoric acid plants DAP, DCP and ammonium nitrate) and SKHIRA (phosphoric acid plant).

Tunisia is the second country in the world to enhance large percentage of its phosphate production (nearly 80%).

SUMMARY

POTENTIAL RESSOURCES OF PHOSPHATES

POTENTIAL RESSOURCES OF URANIUM FROM PHOSPHORIC ACID

RECOVERY OF URANIUM FROM PHOSPHORIC ACID (GCT EXPERIENCE

DEPA-TOPO PROCESS

CHALLENGES

POTENTIAL RESSOURCES OF PHOSPHATES

URANIUM FROM PHOSPHATE ROCK

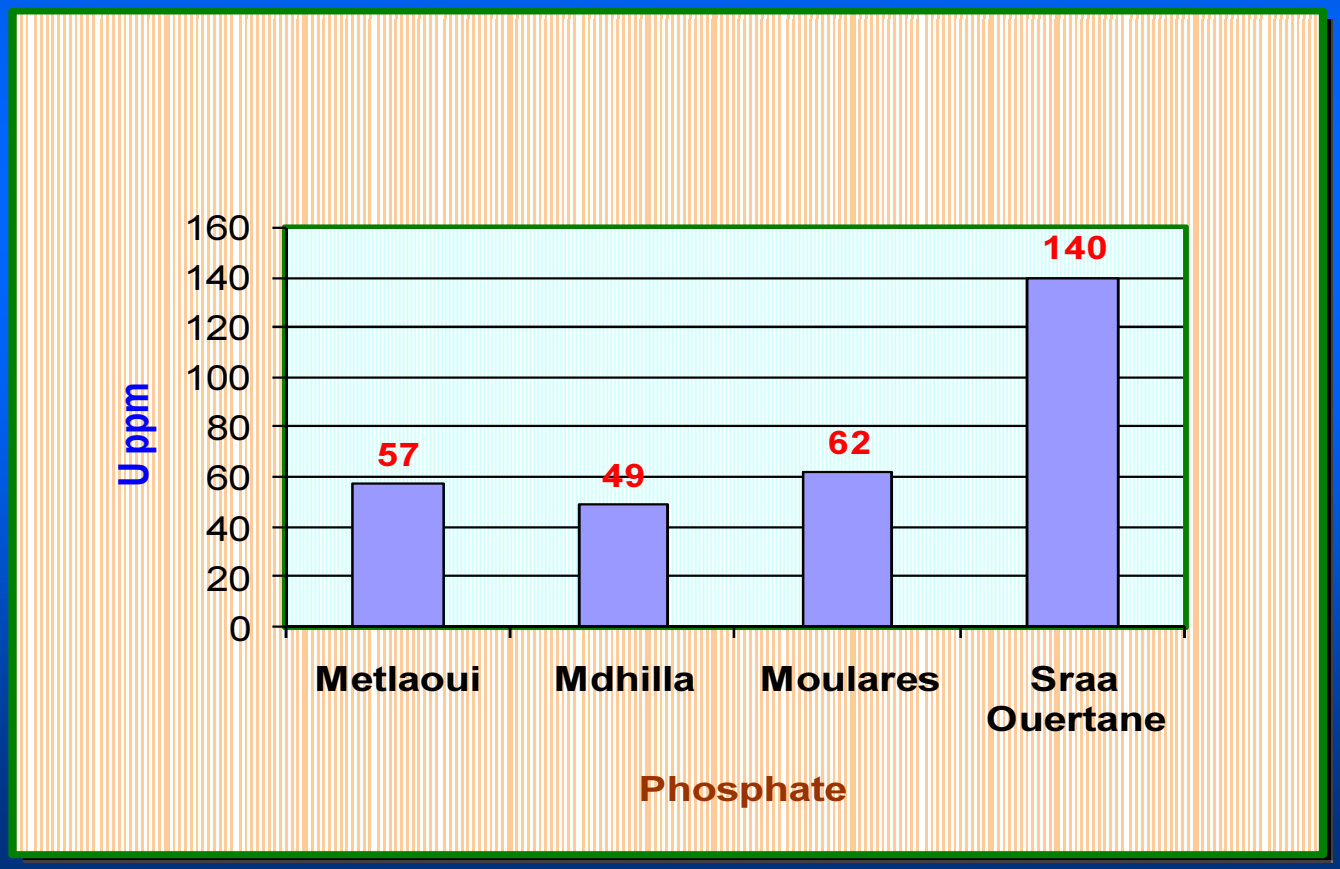
- Phosphate Reserves: about one billion tonnes ;
- Tunisian Phosphate rock is located in the south western and in the north eastern of the country;
- A major proportion of this phosphate contains uranium: 40 to 50 ppm;
- Phosphate Production in 2008: 8 million tons/y with 50 ppm of U;
- The mine of future Sraa Ouertane (ten billion tonnes) reserves contains 100-140 ppm.

URANIUM IN PHOSPHATES

PAYS	U_3O_8 (ppm)	
	Min	Max
Algérie	110	140
Brésil	50	250
Egypte	70	140
Jordanie	50	150
Maroc	90	160
Sénégal	120	180
Syrie	60	160
Togo	80	100
Tunisie	30	150*
US Floride	100	150
US C. Nord	60	80

URANIUM IN TUNISIAN PHOSPHATES

A recent chemical analysis of uranium in phosphates Tunisian (29-30% P_2O_5) has identified the values in the following table:



STATE OF OXIDATION OF U IN THE PHOSPHATES

Uranium is present in the phosphate substitution in calcium Ca^{2+} in the crystal lattice of apatite.

This uranium is found in the tetravalent oxidation states (+4) (UO_2) and hexavalent (+6) form $(UO_2)^{2+}$ in various proportions.

We have:

- **Uranium U^{+4} substituted 2 calcium ions Ca^{2+},**
- **Uranium U^{+6} substituted 3 calcium ions Ca^{2+} .**

POTENTIAL RESSOURCES OF URANIUM FROM PHOSPHORIC ACID

INTRODUCTION

The GCT annually processes approximately 7 million tons of phosphates, to produce phosphoric acid and fertilizers.

This transformation will take place through its various phosphoric acid unit operating with the SIAPE Di Hydrate process.

GCT PA PRODUCTION IN 2008

Total P_2O_5 acid capacity = 1.650 million tons/year

- 1.020 million t/y of P_2O_5 acid in 5 separate units at Gabes;
- 0.150 million t/y of P_2O_5 acid in 1 unit at M'dhilla;
- 0.120 million t/y of P_2O_5 acid in 1 unit at Sfax;
- 0.360 million t/y of P_2O_5 acid in 2 units at Skhira.

URANIUM IN TUNISIAN PHOSPHORIC ACID

- A major proportion of this acid contains uranium: 40 to 50 ppm in the major quality;

- The gisement Sraa Ouertane contains 100-140 ppm with 20-25%P_2O_5

GCT CURRENT POTENTIAL

Assumes phosphate contains 50 ppm of U and recovery is 90% the quantity of U recovery is 265T U/year

During the process, the uranium content of the phosphate ores is preferentially transferred to the phosphoric acid. The uranium material balance is favourable to transfering the uranium to the aqueous phase: Phosphoric acid

GCT POTENTIAL 2011

New Production Plant in Service:

1.500 million T/year of PA

Total GCT Uranium Potential: 332 TU/year

Assumes phosphate contains 50 ppm of U and recovery is 90%

RECOVERY OF URANIUM FROM PHOSPHORIC ACID

(GCT EXPERIENCE)

PHOSPHORIC ACID PRODUCTION

To extract Uranium from phosphate rock we must produce in the first time phosphoric acid.

Phosphoric acid is produced by contacting phosphate ores with sulfuric acid.

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 20H_2O \longrightarrow 2HF + 6H_3PO_4 + 10CaSO_4 2H_2O$$

Uranium balances established after the sulfuric attack of phosphates, show that 85 to 90% of uranium content in these phosphates are found in the phosphoric acid and a small amount is lost in the phosphogypsum.

URANIUM IN PHOSPHORIC ACID

During the process, the uranium content of the phosphate ores is preferentially transferred to the phosphoric acid.

The uranium material balance is favourable to transfering the uranium to the aqueous phase: Phosphoric acid

- **The parameters which relate to the process of transformation must ensure a maximum efficiency of P_2O_5 dissolved in the liquid phase.**

- **These parameters are not necessarily the same ones that guarantee a maximum rate of passage of uranium in aqueous phase.**

CHEMICAL ANALYSES

Phosphate

Élément		Phosphate Lavé	
		mini	max
P_2O_5	%	28,6	29,8
CaO	%	49	51
MgO	%	0,45	0,7
SiO_2	%	2,5	4,5
CO_2	%	6	8
SO_3	%	2,50	4,5
Fe_2O_3	%	0,3	0,38
Al_2O_3	%	0,6	0,8
F	%	3,2	3,6
C. Org	%	0,5	1,4
Uranium (ppm)		50	60

Acide phosphorique

Élément		Acide Phosphorique	
		mini	max
P_2O_5	%	25	26
CaO	%	0,1	0,5
MgO	%	0,5	0,7
SiO_2	%	0,2	0,4
H_2SO_4	%	0,8	1,5
Fe_2O_3	%	0,2	0,3
Al_2O_3	%	0,3	0,4
F	%	0,7	1
C. Org	%	0,035	0,05
Uranium	ppm	35	45

PROCESS IMPLEMENTATION

n general, the processes of liquid-liquid differ by:

- The nature of the solvent ;
- The extraction technique implementation.

The main objective is to ensure intimate contact between the organic and aqueous phases to maximize the recovery yield of solute (uranium).

To do this, existing facilities are classified in two types:

- Mixer settler ;
- Columns packed mobile or fixed.

SOLVENT USED

The solvents used in industrial scale are the following:

- **DEPA-TOPO:** Diethylhexyl Phosphoric Acid and Tri Octyl Phosphine Oxide
- **OPAP:** Octyl Phenyl Phosphoric Acid
- **OPPA:** Octyl Pyro Phosphoric Acid

According to the IAEA report published in 1989, the method based on the DEPA-TOPO solvent this technology the most efficient.

BACKGROUND

The GGT was interested in the recovery of uranium from phosphoric acid twice:

- **In the late '70s, the program was motivated primarily by rising uranium prices and mastery of new technologies in the field of phosphoric acid;**

- **From 2008 a new program was initiated.**

RESULTS OF PREVIOUS TESTS

The experience of GCT in the extraction of uranium from phosphoric acid, dates back to 1978. Although a considerable amount of research and development, the research carried out has enabled:

- **Period 1978-1981: achievement test extraction of uranium from Tunisian acid micro-scale pilot process by Gardinier PUK;**
- **Period 1982-1984: Installation and implementation of a pilot plant at Gabes.**

DESCRIPTION OF PILOT UNIT

This pilot unit dimensioned for a capacity of 200 l/h of dilute acid (28% P_2O_5) at the entrance is composed of two sections:

- Acid pretreatment section;
- A section of extraction and stripping of uranium.

PROCESS DESCRIPTION

The process is based on the following principles:

- The solvent used is OPPA (Octyl Pyro Phosphoric Acid) in kerosene;
- Uranium is extracted from the acid to 28% P_2O_5;
- Uranium is mined by valence 4;

The technique of extraction of uranium is based on the use of a battery of 4 mixers settlers.

STEPS OF THE PROCESS

The process is based on the following steps:

- Pretreatment and Conditioning acid;
- Extraction of Uranium;
- Precipitation of uranium tetra fluoride: UF_4;
- Separation of three phases: Aqueous (HF) organic (solvent), Solid (UF_4) by centrifugation;
- Washing UF_4;
- Washing and recycling of the solvent;
- Recycling of the aqueous HF;
- Purification of uranium to the stage "ADU".

RESULTS OF WORK

The research conducted at the pilot plant have:

- To study the adaptation process to the Tunisian phosphoric acid;
- To define the operating parameters, material balances an consumption of specific chemicals consumed;
- To study the compatibility of the acid (without uranium) with existing downstream manufacturing;
- Provide staff training in techniques of extracting uraniun

DEPA-TOPO PROCESS

PROCESS DESCRIPTION

The DEPA-TOPO process includes the following main steps

- Pretreatment of acid;
- First cycle extraction;
- First stage of stripping;
- Second cycle extraction;
- Second round of stripping;
- Precipitation and purification of uranium;
- Solvent regeneration.

PROCESS CONDITIONS

- The solvent used is the DEPA-TOPO, it is a mixture of two solvents to a given proportion. This combination provides a synergistic effect in favor of a more efficient recovery of uranium and better selectivity;
- Uranium is extracted from the acid at a concentration of $P_2O_5 < 30\%$;
- Uranium is extracted by valence 6;
- The recovered uranium is in the form of U_3O_8.

ADVANTAGES OF THE DEPA-TOPO PROCESS

This process has advantages over the OPPA process. These advantages are mainly:

- The solvent used is more stable and more selective;
- Uranium is extracted by valence 6;
- Uranium is recovered directly in the form of UO_2 or U_3O_8 conform to standards of purity required.

CHALLENGES

- Extraction Uranium from MG phosphoric acid;
- Solvent extraction able to extract Uranium with more efficiency;
- Extraction Uranium by a novel technology in our pilot purification plant based on Pulsed column and not mixer settler method.

Thank you for your attention