

# **THE RECOVERY OF URANIUM FROM PHOSPHORIC ACID**

**REPORT OF AN ADVISORY GROUP MEETING  
ORGANIZED BY THE  
INTERNATIONAL ATOMIC ENERGY AGENCY  
AND HELD IN VIENNA, 16–19 MARCH 1987**



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## FOREWORD

Phosphoric acid is an important alternate source of uranium: the world's reserves of phosphoric rock are estimated to be about 18 000 million tonnes and there are approximately 400 wet-process phosphoric acid plants in operation from which some 13 000 metric tonnes of  $U_3O_8$  could in principle be recovered each year.

The recovery of uranium from wet-process phosphoric acid is a proven technology that is being used commercially, albeit on a limited scale because currently prevailing market conditions make it marginally economic. This situation may eventually change either when the price of uranium increases in real terms or by technological improvements leading to more favorable process economics.

Nevertheless, many developing countries are interested in the recovery of uranium from phosphoric acid for use in their own nuclear power programmes. Several important reasons, such as assurance of supply, savings in foreign currency, acquisition of technology and generation of employment, may render this operation attractive in spite of the marginal economics.

In view of the interest shown by several Member States, the International Atomic Energy Agency convened an Advisory Group Meeting on the Recovery of Uranium from Phosphoric Acid from 16 to 19 March 1987 with the main objectives of reviewing the current status of the technology and to suggest guidelines for the application of existing processes in developing countries. One of the recommendations made by the Group was that a technical report on this topic should be published. Accordingly, the participants undertook the task of preparing a series of papers, based on the material presented during the Meeting, which are included in this Technical Document.

The Document includes a Summary and Recommendations, followed by two review papers which discuss the current status of the technology and industrial practice of uranium recovery from phosphoric acid. Other papers discuss operating experience and current research and development work. Two Panel Discussions are also included, one on capital and operating costs and the other on guidelines for the preparation of feasibility studies.

The Agency wishes to thank the experts and institutions who contributed to this Meeting with their papers and their participation. The meeting was organized and chaired by Mr. S. Ajuria of the Division of Nuclear Fuel Cycle who was also responsible for editing the text.

## **EDITORIAL NOTE**

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## SUMMARY AND RECOMMENDATIONS

### SUMMARY

1. Phosphoric acid is an important alternate source of uranium: the world's reserves of phosphoric rock are estimated to be about 18 000 million tonnes with an average uranium content of 50 to 200 ppm.
2. There are approximately 400 wet-process phosphoric acid plants in operation from which some 13 000 metric tonnes of  $U_3O_8$  could in principle be recovered each year.
3. Several processes have been developed for the recovery of uranium from phosphoric rock. Three of these processes, based on solvent extraction, have reached commercial status:
  - a) The DEPA/TOPO process, developed at the Oak Ridge National Laboratories, using di(2-ethylhexyl) phosphoric acid\* and trioctyl phosphine oxide as extractants,
  - b) The OPAP process, also developed at Oak Ridge but using octyl phenyl acid phosphate as extractant, and
  - c) The OPPA process, developed by Dow and using octyl pyro phosphoric acid as extractant.
4. Eight plants for the recovery of uranium from phosphoric acid have been built and operated in the United States since 1976. Plants have also been built in Belgium, Canada and Taiwan, China.
5. Capital and operating costs for a uranium recovery plant depend strongly on the uranium content and other characteristics of the phosphoric acid and on the size of the plant. Other project-specific conditions such as plant location and availability of manpower and supporting services are also important.
6. Historical operating costs (summarized in the report from Panel 1) range from 22 to 54 U.S. dollars/lb  $U_3O_8$ .
7. Given the current status of the uranium market, the economics of recovering uranium from phosphoric acid are marginal under the best conditions, i.e. in the case of a large plant, located on a site where manpower and supporting services are easily available and which is processing an acid with a high concentration of uranium.

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\* In the present report, this substance is variously abbreviated as DEPA/TOPO, DEHPA/TOPO and D2EHPA/TOPO.



8. No new commercial plants have been recently built and most of the existing plants have closed. The few plants that remain currently active are based on the DEPA/TOPO process and, being older plants, all are fully or largely amortized. Several plants operate intermittently depending on the price of uranium concentrates.
9. Research and development activities on the recovery of uranium from phosphoric acid are continuing along three main lines:
  - a) Improvements on the DEPA/TOPO process to further enhance its flexibility and economy,
  - b) Development of new liquid-liquid extractants,
  - c) Development of other processes such as ion-exchange (using solid ion exchangers), liquid membranes and processes compatible with the hemi-hydrate process for the production of phosphoric acid.

## RECOMMENDATIONS

One of the main objectives of this Meeting was to suggest guidelines for the possible application of existing processes in developing countries. The main conclusion reached by the Group is that, given the current status of the market, the recovery of uranium from phosphoric acid is marginally economic under the best conditions. The recommendations that follow are derived from this salient fact.

1. Whenever possible, preference should be given to the development and exploitation of conventional uranium resources as compared to recovery from phosphoric acid.
2. The construction of a new plant for the recovery of uranium from phosphoric acid for export purposes is virtually ruled out under present market conditions.
3. Even when phosphoric acid represents the only viable source of uranium, careful consideration should be given to the country's actual uranium requirements: whether or not the country has a nuclear power plant in operation, under construction, or committed, what are the amounts of uranium concentrates required by such plants and when they are needed and whether or not such concentrates can be purchased abroad at less cost.
4. Unless there are specific and compelling reasons to do otherwise, it is advisable to use the DEPA/TOPO process because this is well-proven, does not present any major engineering problems and allows economic analyses and projections with a high degree of confidence.
5. Given the currently prevailing conditions of the uranium market and the comparatively high costs of recovering uranium from phosphoric acid it is especially important to perform a thorough pre-feasibility study and project evaluation before embarking on a new venture. Such a study and evaluation should follow generally accepted industrial practice.

# RECOVERY OF URANIUM FROM PHOSPHATES: CURRENT STATUS AND TRENDS

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## Abstract

Commercialization of three processes (OPPA, DEPA-TOPO and OPAP) has shown that the DEPA-TOPO process offers the best technology available today for the recovery of uranium from wet-process phosphoric acid. Uranium recovery plants using this process have been successfully operated in the United States, Belgium, Canada and Taiwan. Operating experience from these plants has led to a significant reduction in both capital and operating costs making the DEPA-TOPO process more attractive in today's depressed uranium market. The main process improvements developed at the Oak Ridge National Laboratories are summarized and current process economics are reviewed. New processes now being studied are discussed, including processes using new extractants, ion-exchange resins and liquid membranes and processes for the recovery of uranium from the hemi-hydrate phosphoric acid process.

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## 1. CURRENT STATUS

Wet-process phosphoric acid is a very important source of uranium which is needed to fuel nuclear power reactors. Commercialization of three processes (OPPA, DEPA-TOPO and OPAP)\* has shown that the DEPA-TOPO process offers the best technology available today (1988) for the recovery of this uranium. Since 1976, eight plants for the recovery of uranium from phosphoric acid have been built and operated in the United States. Six of the plants use or used the DEPA-TOPO process, one used the OPPA process and the other one used the OPAP process. The OPPA plant and the OPAP plant have ceased operation because of problems that led to untenable costs. Five DEPA-TOPO plants are being operated successfully. One DEPA-TOPO plant was closed because of a major reduction in the production of wet-process acid, and the processing of a rock with a very low uranium content. Its closing was not due to problems with the uranium recovery process. These activities are summarized in Table 1.

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*OPPA	- octyl pyro phosphoric acid (Dow process)
DEPA-TOPO	- di(2-ethylhexyl) phosphoric acid-trioctyl phosphine oxide (ORNL process)
OPAP	- octyl phenyl acid phosphate (ORNL process)

Table 1. Uranium Recovery from Wet-Process Phosphoric Acid

Country Name	Facility Name/Location	Owner/ Operator	Process	Capacity TP <sub>2</sub> O <sub>5</sub> /A	Year	
					Start	Close
Belgium	Umipray S.A./Puurs and Engis	Prayon	DEPA-TOPO	130,000	1980	
Canada	Earth Sciences Extraction Co./ Western Co-op Plant in Calgary	Earth Sciences Inc. and Urangesellschaft Canada, Ltd.	OPAP	110,000	1980	1981
			DEPA-TOPO		1983	1987
United States	Uranium Recovery Corp./ W. R. Grace Plant, Bartow, Fla.	United Nuclear Corporation	OPAP	330,000	1976	1980
	Farmland/Pierce, Fla.	Wyoming Minerals Corporation*	DEPA-TOPO	450,000	1978	1981
	Uncle Sam/Convent, La.	Freeport Uranium Recovery Company	DEPA-TOPO	820,000	1978	
	Gardinier/Tampa, Fla.	Gardinier	OPPA	450,000	1979	1982
	IMC/New Wales, Fla.	International Minerals & Chemicals Corporation (IMC)	DEPA-TOPO	1,500,000	1980	
	CF Industries/ Plant City, Fla. Bartow, Fla.	CF Industries/ IMC	DEPA-TOPO	750,000	1980	
			DEPA-TOPO	600,000	1980	**
	Sunshine Bridge/ Donaldsonville, La.	Freeport Uranium Recovery Company	DEPA-TOPO	480,000	1981	
Taiwan	China Phosphate/Lung Tan	Institute of Nuclear Research (NERI)	DEPA-TOPO	33,000	1981	

\*Uranium recovery plant has been purchased by Urangesellschaft for future operation.

\*\*Fertilizer plant is temporarily down.

Uranium recovery plants using the DEPA-TOPO process have been and are being successfully operated in Belgium, Canada and Taiwan. Earth Sciences Incorporated started operations at the Western Cooperative phosphoric acid plant in Calgary, Canada using a version of the ORNL OPAP process, but later, in a cooperative venture with Urangesellschaft Canada Ltd., modified their plant to the DEPA-TOPO system, because of problems associated with the OPAP process. The modified plant was working well until it was forced to shut down in September, 1987 because of the closure of the phosphate plant by Western Cooperative. As shown in Table 1, these companies are or were operating with small throughputs of acid, which many people think are uneconomical.

## 2. IMPROVEMENTS IN THE DEPA-TOPO PROCESS

Feedback from the operating plants indicated several areas where improvements are needed. These include improvement in the transference of uranium from the rock to the acid rather than to the gypsum during acidulation of the rock, improvement in the methods for removal of humic materials that form crud with the solvent phase and which result in high losses of the expensive extractant, a better knowledge of uranium transfer rates during extraction, and a way to increase the efficiency of the reductive strip while minimizing the addition of iron metal in order to completely reduce the uranium to the tetravalent state.

As described below, a partial solution to these problems has led to a significant reduction in both capital and operating costs, and is making the cost of building and operating uranium recovery plants more attractive in today's depressed uranium market.

The initial DEPA-TOPO process has been well documented<sup>2,3</sup> and a reissue patent<sup>4</sup> was granted to the U.S. Government after a lengthy lawsuit with two American companies. Since that time, several important improvements in the process have been published by ORNL workers.<sup>5-8</sup> These are summarized below:

- (1) The provision of oxidizing conditions during acidulation of the phosphate rock can lead to significantly higher concentrations of uranium in the acid, whereas reducing conditions can lead to significant losses of uranium to the waste gypsum.

- (2) The use of activated carbon columns to remove humus from the acid appears to be justified by both laboratory tests and plant practice, in spite of its added cost. Tests have shown that the elimination of this material greatly reduces the formation of crud during extraction and reduces the loss of extractant by entrainment and degradation. It also results in more rapid extraction of the uranium which allows the use of smaller mixers.
- (3) The rate of uranium extraction from even chemically pure 5 to 6 M phosphoric acid with DEPA-TOPO extractant is known to be relatively slow under the best conditions. Tests that were made using high pressure liquid chromatography with very small cation exchange resins have shown that at least two species of uranium (VI)-phosphate coexist in these solutions, which are not in rapid equilibrium with one another. The rate of extraction is probably dependent on the rate of interconversion of unextractable species to extractable ones. This rate is decreased as the phosphoric acid concentration is increased. In addition to humic matter, certain defoamers added during rock digestion can also decrease extraction. The rate can be increased by raising the temperature.
- (4) Tests have shown that the elimination of dissolved oxygen from the pregnant DEPA-TOPO extract by sparging it with an inert gas such as carbon dioxide or nitrogen, along with the elimination of oxygen from the free space in the stripping units by an overpressure of the gas, can greatly improve the efficiency of the reductive strip step. This will lead to a reduction in equipment size and in solvent inventory.
- (5) Equilibrium and kinetic studies of the reductive stripping of uranium from loaded DEPA-TOPO extract has shown that the efficiency of this key process operation can be significantly increased by the use of a more concentrated 8 to 10 M phosphoric acid strip solution rather than the 5 to 6 M raffinate acid recommended in the initial flowsheet. This procedure greatly improves the reduction kinetics allowing decreased retention times in the mixers, use of lower Fe(II) concentrations, and smaller process equipment. All of these improvements can decrease capital and operating costs significantly.

### 3. ECONOMIC CONSIDERATIONS

The economic conditions for the recovery of uranium from wet-process phosphoric acid are not very favorable at the present time (1988) because of the relatively high production costs and the low price of uranium. At the present time (1988), uranium can be purchased on the spot market for less than US \$ 20 per pound of  $U_3O_8$ <sup>1</sup> and all indications are that it will not show a significant increase until the early 1990s, at which time it may rise rapidly as current inventories become exhausted and new nuclear plants go onstream.

No official cost information has been released by the operating companies, but reliable sources indicate that operating costs in the large companies (over 500 000 t  $P_2O_5$ /yr) in the USA have been reduced to a point that they can sell uranium for a profit at the current spot market price of US \$17 per lb  $U_3O_8$ . Most of these companies have had long term contracts for the sale of their uranium at prices of US \$40 to \$50 per lb. This has allowed them to survive initial startup problems and to make improvements and refinements in the process.

It should be pointed out, however, that the philosophy in many countries is that they are willing to subsidize the domestic processing of phosphate rock for uranium recovery, rather than purchasing it on the open market. Local recovery can lead to security of supply, economy of foreign currency, the acquisition of technology, and to the resolution of environmental problems.

### 4. NEW PROCESSES

A large number of establishments have been working to develop new processes as well as to improve the old ones. Many are trying to develop new, more powerful extractants. One of the most attractive of these is the so-called Super-TOPO developed in France. It is a more powerful uranium extractant than regular TOPO, but this advantage is offset by its much higher cost. One new process being developed by Uraphos Chemie GmbH, a subsidiary of Urangesellschaft, uses an amine to extract the uranium. A major problem with this process is that it requires a drastic change in the character of the acid in order to make the uranium extractable. Most phosphate producers could not cope with these changes.

Installations in Israel and England have been pursuing the use of solid ion exchangers for the recovery of uranium. Many advances in the technology are being made and new, more selective resins are being developed. However, problems of low selectivity and capacity as well as slow kinetics and the use of non-continuous systems still hinder this technique's competition with solvent extraction.

Liquid membrane processes have been thoroughly studied and developed and seem to offer certain advantages over solvent extraction. However, some problems remain to be solved such as the processing of dirty solutions and the breakage of the emulsion to recover the uranium.

Most of the research carried on so far has been directed toward the recovery of uranium from the 28-32%  $P_2O_5$  acid produced by the popular dihydrate process. Current processes do not work well for the more concentrated 40-45%  $P_2O_5$  acid produced by a hemi-hydrate process. Most of the hemi-hydrate plants currently in operation are very small and offer only a small uranium recovery potential.

One interesting development for the recovery of uranium in a hemi-dihydrate process, such as the Nissan Process, is a novel precipitation method which is called the phosphogypsum process. In this process, the uranium is co-precipitated with the gypsum by creating a highly reducing condition during rock acidulation. The uranium which is precipitated with the calcium sulfate hemihydrate is released during the hydration step and can be easily recovered by processing a dilute acid side stream. Several review articles discuss in detail these and other activities throughout the world.<sup>9-12</sup>

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# RECOVERY OF URANIUM FROM PHOSPHORIC ACID: AN OVERVIEW

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## Abstract

Wet-process phosphoric acid is one of the most important potential sources of uranium. In spite of the current low market price of uranium, there are many reasons which can make the recovery of this material from phosphoric acid attractive, specially in countries without conventional uranium ore bodies. Several processes, types of equipment and reagents have been studied in order to improve the economics of uranium recovery therefore making this alternative resource more attractive in comparison to conventional ores.

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## 1. INTRODUCTION

Phosphate rock has been the most suitable alternative source for the recovery of uranium. Important amounts of uranium have already been obtained from wet process phosphoric acid.

It is well known that the phosphate ion in the fluo-apatite structure  $[3 \text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2]$  can sometimes be partly replaced by vanadate, silicate, sulfate, or carbonate ions. Rare earths, chromium, iron and uranium are other common impurities. Average concentrations of this last metal can be 50 to 200 ppm U. The potential uranium content of known phosphate rock world reserves is in the range of 5 to  $15 \times 10^6$  t U (1,2).

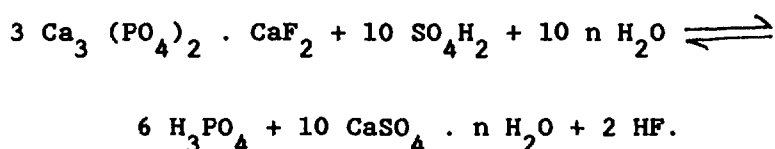
According to estimates as of 1 January 1985 (3), these amounts are higher than conventional reserves of uranium in the world (not including the USSR), exploitable at costs of less than \$130 / Kg U. This is

considering the NEA/IAEA categories of RAR (Reasonably Assured Resources) and EAR-I (Estimated Additional Resources - Category I), which are about  $3.5 \times 10^6$  t U. In the last case, the concentration of uranium in the ores (500 - 2,000 ppm U) is more than 10 times higher than that in phosphate rocks.

## 2. PRODUCTION OF URANIUM IN THE FERTILIZER INDUSTRY

The processes for milling mined phosphate rock can be divided into three major categories, namely, thermal, wet, and rock crushing and calcining. Because of metallurgical reasons, the recovery of uranium is restricted to the wet processes. In a phosphoric acid plant, phosphate rock is digested with any common mineral acid. There are several commercial processes using hydrochloric, nitric or sulphuric acids, or mixtures of them, for the direct production of fertilizers. Sulphuric acid is the most widely used, because of its lower cost and the ease of separation of the reaction products (phosphoric acid and calcium sulfate).

The reaction is as follows :



Depending on operating conditions, mainly temperature and acid concentration, there are the following processes:

<u>n</u>	<u>Process</u>	<u>Temperature</u>	<u>Acid Concentration</u>
2	Dihydrate	68 - 78 °C	28 - 30 %
1/2	Hemihydrate	70 - 100 °C	42 - 45 %
0	Anhydrite	120 - 130 °C	50 - 55 %

The dihydrate process is the most frequently used. Nevertheless there is a trend to obtain more concentrated acid by the hemihydrate process, because of large potential savings in energy and capital costs (4). Nearly two tons of gypsum are produced from each ton of rock

treated. The gypsum thus produced contains the nuclides of the radioactive series of uranium, because the radium remains practically insoluble (5).

Most of the uranium is dissolved with the phosphoric acid. Considering an average concentration of 100 ppm U in the rock, for a worldwide annual production of  $100 \cdot 10^6$  t ( $30 \cdot 10^6$  t  $P_2O_5$ ), the potential recovery is about 10 000 t U. This is slightly less than a third of the Occidental World production of uranium (36 250 t U in 1985) (3).

In spite of this favorable situation, the recovery of uranium from wet-phosphoric acid has only been done on a commercial scale in few instances and without much emphasis on the total production. Although this process has been used since the late 1950's, the maximum activity in this field was between 1978 and 1983. In this period uranium recovered from phosphoric acid represented nearly 5% of world production (1500–2000t U) (6).

### 3. PROCESSES FOR URANIUM RECOVERY

Wet phosphoric acid is normally an unstable physico-chemical system, with stringent requirements for equipment materials. The hydrometallurgical techniques generally used to recover uranium from phosphoric acid are conventional: solvent extraction, ion exchange and precipitation.

#### 3.1 Solvent extraction

Until now, uranium extraction with organic solvents has been the only important process applied on a commercial scale. This process has important advantages : it is easy to apply in a continuous system, the equipment is not too expensive, and it is a well-known operation. Its disadvantages are that:

- a) a previous stage of acid conditioning is necessary with large investment and operating costs;

- b) the treated phosphoric acid may be contaminated by organic solvents;
- c) the economy of the process is strongly affected by the uranium concentration, because the investment and operating costs depend on the acid throughput.

Uranium may be extracted from phosphoric acid by either cationic, anionic or neutral reagents, depending on the ionic form present.

### 3.1.1 Cationic reagents

Cationic liquid exchangers used commercially include the organo-phosphoric acids, which are the more usual reagents for the industrial recovery of uranium from phosphoric acid manufactured by the dihydrate process (28-30 %  $P_2O_5$ ). The main reagents used are:

- The synergistic combination of di-2-ethyl-hexyl-phosphoric acid (D2EHPA) and trioctyl-phosphine oxide (TOPO), which extracts hexavalent uranium (14, 15, 16).
- The mixture of mono and di-phenyl phosphoric acid (OPAP) (17) which extracts uranium in the tetravalent state.
- Octyl-pyrophosphoric acid (OPPA), made on site by combining phosphorous pentoxide and octyl alcohol to form an ester. It extracts both  $U^{4+}$  and  $U^{6+}$ , but preferentially extracts  $U^{4+}$  (18).

These three general processes have been reviewed on several occasions. They are based on the extraction of uranium as a cation. In a general sense, they comprise the following stages of treatment:

- a) Acid conditioning with the purpose of bringing the acid to an optimum redox condition and temperature for extraction and also to remove solids and organic matter to reduce "crud" formation in the extraction stage. Several treatment flowsheets have been developed (19, 20).

b) Separation of the uranium from the acid, by means of a first extraction cycle with one of the solvents mentioned above. In the D2EHPA-TOPO and OPAP systems uranium is stripped with concentrated phosphoric acid (6-10 M), in the opposite redox conditions to those of the extraction step. The OPAP system requires an uranium complexing agent as hydrofluoric acid which precipitates the hydrated uranium tetrafluoride ( $UF_4 \cdot 2H_2O$ ) called "green cake".

c) Purification of uranium and precipitation of concentrates, by means of a second cycle of solvent extraction. In systems in which concentrated phosphoric acid is used as a stripping agent (D2EHPA-TOPO and OPAP processes) the acid is diluted and oxidized (should it be necessary), and further purified by a second solvent extraction step using a less concentrated D2EHPA-TOPO mixture. Uranium is stripped with carbonate, either under precipitating conditions (ammonium carbonate) or in solution (sodium carbonate). The final product can be ammonium uranyl tricarbonate (AUTC) or ammonium diuranate (ADU). In the OPAP process, the green salt is dissolved with nitric acid and subsequently purified by solvent extraction with TBP (tri-butyl-phosphate) and stripped with  $H_2O$ . Finally, uranium is precipitated with ammonia and recovered as ADU.

In all cases, the barren phosphoric acid is treated either by an activated charcoal system or by an air flotation system and recycled to the fertilizer plant. The recycled acid conserves its main chemical characteristics (acidity, chemical composition of the rest of ions) but is free of uranium, humic acids and suspended solids.

Among the recovery processes discussed above the OPAP system has the largest extraction coefficient (100 versus 25-30 for OPAP system and 4-10 for D2EHPA-TOPO system) considering a 28-30%  $P_2O_5$  phosphoric acid. In addition OPAP is less expensive than OPAP and, until now, than D2EHPA-TOPO.

Nevertheless, D2EHPA-TOPO is a more stable and selective reagent (specially against iron), and can be used for both extraction cycles. With the exception of two commercial plants which use the OPAP and OPAP

processes, the rest (9 facilities) use the D2EHPA-TOPO system. The Calgary plant (Canada) owned by Earth Sciences is a relevant case, because it was started in 1980 with the OPAP process and after 1983 was changed to the D2EHPA-TOPO process after 1983.

The treatment of phosphoric acid manufactured from Mediterranean and North Africa phosphate rock by the D2EHPA-TOPO process has an additional advantage : since the uranium is usually present in the hexavalent form, the use of this reagent saves oxidant and avoids phosphoric acid contamination with iron scrap, which is the reagent most commonly used for reducing uranium in the other processes.

### 3.1.2 Anionic reagents

Uraphos Chemie GmbH has piloted a process (the Uraphos process) using a tertiary amine (TDDA or trillauryl amine) as extractant. This reagent extracts tetravalent uranium only.

It is well known that the amines are less powerful extractants than organo-phosphoric compounds. The extraction of uranium is strongly affected by the total acidity and the content of foreign ions, mainly fluoride and ferric iron. To make uranium recovery possible it is necessary to pre-treat the acid, changing some of its chemical characteristics and adding complexing agents like sodium polyphosphate. The process involves the following steps:

#### a) Phosphoric acid conditioning, including :

- Reduction of the acidity and of the concentration of competitive ions, by addition of  $\text{CaO}$ ,  $\text{NaOH}$  and  $\text{SiO}_2$ . A partial neutralization of acid decreases the concentration of fluoride ions (such as sodium fluosilicate,  $\text{Na F}_6 \text{ Si}$ ) and sulphate (as calcium sulphate,  $\text{CaSO}_4$ ) in solution.
- Solid-liquid separation, to remove fluosilicate and gypsum. The process must be tailored to the specific acid characteristics and may include the operations of ageing, flocculation, decantation and filtration.

- Reduction of organic matter content with activated charcoal.
- Adjustment of the redox potential with iron scrap.

b) First cycle extraction. The pre-treated acid is mixed with sodium polyphosphate and uranium is extracted with TDDA. The loaded organic phase is scrubbed with sulphuric acid and stripped with a buffer solution of  $\text{Na}_2\text{CO}_3$  and NaOH. The final product is a sodium di-urnate precipitate, obtained by adding NaOH to the aqueous extract.

Second cycle extraction, where the prior precipitate is dissolved with sulphuric acid and uranium is extracted with the same organic phase and stripping agent as in the first cycle. A precipitate of sodium diuranate is finally obtained.

In order to demonstrate the feasibility of the process, Uraphos has constructed a modular and mobile pilot plant capable of continuous operation with a throughput of 200 l/h of phosphoric acid.

Although the extractant used is less expensive than the organo-phosphoric compounds, reagent costs are 2 - 3 times higher than in for the D2EHPA process. Investment costs should be comparable to those of plants using cationic reagents, because the acid pre-treatment and the first cycle extraction are very similar.

This process also could be adequate, a priori, for treating a more concentrated phosphoric acid manufactured by the hemihydrate process (40-45 %  $\text{P}_2\text{O}_5$ ), as a consequence of the previous treatment of the acid, specially in relation to neutralization. This last aspect is a drawback for the process, because phosphoric acid manufacturers are very sensitive to any change in acid composition, specially when the market value of the recovered uranium is generally expected to be less than 10% of that of the main product.

### 3.1.3 Neutral reagents

Neutral organic compounds of phosphorus, as phosphine, phosphinate and phosphate oxides, have been applied at the different

treatment stages to recover and purify uranium solutions, mainly in nitric medium. Uranium is extracted as uranyl nitrate. The most common reagent is tributyl phosphate (TBP).

The high content of ions which can form anionic or cationic complexes makes the extraction difficult. For that reason the use of this system has only been limited to processes in which phosphate rock is digested with nitric acid, or processes such as the OPPA, where  $UF_4$  is dissolved with nitric acid.

Rare earths could also be recovered using these reagents. These are present in phosphate rocks in amounts 100 times higher than uranium (about 1%). Interest in the TBP process is growing as a result of the trend to use nitric acid to up-grade phosphates. This way the product contains more than one nutrient (Nitrogen and phosphorus) and is a more effective fertilizer.

### .3.2 Ion exchange

The use of solid ion exchangers for the recovery of uranium from phosphoric acid, and from sulphate liquors, has become attractive in the last few years. The development of more selective resins and the recent successful installation of several plants using continuous ion-exchange (CIX) systems, have promoted interest in this technology.

The Ion exchange processes have potential advantages in relation to solvent extraction processes because:

- a) They can treat phosphoric acid with low uranium concentrations at a lower cost than other processes;
- b) They do not contaminate the phosphoric acid with organic solvents;
- c) The recovery of uranium is less affected by the concentration of phosphoric acid and by temperature;
- d) If fluidized bed continuous systems can be used there may be important savings in acid clarification.



Nevertheless the low selectivity and capacity of available resins for the extraction of uranium in  $P_2O_5$  solutions and their low density compared with that of the acid have limited their use until now. The density and viscosity of phosphoric acid is such that they make resin beads float. Several studies at laboratory scale have been done (22, 23, 24), where two alternative cation exchangers have been studied:

- Resins impregnated with the mixture D2EHPA-TOPO. The Resin matrices used were poly styrene-divinylbenzene or methylmethacrylate.
- Macroporous copolymer of styrene-divinylbenzene with amino-phosphonic functional groups. This is manufactured by Duolite International under the trade name of DES-467.

Both ion exchangers have shown to be potentially suitable for the recovery of uranium from phosphoric acid. Impregnated resins have faster kinetics, but uranium loading was 4 - 6 times higher in the Duolite - ES-467 resin, which could be also used at temperatures near  $60^{\circ}C$ . The eluant for the resin impregnated with D2EHPA-TOPO was phosphoric acid at reducing conditions (with  $Fe^{2+}$ ) and the aminophosphoric resin was eluted by ammonium carbonate solutions. The organic matter present in the phosphoric acid was carried-over to the eluate solution along with the uranium. In a general way, a second cycle may be needed in order to attain satisfactory purification of the uranium.

No continuous ion-exchange processes have been developed. These would have the advantage of requiring little or no clarification of the acid. The availability of high density resins (with a density higher than  $1,3 \text{ g/cm}^3$ ) could make the use of the fluidized bed systems possible, saving costs on acid clarification.

### 3.3 Precipitation

The first method to be commercially used in the recovery of uranium from phosphoric acid in the early 1950s was a precipitation method (25). The Blockson Chemical Company developed a process, whereby uranium was reduced and precipitated with sodium hydrosulfate ( $Na_2S_2O_4$ ). The filter cake was washed and redissolved in a

solution of sulfuric acid under oxidizing conditions. Uranium was then reprecipitated with sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). The dry precipitate contained 40 to 60% uranium as  $\text{U}_3\text{O}_8$ .

Another method to recover uranium from phosphoric acid is by coprecipitation of tetravalent uranium with gypsum. In this process (called the "phosphogypsum process") the phosphate rock is digested in sulfuric acid under reductive conditions with metallic iron. The uranium, together with gypsum is removed by filtration of the phosphoric acid.

The precipitated uranium can be redissolved with a mineral acid, preferably sulfuric acid. The uranium solution can then be processed by conventional operations, either ion exchange, solvent extraction or both in series (26). Another method which has been tested is the digestion of the precipitate with phosphoric acid, using the original acid (27). The coprecipitation of tetravalent uranium with ammonium fluoride and subsequent recovery of rare earths, yttrium and vanadium, has also been studied (28).

The co-precipitation of uranium is affected by the concentration of ions present in solution. A higher content of fluoride allows a more efficient precipitation. Uranium is also precipitated more easily and efficiently from the hemihydrate gypsum than from dihydrate gypsum. The redissolution of uranium from the phosphogypsum does not present any special problems.

These precipitation processes have some advantages :

- a) They can be applied to the phosphoric acid obtained by the hemihydrate method (40-45 %  $\text{P}_2\text{O}_5$ ) as well as by the dihydrate method (28-30 %  $\text{P}_2\text{O}_5$ ).
- b) Risks of acid contamination with organic solvents are eliminated.
- c) After leaching the uranium from the phosphogypsum, its recovery is easy and inexpensive.

On the other hand, the process is strongly affected by the phosphate. Besides the higher iron concentration in the phosphoric acid during the digestion of the rock decreases its quality and generates additional corrosion problems which require the use of special materials.

### 3.4 Other methods

Other methods for the recovery of uranium from phosphoric acid are being studied. Liquid membranes and froth flotation seem to be the most promising.

#### 3.4.1 Liquid membrane process

A liquid membrane is a thin liquid film that selectively permits the passage of a particular component of a mixture. There are two types of liquid membranes : thin films supported by a solid structure and emulsions (29).

In the first type the liquid is impregnated into the pores of a solid membrane, such as a flat polymer sheet, or spiral-wound or hollow fibres. The liquid contains an extraction reagent which separates the uranium and transfers it through the membrane to the stripping agent. The extraction reagent is returned to the process.

Emulsion membranes, also called liquid surfactant membranes, are a stabilized dispersion of aqueous phase droplets in an organic phase. The internal phase is the stripping agent stabilized by the addition of a surfactant agent into the extraction agent.

The application of both kinds of liquid membranes to the uranium-phosphoric acid system has been studied using both (30, 31). D2EHPA-TOPO and OPPA as extractants. The process has been developed successfully to the stage of continuous tests in a laboratory scale.

The advantages of liquid membranes over solvent extraction and ion exchange are derived mainly from the favourable kinetics. The equipment required is smaller, and it is possible to treat phosphoric acid under more difficult conditions such as higher temperature (eliminating the cooling stage) and higher acid concentrations. The process could be applied to the recovery of uranium from hemihydrate acid.

### 3.4.2 Froth flotation

Flotation methods used to concentrate diluted liquors from uranium ores (32, 33) have also been studied to recover uranium from phosphoric acid.

In froth flotation techniques, compounds without surface activity are floated by adding a surface-active agent (collector). Several compounds can be removed from dissolved ions when these species form either an insoluble froth with the collector (ionic flotation) or an insoluble compound which is precipitated previously by adding a reagent different from the collector (precipitate flotation). Because of the addition of the collector and their hydrophobic character, the compounds formed by any one of the two methods, are absorbed into the bubbles of gas (air, nitrogen) which traverse the liquid upward. The floated species is collected in solid form at the surface of the liquid.

The ionic flotation technique has been applied to concentrate tetravalent uranium in phosphoric acid, because it is possible to form some floatable complexes with anionic collectors (34). This way, a final precipitate with a uranium content between 12 and 17 % is recovered. This product can be treated by a conventional process to obtain a commercial uranium concentrate.

### 3.5 Discussion of process applications

As shown in this review there are many methods that, in principle, can be used to recover uranium from phosphoric acid. Moreover, there are many variations of each method. New reagents are being developed which have not been mentioned in this paper and there are several possible combinations of processes and reagents. The main points to consider when analysing the applicability of the different processes are:

a) Range of acid concentration in which the method can be applied. Processes which can treat phosphoric acid obtained by any of the three existing methods (dihydrate, hemihydrate or anhydrite) in a range of concentrations between 25 and 55 %  $P_2O_5$  are favoured. This is the case of ion exchange and precipitation processes. Among the processes which use organic solvents, liquid membrane processes are the most suitable from this point of view.

b) Risk of contamination or modification of the quality of the original phosphoric acid. From this point of view, processes which use organic solvents or which introduce foreign ions (e.g. iron at the phosphogypsum process) are at a disadvantage.

c) Acid of pre-conditioning requirements, in relation to the temperature and content of organic matter and solids. Liquid-liquid extraction processes have more stringent pre-conditioning requirements than ion exchange and precipitation methods.

d) Efficiency of uranium recovery. This is generally higher with solvent extraction methods although liquid membranes and some organic solvents (OPPA, OPAP) have a higher loading capacity than the other reagents.

e) Kinetics of the process. Liquid membrane processes have faster kinetics while ion exchange processes are the slowest.

f) Selectivity of the reagents. Organic solvents and impregnated resins have the highest selectivity.

g) Chemical and physical stability of the reagents. Impregnated resins and some organic solvents (OPPA, OPAP) are degraded more easily than the other reagents.

h) Availability of continuous equipment for industrial use. Mixer-settlers for liquid-liquid extraction are commercial systems with lower investment costs and are easy to operate.

i) Economics. An economic comparison among the different processes is difficult, because of the different scales of application. Only the data referring to the processes based on solvent extraction are precise enough for economic studies, because of their widespread commercial acceptance.

Processes for the recovery of uranium from phosphoric acid must be considered in the light of current treatment trends for up-grading phosphates. The possibility of using other acids (nitric or hydrochloric acid) and of recovering other associated elements (rare earths, vanadium,

chromium, yttrium, etc) must also be taken into account. Designing the most suitable processes for the recovery of uranium from phosphoric acid is a challenge which will lead to advances in hydrometallurgy.

#### 4. ECONOMIC FEASIBILITY OF URANIUM RECOVERY PROCESSES

The costs of recovering uranium from phosphoric acid depend mainly on :

- plant capacity
- the concentration of uranium in the phosphoric acid
- the recovery process applied, especially regarding conditioning of the acid and the first cycle, where all the acid throughput is treated.

Several studies done at the beginning of the eighties (7, 8), showed that uranium recovery was economically feasible for treatment plants treating more than 150 000 t  $P_2O_5$ /year with uranium concentrations over 120 g U/cubic meter, taking into account the maximum price reached by the uranium between the years 1976 and 1979. The spot market price, which is frequently used as a reference to uranium price trends, was in this period over 40 US \$/lb  $U_3O_8$  (105,72 US \$/Kg U). This is the best indicator of uranium prices, even though only about 10% of the world trade is conducted through the spot market. After 1979, the average spot market price of uranium decreased to a minimum value of about 17 US \$/lb  $U_3O_8$  (44,93 US \$/Kg) in 1984. In the United States this caused the closure of high capacity plants because of their marginal economy (9). Since 1985 only one plant has remained in operation in the North American continent, that of Earth Sciences in Calgary (Canada).

Under currently prevailing conditions of the uranium market (low prices and assured supply), the recovery of this metal from phosphates is not attractive, compared with conventional mining (10). Nevertheless, there are some arguments in favour of utilization of this resource (11, 12, 13)

##### a) Strategic

In several countries, phosphoric acid is the only domestic uranium resource. In particular, this is the case of:

- Countries around the Mediterranean Sea, from Algeria to Iraq, including Tunisia, Egypt, Jordan and Syria.
- Countries on the Atlantic seaboard of Africa-Morocco and Sahara, Senegal and Togo.

The recovery of uranium from phosphates in these countries can be profitable because of:

- i) Savings of foreign currency
  - ii) Security of supply
  - iii) Acquisition of technology
- b) Ecologic
- The extraction of uranium from phosphoric acid is an example of conservation of a natural resource : if the uranium is not recovered, it is lost forever from the economy.
  - This process decontaminates the phosphoric acid. If uranium is not removed it remains in the final products (fertilizers, detergents, etc.), although this has not been proven to represent a health hazard.
- c) Economic
- Investment costs for a plant to recover uranium from phosphoric acid are lower than those for a conventional uranium mine and mill. Besides, the uranium is quickly available (with lead times of 3-5 years versus 12-13 years for conventional mines).

**Flexibility :** In times of uranium oversupply, the economic and social costs of putting an uranium from phosphoric acid unit on stand-by are lower than in the case of a conventional mine and mill.

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# **IMPROVEMENTS AND RESULTS ACQUIRED THROUGH SIX YEARS OF INDUSTRIAL URANIUM EXTRACTION FROM PHOSPHORIC ACID BY THE PRAYON PROCESS**

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## **Abstract**

UMIPRAY, S.A. has been recovering uranium from phosphoric acid since 1980 using the DEHPA/TOPO process. The main characteristics of the process are described and recent process innovations are discussed. These include the use of low-level flash coolers for acid cooling during pretreatment, improved control of the first-cycle reductive stripping, improved post-treatment of the first-cycle raffinate using a lamella settler and air-induced flotation, the use of gaseous oxygen instead of hydrogen peroxide for second-cycle acid oxidation, improved filtering and dewatering of the uranium concentrate and progressive introduction of automatic control for plant operation.

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## **The UMIPRAY plant extracts uranium from phos-acid since 1980 by the PRAYON Process**

UMIPRAY S.A., a Belgian Limited Company wholly owned by PRAYON, started recovering uranium from phosphoric acid in May 1980.

The PRAYON process used is based upon fundamental works of the Oak Ridge National Laboratory, U.S.A. (1), (2), (3) and utilizes the two-cycle extraction/stripping technique with the DEHPA/TOPO\* as solvent (\* see last page). From the origin and during the six-year operation now completed, important and particular design features have been introduced in the process, making it different from other processes using the same DEHPA/TOPO solvent and operated in North America.

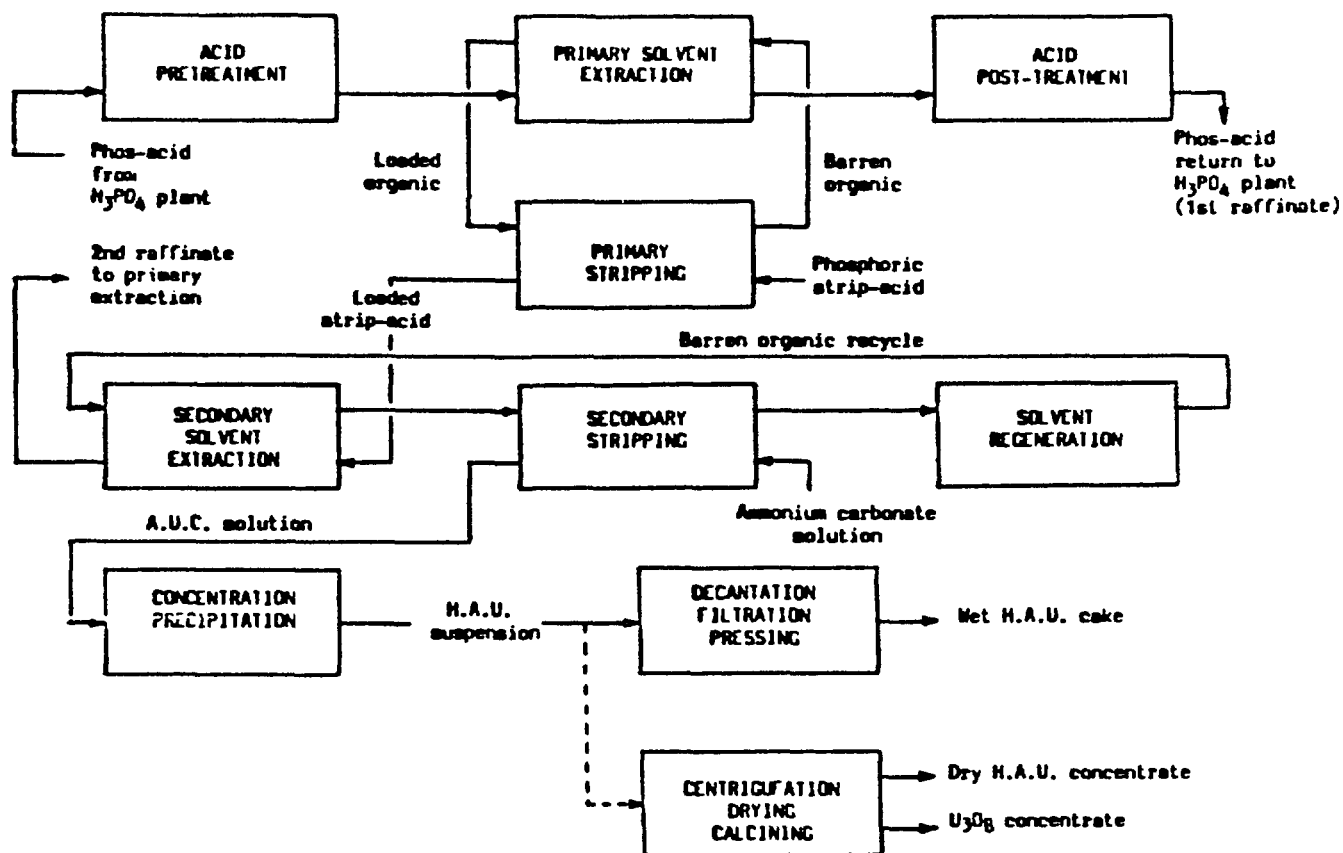
In spite of the depressed price displayed by the uranium since several years, the UMIPRAY plant is still in profitable operation and is the only one remaining on stream outside America. This is due to the high level of reliability, efficiency of operation and quality of uranium concentrate achieved by the process.

## **The main characteristics of the PRAYON uranium recovery process**

The PRAYON process (formely called I.M.C./PRAYON process), is the property of PRAYON DEVELOPPEMENT S.A., the Engineering Division of PRAYON and has been developed in 1978-79.

To this end, PRAYON has entrusted METALLURGIE HOBOKEN-OVERPELT, a world leader in liquid/liquid extraction of non ferrous metals, with the extraction part of the research and has shared with I.M.C. the first year of industrial experience of their respective plants.

Basically, the process is outlined in the block-diagram hereafter. It has been described in several papers (4), (5), (6) and we only recall here some of its features.



BLOCK DIAGRAM OF PRAYON URANIUM RECOVERY PROCESS

### 1. The phosphoric acid pretreatment

From our view-point, the acid pretreatment is nearly as important as the extraction itself.

High performances in extraction step depend, indeed, on a strict control of the solvent and acid flows, on a clear-cut division between the two phases after each mixing, on the absence of any "organic cruds" formation that would inevitably reduce the efficiency and cause losses of acid and solvent. That is why we give the primary phosphoric acid an extensive preparation including cooling, desaturation, clay treatment, filtration and adsorption through activated carbon.

In these conditions, the resulting clear "GREEN ACID" is perfectly desaturated, free of any mineral or organic solid, free of its soluble humic material and is prepared to be processed by liquid/liquid extraction.

## 2. First Cycle of Extraction/Stripping

Both extraction and stripping are made in a 3 or 4-stage battery of rectangular mixer-settler units.

The DEHPA/TOPO solvent requires the uranium to be at the  $U^{6+}$  state for the extraction and, inversely, to be at the  $U^{4+}$  state for the reductive stripping.

The judicious utilization of scrap iron added to the small flow of phosphoric strip acid to lower its Redox potential during the stripping is a major factor for the operation of the plant.

After the extraction step and the separation of the solvent entrained, the main flow of phosphoric acid (the 1<sup>st</sup> raffinate) returns to the  $H_3PO_4$  facility with the same clean aspect as the "green acid".

## 3. Second Cycle and Refinery

The same DEHPA/TOPO solvent is utilized in the 2<sup>nd</sup> cycle but with slightly different concentrations. The strip acid from 1<sup>st</sup> cycle enters the secondary extraction with a concentration of 10 to 12 g  $U_3O_8$ /litre.

The secondary stripping is made in a precise range of conditions such that the ammonium-uranium carbonate formed (A.U.C.) remains perfectly soluble, while other metallic compounds can precipitate.

Uranium precipitates naturally by concentration of the clear A.U.C. solution and gives a hydrated salt ( $3 UO_3 \cdot NH_4 \cdot 5H_2O$ ) called H.A.U. The purity of this product lies well beyond the requirements of all the converters.

Two ways of conditioning are then possible :

1°- The H.A.U. suspension is filtered and washed in a pressure filter and the WET YELLOW CAKE can be put directly in drums.

This concentrate does not need any calcination and it does not create any problem of radioactive dust recovery and environment protection.

2°- The H.A.U. precipitate can be, at will, either dried or calcined, giving in this case a  $U_3O_8$  concentrate with more than 80 % U.

### A few data about the UMIPRAY plant

<u>Location</u> : <u>at Puurs</u> (near Antwerp)	<u>at Engis</u> (near Liège)
- Pretreatment of acid	- Cycle II
- Cycle I	- Refinery
<u>Capacity</u> : 130.000 t P <sub>2</sub> O <sub>5</sub> /year (outside UMIPRAY plant)	55 t U <sub>3</sub> O <sub>8</sub> /year (presently) 115 t U <sub>3</sub> O <sub>8</sub> /year (by possible modification)
<u>Current output</u> : about 115.000 t P <sub>2</sub> O <sub>5</sub> /year	45 to 50 t U <sub>3</sub> O <sub>8</sub> /year

Phosphate raw material : Khouribga 70-71 BPL with 115-125 ppm U

Phosphoric acid to Sx-U : 45 to 50 m<sup>3</sup>/hour with 30-32 % P<sub>2</sub>O<sub>5</sub>

### Table of main performance figures :

Year	Uranium Concentrate Production (t U <sub>3</sub> O <sub>8</sub> )	Phosphoric Acid available		Uranium. Extraction Yield (%)	Operating Factor (vs. time available)
		P <sub>2</sub> O <sub>5</sub> content (%)	U <sub>3</sub> O <sub>8</sub> content (ppm)		
1980	20,4 (a)	28,92	129	91,1	87,0
1981	41,1	28,96	129	94,8	96,7
1982	43,7	29,0	124	96,5	99,0
1983	45,1	30,1	132	96,8	98,2
1984	50,3	29,8	135	97,0	99,2
1985	44,1 (b)	31,2	125	94,0 (c)	99,0

(a) : 6 months of operation in 1980

(b) : the production is evidently subject to the U<sub>3</sub>O<sub>8</sub> content of phosphate.  
A changement of phosphate rock composition has effected the production in 1985.

(c) : the new phosphate, strongly laden with humic material has caused a reduction of yield in 1985.

### Recent innovations brought to the process with a view to improve its efficiency and reduce the production cost

#### 1. Improvement of the phosphoric acid cooling in the Pretreatment by the use of two Low Level Flash Coolers working in series

The two-superposed-stage evaporator utilized originally has several process and operation disadvantages : incrustation build-up in the apparatus due to a high temperature drop, important kWh and water consumption, etc.

The new design includes two "Low Level Flash Coolers" (L.L.F.C.) similar to the ones used successfully in recent PRAYON phosphoric acid plants, working with a very low temperature drop (1 to 2 K) and a high circulation flow. These coolers are installed at a much lower level and partially flooded by the acid when put under vacuum. The circulation of acid is ensured by an axial-flow circulator with low manometric head. Each cooler has an individual circulation tank, the acid overflowing freely from 1<sup>st</sup> cooling circuit to 2<sup>nd</sup> one.

This design brings important savings of investment and operation costs to the acid pretreatment :

- less kWh consumed by the circulators (large capacity but very low manometric head);
- less cooling water needed by the condenser thanks to the higher temperature of water vapours leaving the 1<sup>st</sup> circuit;
- less steam for the ejectors of the vacuum unit (less dissolved air to be exhausted from the cooling water).

The following table gives the main figures for new and previous cooling designs on the basis of a 1.500 t P<sub>2</sub>O<sub>5</sub>/day pretreatment unit :

	Previous device	Use of 2 L.L.F.C.	Saving
Investment * (M FB)	16,7	12,3	26 %
Electrical power (kWh/h)	84,5	14,4	83 %
Cooling sea water (m <sup>3</sup> /h)	447	312	30 %
Steam for ejectors (kg/h)	600	500	17 %

\* investment relating to equipments differing in the two alternatives.

## 2. Improved control of the reductive stripping of uranium in the first cycle

The limitation of iron consumption during the stripping step of uranium is a major concern. Presence of Fe<sup>2+</sup> ions is permanently required in the strip acid to reduce U<sup>6+</sup> to U<sup>4+</sup>, but both iron and uranium are exposed to re-oxidation by the ambient air. The resulting ferric iron passing into the acid can cause undesired precipitation of ferric phosphate compounds in the mixer-settler units.

A patented device of "interstage reduction" has been implemented in our process. Controlled amounts of scrap iron are dynamically dissolved at every stripping stage, ensuring a constant and minimum presence of Fe<sup>2+</sup> ions at the right place with a minimum of fatal ferric iron passing in the acid.



In terms of consumption, the following figures have been recorded at UMIPRAY plant :

	kg scrap iron per t $P_2O_5$ available	kg scrap iron per kg $U_3O_8$
Average for 1982	1,43	3,54
Average for 1983	1,60	3,76
<u>After start-up of new device :</u>		
2 <sup>nd</sup> half-year 1984	1,18	2,67
Average for 1985	1,17	3,12

### 3. Modification of the post-treatment of first raffinate

The first raffinate, that is the main flow of acid going back to the  $H_3PO_4$  facility, is polluted by traces of solvent (DEHPA, TOPO and their diluent kerosene). For economical and technical reasons, it is important to sharply separate them. In UMIPRAY plant, the post-treatment presently includes one lamellas-settler followed by two activated carbon columns. The final quality of the raffinate is excellent, but the carbon must be periodically regenerated and the solvent absorbed in the columns is lost.

Another scheme of post-treatment has been experimented at industrial scale. After the lamellas-settler, the raffinate is treated in air-induced flotation cells. They practically require no maintenance and deliver the acid with less than 25 ppm (vol/vol) of solvent. The additional recovery of solvent is estimated to be 75 ppm of the raffinate volume (the average in/out contents being 100/25 ppm).

The corresponding saving in DEHPA + TOPO amounts to  $16/g\ m^3$  of raffinate, i.e. 95 g/kg  $U_3O_8$  in the yellow cake. This represents about one third of the DEHPA + TOPO consumption of the first cycle.

### 4. Reduction of the cost of oxidation agent in the second cycle by utilization of gaseous oxygen

The substitution of gaseous oxygen to hydrogen peroxide for the oxidation of the uranium-loaded acid entering the 2<sup>nd</sup> cycle is gradually proceeding in the UMIPRAY plant. When the full chagement will be achieved, it is expected that the cost of this reactive will be cut by four.

The efficiency of gaseous oxygen is less good than the one of hydrogen peroxide but this is amply compensated by its low cost.

So far, the oxidation cost evolves as follows :

YEAR	Cons. per kg U <sub>3</sub> O <sub>8</sub>	Unit cost	Cost per kg U <sub>3</sub> O <sub>8</sub>
1982+83	2,10 kg H <sub>2</sub> O <sub>2</sub> (35 %)	25 FB/kg	52,5 FB
1984	1,01 kg H <sub>2</sub> O <sub>2</sub> (35 %) 0,53 Nm <sup>3</sup> O <sub>2</sub>	25 FB/kg 4,8 FB/Nm <sup>3</sup>	25,25 ) 27,8 FB 2,55 )
1985	0,66 kg H <sub>2</sub> O <sub>2</sub> (35 %) 0,74 Nm <sup>3</sup> O <sub>2</sub>	25 FB/kg 4,8 FB/Nm <sup>3</sup>	16,5 ) 20,05 FB 3,55 )

##### 5. Improvement of the yellow cake purity and moisture

The handling and dissolution of the wet yellow cake (H.A.U.) at the converter's facility had given some unpleasant annoyance due to the :

- appearance of some spongy "gums" during dissolution of Y.C. in nitric acid (and caused by traces of solvent trapped in the H.A.U. precipitate);
- difficulty of handling the wet and sticky cake.

The origin of the first trouble has been quickly identified by laboratory tests. A simple solution has solved this problem : the A.U.C. solution is polished by filtering it through a paper-filter before entering the lamellas-settler. The bright clear solution then flows to the precipitation step.

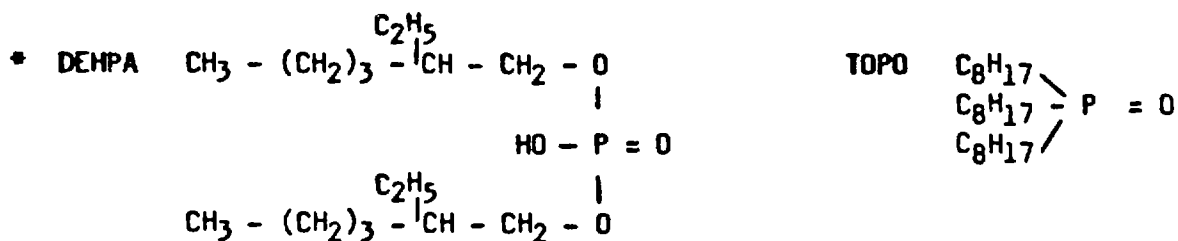
The second problem has been definitely solved by pressing the H.A.U. cake in a tube-press under a pressure of about 120 bars.

The dewatered cake falls from the tube-press in the form of narrow strips having a compact and solid aspect and withholding only 10 to 15 % moisture. This yellow cake is now easy to handle and has lost its thixotropic character.

##### 6. Advance in the monitoring of uranium through the process, leading to a automatic control of the operation

The plant has demonstrated to be easily controlled and technical performances have reached a high level. The next task of our R & D staff is now to progressively introduce an automatic control of the operation in the plant. The first step is the development, in laboratory, of a "continuous flow" uranium analysis method valid for organic and aqueous phases. This has been achieved last year and it is based on the photo-colorimetric technique.

The next step will include the construction of a semi-automatic apparatus and its experimentation in cycle II of the plant.



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## THE D/T EXTRACTION PROCESS AND ITS APPLICATION TO A PHOSPHORIC ACID

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### Abstract

The DEHPA/TOPO process used by the Uraphos Chemie plant in Florida and the Uraphos amine/polyphosphate (A/P) uranium extraction process are described. The industrial plant in Florida uses a conventional DEHPA/TOPO process with acid preconditioning, first cycle extraction in six mixer-settlers, raffinate post treatment, second-cycle extraction in four stages, stripping and precipitation. The Uraphos A/P process uses a tertiary amine (2% trilaurylamine) as extractant and a long-chain polyphosphate as complexing agent for tetravalent uranium. The process includes acid pretreatment, first-cycle extraction and stripping, precipitation of  $\text{Na}_2\text{U}_2\text{O}_7$  as an intermediate product, dissolution of the intermediate product, second-stage extraction and stripping and precipitation of sodium diuranate as a final product. A mobile pilot plant with a capacity of 200 L of phosphoric acid per hour has been built to demonstrate the process. A test programme to study the suitability of the DEHPA/TOPO process or the A/P process for the treatment of a given phosphoric acid is outlined.

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The process can be split up into 4 unit operations which are

- (1) Acid preconditioning and gunk removal
- (2) First cycle extraction and strip
- (3) Raffinate post treatment
- (4) Second cycle extraction, strip and uranium precipitation.

Figure (1) shows a simplified pictorial flow sheet of the DEHPA/TOPO process as used in our extraction plant in Florida/USA.

- 1.1 The acid preconditioning and gunk removal includes the
  - acid coolingperformed in a two stage flash cooling system reducing the acids temperature from approx. 65° to 40° C; the
  - acid clarificationwhich takes place in a raked clarifier of 1000 m<sup>2</sup> settling area. The overflow, essentially free of solids is pumped into an oxidation reactor tank where the
  - acid oxidation

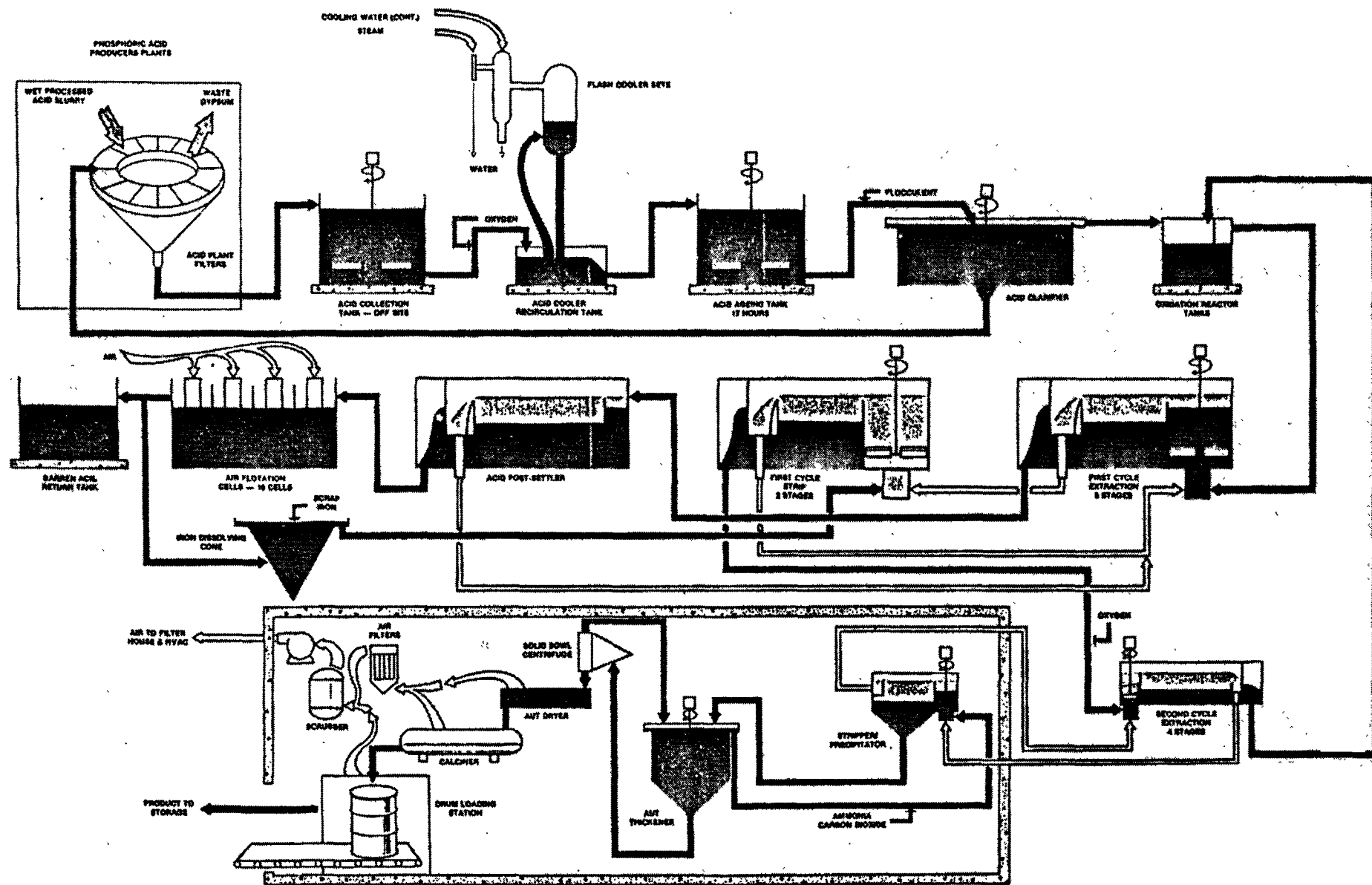


FIG. 1. Flow sheet of the DEHPA/TOPO process.

actually an oxidation of uranium and divalent iron, is accomplished in an oxidation reactor by having injected oxygen into the phosphoric acid transfer pump sections prior to flash cooling. In addition, as a back up, a hydrogen peroxide polishing system is installed to introduce  $H_2O_2$  to the phosphoric acid assuring a hexavalent uranium and a trivalent iron ion in solution.

The last step of the acid preconditioning the  
- gunk removal

can already be considered a part of the next unit operation, the first extraction cycle.

Whenever phosphoric acid containing humic solids is contacted with a kerosene-based organic solvent, and the resulting mixture is allowed to settle, an oily, viscous emulsion will form at the interface between the organic and aqueous layers. This interfacial emulsion has been given the name "gunk". If the gunk were allowed to collect at the interface of a settler, it would soon interfere with normal operation. The purpose of the gunk-removal mixer-settler is to thoroughly mix the acid with the first cycle organic, and to cause most of the gunk to form in one area, where it can be handled with special equipment.

The gunk layer in the settler is allowed to grow to the point where it overflows with the organic into the organic clarifier, where the gunk is allowed to separate and compact. The clarified organic overflows to the organic make up feed tank where it is pumped to first cycle stripping and recycled to the gunk mixer-settler. The acid stream, now essentially free of its organic solids, flows to first cycle extraction.

## 1.2 First Cycle Extraction and Strip

The purpose of first cycle extraction is to effectively transfer the uranium into the first cycle organic solution. This is accomplished in five mixer-settler units (six including the gunk mixer-settler) with the organic flowing countercurrent to the acid in a flow ratio of 0.5 to 1 O/A. There is intrastage recycle of the organic to maintain a phase ratio of 1.5 to 1 O/A in the mixers. The loaded organic proceeds through the gunk mixer-

settler and on through first cycle stripping delivering the uranium to the stripping acid, and the barren organic is recycled to the final extraction stage. The barren acid (raffinate) flows into the raffinate treatment section before being returned to the phosphoric acid producer.

Stripping of the uranium from the loaded solvent is accomplished by borrowing a small portion of the uranium-barren raffinate from the main acid stream and adding iron metal to it. The reduced acid is pumped to the first cycle stripper where it flows countercurrently to loaded organic. A large aqueous intrastage recycle is maintained for an aqueous-continuous phase. As the loaded organic intensively contacts the reduced acid, the uranium is reduced to  $U^{+4}$  and is rejected by the organic.

### 1.3 Raffinate post treatment

The acid stream from the extractor loop contains enough entrained organic solvent to be harmful to the equipment of the acid producer. The larger proportion of this organic solvent is removed by allowing the acid to flow gently through a tank with a large surface area where phase disengagement can take place.

A series of air flotation cells remove the remainder by causing this organic solvent to adhere to dispersed air bubbles that float the organic solvent to the surface as a foam (froth). Finally the acid is reheated to its original temperature before being returned to the acid producer. Reheating is needed to prevent a loss of evaporator capacity for the acid producer.

### 1.4 Second Cycle Extraction, Strip and Uranium Precipitation

The second cycle extraction system is identical in principle to first extraction, but has only four stages. A small intrastage recycle of organic is maintained. The raffinate from the fourth mixer-settler is collected and returned to second stage of first cycle extraction, thus returning the acid that was "borrowed" from the main acid stream.

The uranium loaded organic flows to a two stage stripping unit where it is contacted with ammonium carbonate solution. By maintaining a specific ammonia level and lead pH in the solution uranium precipitates as ammonium uranyl tricarbonate (AUT) which is collected at the bottom of the conical settlers. The settler underflow is brought to a drying and calcining unit to produce the  $U_3O_8$  final product. The  $NH_3$  and  $CO_2$  gas from the calcining unit is used in fortification of the aqueous stripping solution.

## 2. UC'S OWN AMIN/POLYPHOSPHATE (A/P) URANIUM EXTRACTION PROCESS

Again we would like to outline the process using a simplified process flow sheet (Figure 2). The process divides readily into 3 logical unit operations which are

- acid pretreatment
- extraction, stripping cycle 1 and intermediate product precipitation
- purification cycle and precipitation of final product.

This process is based on the well known amin technology employing a tertiary amin as a liquid ion exchange media. A long chain polyphosphate is used as complexing agent for the tetravalent uranium, making it necessary to reduce all uranium to the tetravalent stage.

### 2.1 The acid pretreatment includes the

- reduction of interfering ions such as  $F^-$  and  $SO_4^{2-}$ . The tolerable levels for  $F^-$  and  $SO_4^{2-}$  in terms of g/kg of acid are 5.0 and 20.0 respectively. The excess of both  $F^-$  and  $SO_4^{2-}$  are precipitated as insoluble solids e.g.  $Na_2SiF_6$  and  $CaSO_4$ . After thickening and filtration the uranium values in the acid have to undergo an

- EMF adjustment

which is accomplished by adding elemental iron to the phosphoric acid. EMF values of 220 mV are usually sufficient to guarantee a good uranium loading of the light phase. In case black acids have to be used as an extraction feed the

- reduction of humates

will be achieved using activated carbon columns.



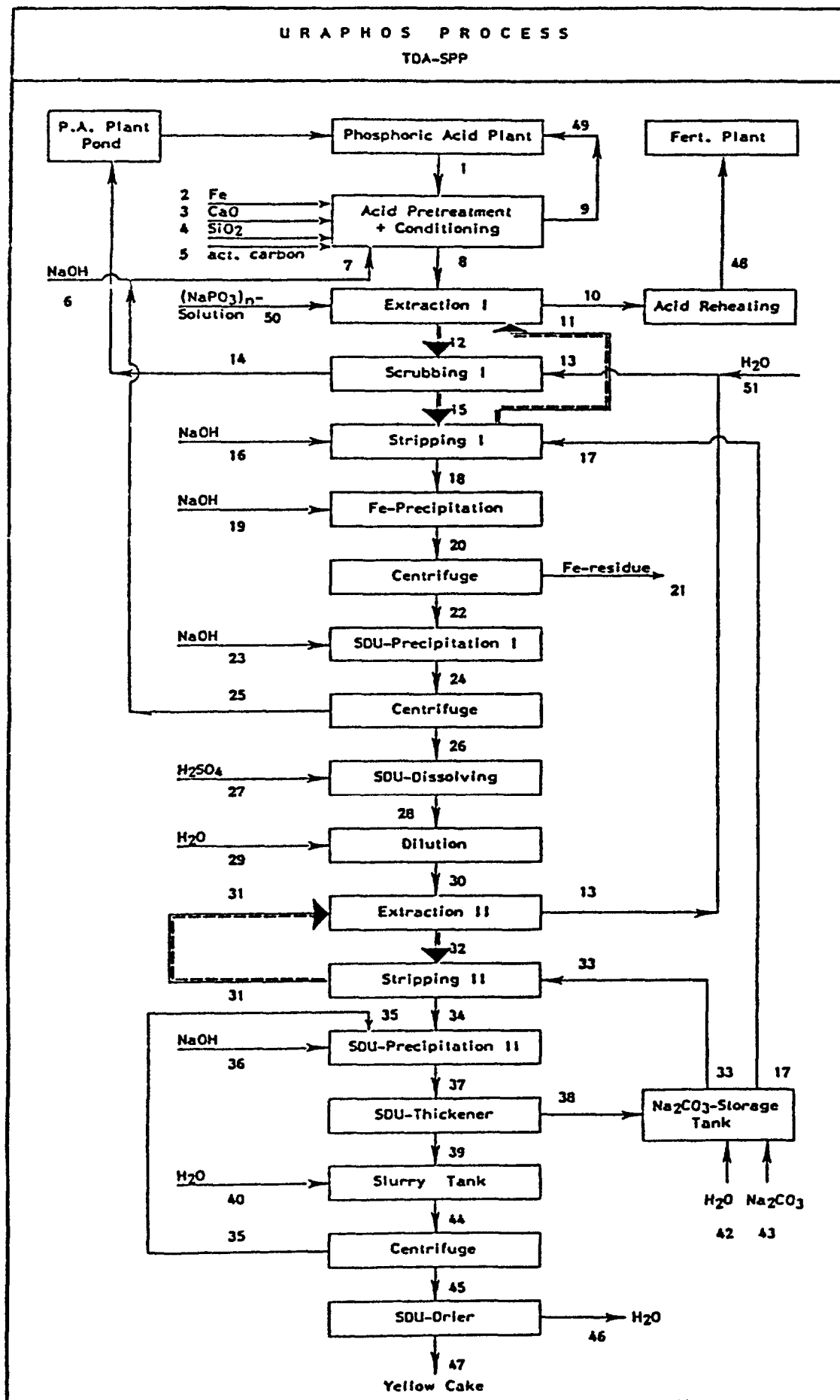


FIG.2. Uraphos process flow sheet.

## 2.2 Extraction, Stripping Cycle 1 and Intermediate Product Precipitation

The pretreated reduced acid essentially free of solids and humic matter enters the first extraction and stripping cycle, at the end of which a crude intermediate sodiumdiurante is precipitated. As already mentioned earlier the A/P technology can be defined as a liquid ion exchange process employing a solution of 2 % trilaurylamine in Exsol D 200/240. Therefore the transfer of uranium from the aqueous to the organic phase being an ionic reaction, will be easily accomplished in two to three mixer settler stages operated in a countercurrent mode. The light phase is riddened of coextracted iron and entrained  $P_2O_5$  values in a solvent scrubbing stage. The uranium pregnant light phase then is stripped with a sodium carbonate solution in a three stage countercurrent stripping cycle. This carbonate solution carries approx. 10 g of uranium/l. The uranium is precipitated as  $Na_2U_2O_7$  using a 50 % NaOH solution. The next slide (6) shows the composition of a typical crude yellow cake produced with the A/P process.

## 2.3 Purification Cycle and Precipitation of the Final Product

The two main impurities of the intermediate product,  $P_2O_5$  and Fe, have to be separated from the yellow cake. This is accomplished in the purification cycle. The intermediate product is dissolved in sulfuric acid resulting in a solution carrying approx. 10.000 ppm U. This liquid is used as a feed for the two stage countercurrent purification extraction. The spend sulfuric acid raffinate is used as a scrubbing liquid for first cycle organic scrubbing. The organic phase is exactly the same for both extraction cycles, meaning there is no necessity of changing the concentration of the complexing agent or changing the extraction media altogether.

The uranium loaded light phase is again contacted with a sodium carbonate solution and uranium is precipitated from this solution as sodium diuranate using sodium hydroxide. The strip raffinate of this second two stage countercurrent stripping cycle is reused in the first stripping cycle. The composition of the final product is shown on the next slide (7).

### 3. DATA CONCERNING UC'S "MOBILE PILOT PLANT"

The next two Figures (3 and 4) will give a general overview over UC's pilot plant.

#### 3.1 Size and name plate information of the pilot plant see Figure 3.

The extraction plant is able to treat approx. 200 - 300 l of phosphoric acid per hour resulting in approx. 6 t of phosphoric acid per day.

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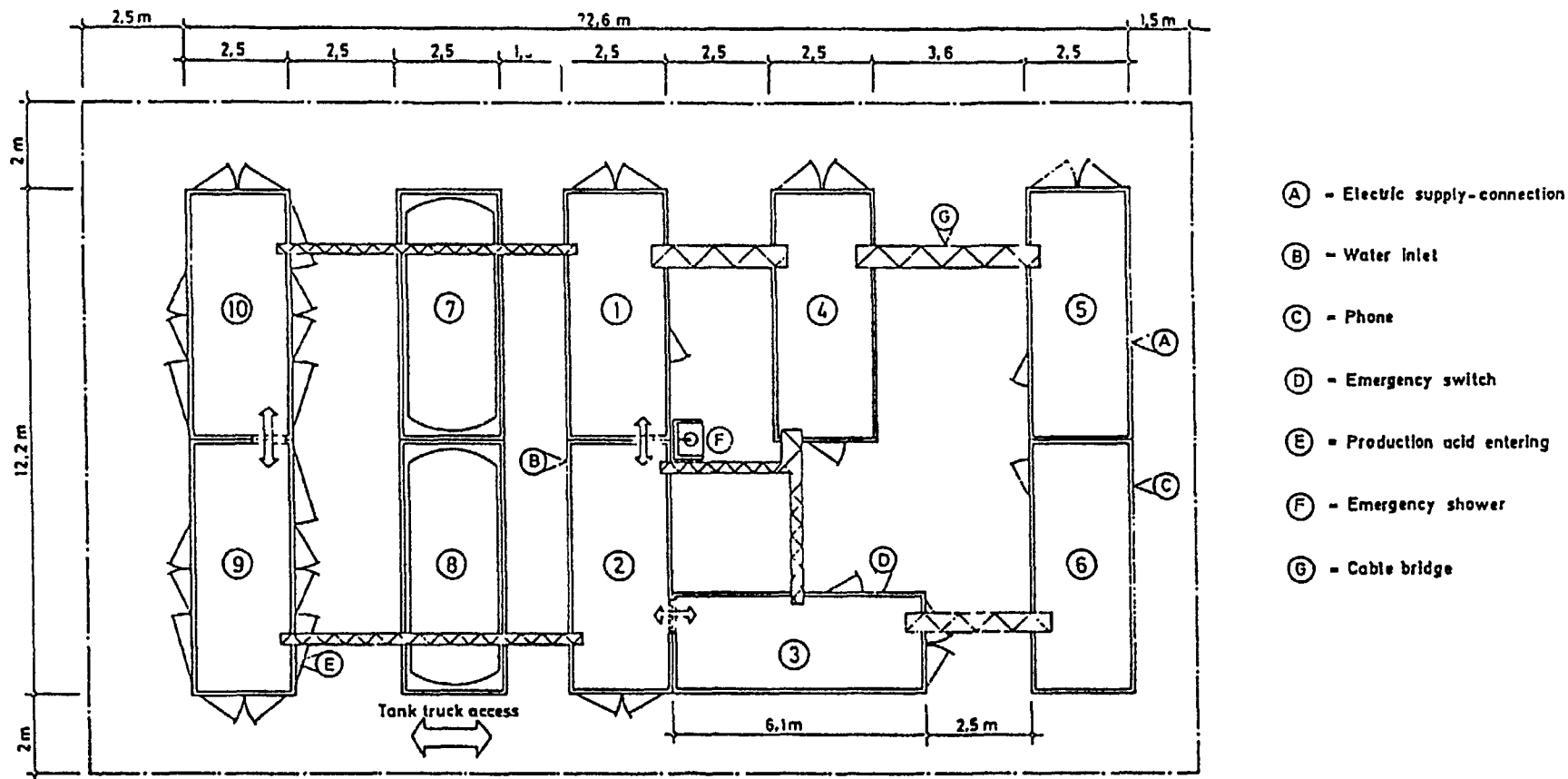
Number of containers:	10
Type of containers:	8 ISO containers 2 ISO tank containers
Measures:	20' x 8'6" (8 units) 20' x 8' (2 units)
Area required for plant:	approximately 430 m <sup>2</sup> (see outline below)
Electrical connection:	approximately 120 kW 380 - 660 V 50 Hz
Throughput of phosphoric acid:	approximately 200 l/h
Operating staff:	3-4 men/shift

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FIG.3. Data of the mobile Uraphos pilot plant.

#### 3.2 Arrangement of containers, set up and area requirement

Figure 4 shows the set up of the pilotplant and the unit operations located in each container.



NECESSARY LOCATION AREA  $26.6\text{ m} \times 16.2\text{ m} = 431\text{ m}^2 = (87.27\text{ ft.} \times 53.15\text{ ft.} = 4639\text{ sq.ft. (us + imp.)}$

- |  |  |
|--|--|
| Container ① - Extraction I                                       | Container ⑧ - X-ray fluorescent analysis<br>Measuring and control room |
| Container ② - Solvent-regeneration                               | Container ⑦ - Phosphoric acid tank                                     |
| Container ③ - Re-extraction I, extraction II<br>Re-extraction II | Container ⑥ - Phosphoric acid tank                                     |
| Container ④ - Iron-precipitation<br>Uranium-precipitation        | Container ⑨ - Phosphoric acid conditioning                             |
| Container ⑤ - Electric power, store                              | Container ⑩ - Phosphoric acid conditioning                             |

FIG.4. Location plan of the Uraphos pilot plant.

### 3.3 Essay of yellow cake produced in a test campaign

Figures 5 and 6 show the analysis of the yellow cake products achievable using the amin/polyphosphate technology.

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$\text{U}_3\text{O}_8$	57.1 %
$\text{P}_2\text{O}_5$	6.3 %
$\text{Fe}_2\text{O}_3$	1.1 %
$\text{CaO}$	0.5 %
$\text{SiO}_2$	0.3 %
$\text{H}_2\text{SO}_4$	1.1 %
$\text{Na}_2\text{O}$	17.5 %
$\text{CO}_3$	10.8 %

---

FIG.5. Essay of the unwashed intermediate yellow cake produced by the A/P process.

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$\text{U}_3\text{O}_8$	81.6 %
$\text{P}_2\text{O}_5$	0.3 %
$\text{Fe}_2\text{O}_3$	0.2 %
$\text{CaO}$	0.3 %
$\text{SiO}_2$	0.05 %
$\text{H}_2\text{SO}_4$	0.7 %
$\text{Na}_2\text{O}$	9.13 %
$\text{K}_2\text{O}$	0.05 %
$\text{V}_2\text{O}_5$	0.05 %
$\text{TiO}_2$	0.08 %

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FIG.6. Essay of the purified yellow cake produced by the A/P process.

## TEST PROGRAM EMPLOYING PHOSPHORIC ACID

### (1) Analysis of rock phosphate, phosphoric acid and gypsum from rock phosphate digestion

For these tests representative samples (appr. 1 kg) of rock phosphate (RP) phosphoric acid (PA) and gypsum (G) will be analyzed for following elements:

Elements	RP	PA	G
P <sub>2</sub> O <sub>5</sub>	x	x	x
CaO	x	x	-
H <sub>2</sub> SO <sub>4</sub>	x	x	x
Fe <sub>2</sub> O <sub>3</sub>	x	x	x
SiO <sub>2</sub>	x	x	x
Al <sub>2</sub> O <sub>3</sub>	x	-	-
MgO	x	-	-
Na <sub>2</sub> O	x	x	x
U <sub>3</sub> O <sub>8</sub>	x	x	x
EMK (mV)	-	x	-
ρ (kg/l)	-	x	-

With this data P<sub>2</sub>O<sub>5</sub> and uranium balances will be established leading to recovery rates (yields) for P<sub>2</sub>O<sub>5</sub> and U<sub>3</sub>O<sub>8</sub>.

Costs of DM 5,000 will be charged for these analysis.

### (2) Prefeasibility study on a 100 l phos acid sample

This test program includes the following activities:

- Analysis of the acid.
- Pretreatment tests (DEHPA/TOPO (D/T) and Amin/Polyphosphates (A/P) technology).
- Extraction tests (single stage, multistage-countercurrent, development of partition coefficients - McCape Thiele plot of results).

- Stripping tests (see extraction tests).
- Determination of operating costs (D/T and A/P).
- Investment costs (guesstimate).

For the prefeasibility study DM 25,000 will be charged to the orderer.

(3) Pilot plant testing using either the D/T or A/P technology

These tests should be performed directly in cooperation with the phosphoric acid producer. The cost breakdown is based on a 6 months campaign employing three specialists of UC and operating personel of the phosphoric acid producer.

The process technology used will be drawn out of the results of the work performed under (1) and (2).

Budget breakdown

- Labor costs
 

Process engineers	DM 760/day	2 x
Lab technician	DM 600/day	1 x

For the 6 months period following time formula is used:

$$\text{DM}(\text{man} \cdot \text{day}) \times n_{\text{days}}^{0,95} = \text{resulting labor costs}$$

$$((2 \times 760/\text{day}) + (1 \times 600/\text{day})) \times 110 \text{ days}^{0,95} = 184,356.70 \text{ DM}$$

-	Travel expenses	
	6 flights	- Germany DM 3,000/flight
	6 x 3,000 DM	18,000.-- DM
-	Telephone, telex, etc.	2,500.-- DM
-	Overheads	
	40 % of labor costs	73,742.68 DM
-	Transportation costs for pilot plant (guesstimate)	150,000.-- DM
-	Insurance for pilot plant	60,000.-- DM
-	Depreciation for pilot plant	
	Time formula: $n_{\text{weeks}}^{0,85} \times 8,000 \text{ DM/week}$	= resulting depreciation
	0,5 a = 26 weeks	
	$26^{0,85} \times 8,000 \text{ DM/week}$	127,590.20 DM
	Subtotal	616,189.58 DM
-	Unexpected expenses	
	10 % of the labor costs	18,435.67 DM
	TOTAL COSTS	<u>634,625.25 DM</u>

The proposed scope of work under title (3) includes all evaluations of test results, a feasibility study, design criteria for an uranium extraction plant and the calculated operating and production costs in terms of US\$/lb  $\text{U}_3\text{O}_8$ .



# RECOVERY OF URANIUM FROM PHOSPHORIC ACID BY ION EXCHANGE

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## Abstract

The ion-exchange process developed by the Nuclear Research Center at Negev and the pilot plant built to demonstrate it are described. The process includes acid pre-treatment, absorption on Duolite ES-467 ion-exchange resin, elution and precipitation. A pilot plant with a capacity of 100 L/hr of fresh phosphoric acid was built adjacent to the Rotem phosphoric acid plant (Negev) and operated intermittently from 1984 to mid-1986. Overall uranium recovery was about 90% and the concentrate produced met commercial specifications. An economic analysis of the process is also given.

---

## 1. Introduction

The ion-exchange route for the recovery of uranium from "wet phosphoric acid (WPA) has been developed by the NRCN as an improved alternative to the currently used solvent extraction processes. It was a result of a long-term research program which was reviewed in a previous publication (1).

Extensive laboratory and bench-scale work carried out mainly during 1983, showed the significant potential advantages of the ion-exchange process over other existing techniques(1). Therefore, a decision was taken to proceed with the development of the process on a semi-industrial scale.

A pilot-plant has been constructed adjacent to the wet-process acid plant of Rotem Fertilizers Ltd., in the Negev (southern part of Israel). It has operated intermittently, for periods of several months each, from the beginning of 1984 until mid-1986. Shut-down periods were utilized to analyse the results, identify problems, perform supporting laboratory research and maintenance.

The basic process flow-scheme shown previously, has been re-designed and improved as a result of this work.

## 2. Description of the process

The process flow-scheme, as evaluated and demonstrated during the operation of the pilot-plant, consisted of the following stages:

### 2.1 Pre-treatment of the acid feed

- Settling of suspended solids
- reduction of the acid with iron powder
- heating (if needed)
- sand-type filtration (if needed)

### 2.2 Loading (adsorption) of uranium on ion-exchanger

- adsorption from tails (scavenging)
- adsorption from fresh acid feed

### 2.3 Preparations for elution

- Oxidation of adsorbed uranium with raw (unreduced) phosphoric acid
- displacement of phosphoric acid from the ion-exchange column with water
- washing of resin bed with water
- neutralization of the ion-exchanger and removal of adsorbed organics with aqueous ammonia
- washing of resin bed with water.

### 2.4 Elution

- Stripping of adsorbed uranium with aqueous ammonium-carbonate solution.



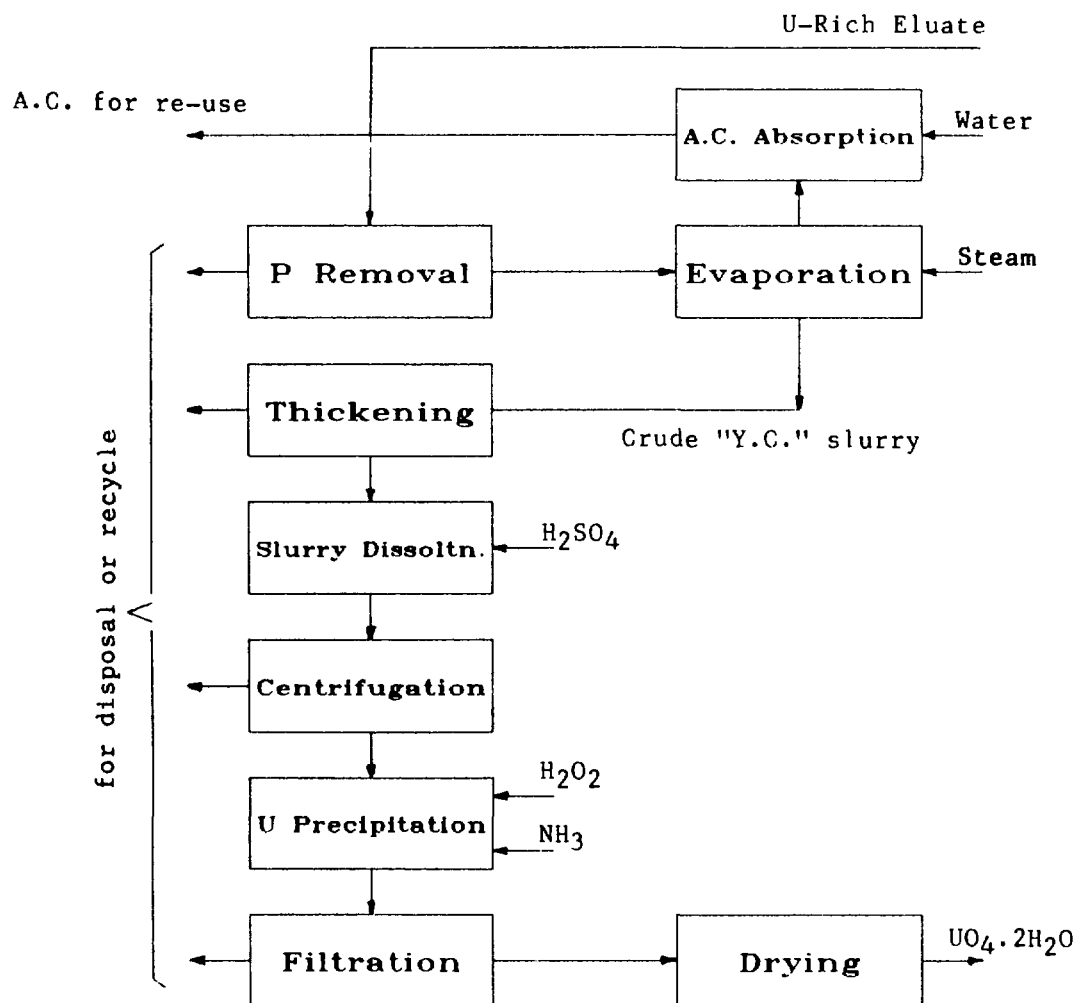


FIG.2. PRECIPITATION OF YELLOW CAKE

The ion-exchange system consisted of four fixed-bed columns, with a diameter of 15 cm and a height of 300 cm each. Phosphoric acid and other reagents were fed directly on top of the resin bed, while wash water were introduced through a "water dome" at the empty upper part of the columns.

Each column was operated batchwise. For achieving an overall continuous operation of the ion-exchange system, the columns were connected in series and operated in a cycled "Merry-Go-Round" arrangement. Experiments could be carried out, however, by separating the columns and operating them in parallel.

Precipitation of crude "yellow-cake" was carried out in a double-effect electrically heated evaporator. Ammonium-carbonate vapors were absorbed for re-use in a circulating water stream by a venturi scrubber.

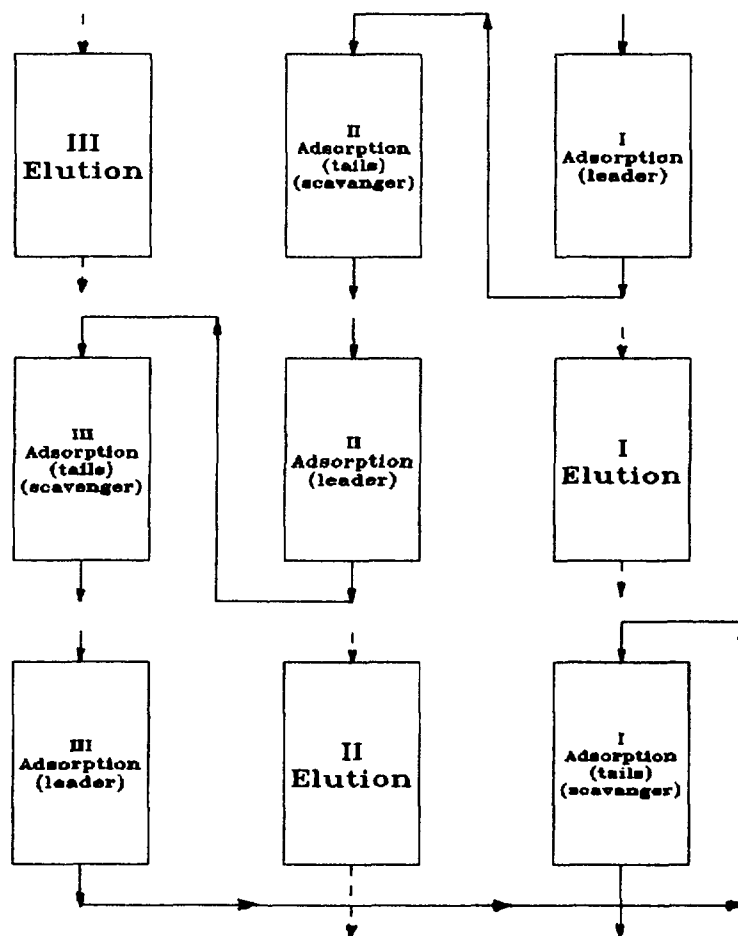


FIG.3 AN EXAMPLE OF A MERRY-GO-ROUND SYSTEM

The operation of the pilot-plant was controlled manually. However, adequate on-line analytical methods have been developed for continuous verification of performance in real-time. Two developments deserve special attention:

- a) Monitoring the performance of the reduction column by continuous determination of residual  $\text{Fe}^{+3}$  concentration. This important problem was solved by adaptation of the common laboratory polarography technique to continuous operation.
- b) Determination of uranium concentrations, varying from a few mgr/lit to over 10 gr/lit, in various process streams. This was accomplished by measuring the 185 KeV peak of the gamma

radiation emitted by the natural occurring  $U^{235}$  isotope. A field apparatus comprising of a GeLi detector and a multichannel analyzer has been built and operated for analyzing uranium at real time.

#### 4. Summary of Results

The design and the working program of the pilot plant had two main objectives:

- a) to verify and confirm laboratory results on a larger scale with fresh WPA.
- b) to evaluate data and procedures for scaling-up the results to a full-scale uranium recovery plant.

From this point of view, attention has been focused mainly on the performance of the ion-exchange system, as it represented the novelty of the process.

It has been proven that the resin used (Duolite ES-467) adsorbes  $U^{+4}$  with high affinity and selectivity. Interference is expected only by  $Fe^{+3}$  which, therefore, must be reduced to  $Fe^{+2}$  prior to adsorption.

Reduction of the uranium and iron content of the WPA feed is therefore a key step in the process-affecting directly the yield of uranium recovery.

Metallic iron powder has been used for carrying out the reduction step. It has been dissolved in the WPA feed batchwise in mixed tanks.

A more efficient and convenient reduction technique has been developed during the operation of the pilot-plant. It applied a continuous "reduction-column" where WPA and iron powder were fed co-currently. As mentioned above, the performance of the column was controlled on-line by a falling mercury drop polarograph.

As compared to the formerly used batch reduction, the continuous operation enabled us to shorten retention times and to reduce excessive iron consumption considerably.

Oxidation of the loaded uranium on the resin phase has been found to be the key step influencing elution efficiency. Because common oxidizing agents cannot be tolerated by the ion-exchanger, raw (unreduced) WPA has been used for this purpose. Oxidation of the  $U^{+4}$  ions took place probably because of the presence of  $Fe^{+3}$  ions in the medium of the unreduced WPA. Excess of unreduced WPA is required for complete oxidation of the adsorbed uranium.

The oxidizing WPA thus emerging from the ion-exchange column is recycled to the reduction step.

Laboratory experiments showed that exposing the ion-exchange resin to common oxidizers (like nitrates, chlorates and hydrogen-peroxide) caused irreversible damage to its performance.

On the other hand, the ion-exchanger was very stable under normal process conditions. Minor resin losses from the pilot-plant columns were only due to spillages caused by operational mistakes.

Overall uranium recovery, measured during the prolonged operation of the pilot-plant, was about 90% based on its concentration in the acid feed.

Precipitation of "yellow-cake" from the rich eluate by partial evaporation of the solution and expelling the ammonium-carbonate is a well-known technique and imposed no special problems.

However, at this stage special attention has been given to the problem of product purity. It has been realized that the "yellow-cake" thus obtained did not meet the commercial specifications for impurities content, and the development of an additional purification step became a necessity.

The most prominent impurity was phosphate which probably came from trapped traces of phosphoric acid and from adsorbed uranium-phosphate complexes. It is reasonable to assume that phosphate contamination is an unavoidable outcome of the ion-exchange process, and therefore should be removed prior to the primary precipitation of uranium from the eluate by evaporation. We have chosen a selective precipitation scheme for this purpose.

TABLE 1. MAIN IMPURITIES IN URANIUM CONCENTRATES

Element	Concentration in Y.C.		Specifications (Comurhex)	
	Crude	Purified	Penalty	Rejection
U <sup>(1)</sup>	63%	69.2%		60%
Organics <sup>(1)</sup>	0.1%	0.03%		0.1%
CO <sub>3</sub> <sup>(2)</sup>	3.00	0.14	2.00	3.00
PO <sub>4</sub> <sup>(2)</sup>	14.40	0.20		1.00
Mo <sup>(2)</sup>	0.04	<0.01	0.10	0.30
SO <sub>4</sub> <sup>(2)</sup>	0.52	1.50	3.00	10.00
V <sup>(2)</sup>	0.60	0.30		0.30
Zr <sup>(2)</sup>	1.95	0.04	0.20	2.00

(1) Based on dried sample (120°C, 24 hours).

(2) %, uranium based.

Other impurities - like Zr, V, Ti, Mo etc.- are characteristic to their concentrations in the WPA feed. Therefore, their existence in the "yellow-cake" depend on the composition of the acid, and measures to remove them may not be a necessity. Further purification of the uranium is therefore an additional step which can, under certain conditions, be skipped.

The additional purification scheme developed by us is based on the well-known technology - re-dissolutive of the crude primary "yellow-cake" and precipitation of uranium as the peroxide complex.

##### 5. Economic Considerations

Although the performance of the process is relatively insensitive to WPA composition (except for P<sub>2</sub>O<sub>5</sub> concentration), it does influence the economics of uranium recovery.



The main factor to be considered is the concentration of uranium in the WPA feed, because of two reasons:

- a) A major part of the investment is a function of the WPA volume to be handled, and not of the quantity of uranium to be recovered.
- b) Chemicals consumption for elution and hence its absolute cost is mainly determined by the chemical properties and the volume of the resin.

The quantity of uranium loaded on the resin, which is a function of its concentration in the WPA does not actually affect elution costs. The same goes for WPA related operations, such as heating.

Another important factor, or to be more specific- the Fe/U ratio in the WPA, determines the consumption of iron powder for reduction, which is a significant cost item.

These parameters, along with other specific local cost items (such as costs of chemicals and utilities, manpower costs, overhead burden, interest, taxes and other charges) vary from site to site. Therefore, it is impossible to give generally valid cost estimates for the process.

Anyhow, several feasibility studies prepared by the NRCN for various different cases and sites lead to the following conclusions:

- a) The approximate distribution of capital costs among the main process sections is 50% for pretreatment, 25% for the ion-exchange system and 25% for precipitation and purification of the yellow-cake.
- b) Overall uranium recovery expenses are usually in the range of 15-25 \$/lb  $U_3O_8$ , depending on local conditions.
- c) Overall expenses, both for investment and operating, are generally in the order of 50% of an equivalent solvent extraction plant, depending again on local conditions.

## 6. Summary

The ion-exchange process developed by the NRCN for the recovery of uranium from phosphoric acid has been demonstrated in a pilot-plant and proven to be simple, reliable and efficient.

We believe that the know-how and operating experience gained during this development work form a good basis for the design and construction of a full-scale uranium recovery facility.

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# **LABORATORY AND PILOT PLANT STUDIES FOR THE RECOVERY OF URANIUM FROM PHOSPHORIC ACID BY THE D2EHPA-TOPO PROCESS**

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## **Abstract**

The activities and costs involved in laboratory and pilot plant studies are discussed as applied to the D2EHPA-TOPO process. The overall capital investment (including engineering) for a plant with a throughput of 12 cubic meters of acid / day has been estimated to be around one million US dollars. Operating costs per year, without considering amortization and labor, are over 20 000 US dollars. A total time of 3,5 years (including engineering, purchase and pilot plant tests) could be needed to obtain the information required for final scale-up.

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## **LABORATORY AND PILOT PLANT STUDIES**

### **1. INTRODUCTION**

Process development for the recovery of uranium from phosphoric acid can be directed according to two different objectives :

a) To improve the technology and economics of recovery, using new reagents and equipment and developing new processes. Several companies and organizations in France (Minemet Recherche, PUK) (35, 16), the United Kingdom (Imperial College, Davy McKee) (36,31), Israel (IAEC) (26), the United States (ORNL) (37, 38) and Germany (Uraphos Chemie) (21), are directing their efforts along these lines.

b) To apply existing processes in countries where phosphoric acid is the most suitable raw material for the production of domestic uranium.

In the second case important advantages can be realized in the engineering of commercial plant, such as :

- Better knowledge of the process and of related analytical methods;
- Training of technical and support personnel in plant operation;

- Possibility of a greater participation of domestic enterprises in process engineering and equipment procurement;
- Establishment of working groups which can develop further activities for the recovery of other metals.

Different strategies for the application of an existing process may be used, depending on several factors (39). The following section reviews a suitable method for the application of the D2EHPA-TOPO process to the recovery of uranium from a particular phosphoric acid. The main stages of the investigation, the activities which should be included, an implementation schedule and the associated costs, are described. Economic data are expressed in US dollars at the exchange rate for mid-1986 (1 US \$ = 160 pesetas).

## 2. LABORATORY STUDIES

The D2EHPA-TOPO process has received the widest commercial acceptance and it has been reviewed on several occasions. Laboratory studies using this process should only be intended to adapt the process parameters to the particular case by relatively small changes around known values. In this way the tests can be completed in a short time and at low cost.

As distinct from subsequent studies, the early tests can be carried out in a laboratory away from the phosphoric acid plant, in order to reduce costs and simplify the operation. Under these conditions, when the acid has been aged for more than a week after being produced it has cooled and is free of solids and is known as "green acid". Obviously, this acid is not suitable for testing processes for acid conditioning, but it is possible to test the solvent extraction process, after removing the solids, adjusting the redox state (should it be necessary) and heating the acid to the appropriate operating temperature.

The first cycle extraction for the separation of uranium from the acid is of central importance in these tests, because :

- it has the highest cost incidence (all the acid passes through it);
- it determines the load of organic phase, the level of recovery of uranium, the operating conditions and the size of equipment.

The main activities which should be carried out are :

a) Chemical characterization of the phosphoric acid, determining mainly: U,  $P_2O_5$ ,  $SO_4$ ,  $SiO_2$ , F, Fe(III), Fe (II), density and redox potential.

b) Bench scale testing of the first cycle of extraction (Determination of kinetics and equilibrium isotherms of both the extraction and stripping stages).

c) Continuous operation of first-cycle extraction and stripping.

Once suitable results had been obtained the second cycle tests can be done using the aqueous extract obtained from the first cycle operation as feed. The tests can cover:

- d) Determination of oxidant consumption;
- e) Continuous operation of the solvent extraction units including extraction, washing, stripping and conditioning of the organic phase;
- f) Uranium precipitation;
- g) Determination of the composition of the concentrate obtained, especially the content of uranium, phosphorous and iron.

After completing these tests, the final report should be prepared summarizing the basic data about the D2EHPA-TOPO process as applied to the phosphoric acid under study. The following points should have been established:

- Preliminary process flowsheet (excluding acid conditioning);
- Recovery of uranium under equilibrium concentrations;
- Number of stages in each operation;
- Operating data of the solvent extraction processes, e.g. mixing phases ratios, mixing times, settling times, and areas, continuous phase and recyclings;
- Reagent consumption in the chemical operations (reduction, oxidation, precipitation);
- Physical behaviour to be expected (crud formation, continuous phase inversion, etc.);
- Quality of intermediate and final products;
- Overall evaluation of the process, showing the stages which must be studied in more detail at the pilot plant scale.

Table I shows an estimate of the capital investment required for these tests, including process equipment (for a throughput of 5-10 l/h) and related analytical systems. The equipment required for acid conditioning is not included, and the same liquid-liquid equipment is used for first and second cycle extraction.

TABLE I. INVESTMENT COSTS FOR LABORATORY TESTS (US \$)

		Estimated Cost
1.	PROCESS EQUIPMENT	
1.1	Set of laboratory mixer-settlers, for acid flow-rates of 5-10 liters per hour (12 stages).	16 000.00
1.2	Metering pumps for phosphoric acid and organic solvents (6 units)	5 000.00
1.3	Agitated tank with heating for phosphoric acid (50 liters).	2 000.00
1.4	General purpose muffle furnace with automatic control, for temperatures up to 1 100°C	2 000.00
	Sub total	25 000.00
2.	ANALYTICAL SYSTEMS	
2.1	UV-visible spectrophotometer	8 000.00
2.2	pH (ion)-meter, with electrodes	6 000.00
2.3	Electronic top-loading balance	2 000.00
2.4	Analytical balance	2 500.00
2.5	Temperature controlled oven, to 300°C	1 500.00
	Sub total	20 000.00
3.	GENERAL PURPOSE LABORATORY EQUIPMENT	
	Conventional analytical and process equipment and laboratory scale materials.	7 000.00
	TOTAL INVESTMENT (US \$)	52 000.00

Note - Utilities such as electricity, water, compressed air and vacuum are assumed to be available.

Table II lists the requirements for the tests, although neither raw material nor labour costs are included.

TABLE II. LIST OF REQUIREMENTS FOR LABORATORY TESTS

	Estimated Cost
1. RAW MATERIAL	
Phosphoric acid : 1 000 - 2 000 liters	
2. REAGENTS (US \$)	
2.1 <u>Process reagents</u>	300.00
D2EHPA : 10 kg	
TOPO : 4 kg	
Kerosene : 60 l	
2.2 <u>Analytical reagents</u>	
Arsenaze III : 10 g	
Analytical grade TOPO : 500 g	
Titriplex III : 1 000 g	
Titriplex IV : 100 g	
2.3 <u>Miscellaneous reagents</u>	2 200.00
Sub-total	6 500.00
3. LABOUR REQUIREMENTS	
3.1 2 Hydrometallurgists: 2 000 man hours (1 analyst/1 process engineer)	
3.2 2 operators : 2 000 man hours	

NOTE : The test period is considered to be 6 - 8 months. Reagent consumption, however, has been calculated for one year.

### 3. PILOT PLANT TESTS

#### 3.1 Objectives

Once the results of laboratory tests have been analysed, and the discrepancies with established commercial processes are known, it is possible to decide whether or not to build a pilot plant.

A pilot plant must be installed at the site of the fertilizer plant, and it must use an acid feed as similar as possible to that of the commercial plant.

The pilot plant must include as a minimum the acid conditioning stage and the first cycle of extraction. The additional cost of equipment required to test the complete process is relatively small (10-15% of total, see Table III), and for this reason it is preferable to

TABLE III. COST OF EQUIPMENT, PIPING AND INSTRUMENTATION  
FOR A PILOT PLANT (US\$)

			Estimated Cost
1.	ACID CONDITIONING		151 000.00
1.1	Flash cooling system	45 000	
1.2	Ageing tanks (2 x 6 m <sup>3</sup> )	25 000	
1.3	System for preparation and metering of flocculant	2 000	
1.4	Clarifier-thickner (1.5 m <sup>2</sup> )	30 000	
1.5	Baryte bed filters	5 000	
1.6	Activated carbon system for adsorption of organic matter	6 000	
1.7	System for preparation and metering of sodium hydroxide	2 000	
1.8	Storage vessels (3 units)	2 000	
1.9	Pumps (10 units)	34 000	
	Sub total	151 000	
2.	FIRST CYCLE OF EXTRACTION		
2.1	Set of extraction mixer-settlers (4 stages)	50 000	
2.2	Set of stripping mixer-settlers (3 stages)	40 000	
2.3	System for preparation of organic phase	2 000	
2.4	System for preparation of stripping agent	6 000	
2.5	Centrifuge for crud treatment	20 000	
2.6	Storage vessels (5 units)	6 500	
2.7	Pumps (5 units)	2 000	
	Sub total	132 000	



TABLE III. COST OF EQUIPMENT, PIPING AND INSTRUMENTS  
FOR A PILOT PLANT (US \$). (CONTINUATION)

		Estimated Cost
3.	SECOND CYCLE EXTRACTION AND PREPARATION OF FINAL CONCENTRATE	
3.1	System for oxidation-dilution of first cycle extract	3 000.00
3.2	Mixer-settlers (10 stages), for flow-rates between 15-25 l/h. Stages : 4 extraction, 3 organic phase washing, 2 stripping, 1 organic phase conditioning	28 000.00
3.3	Water cooling system (200 l/h at 5°C).	3 000.00
3.4	Storage vessels (8 units)	4 000.00
3.5	Oven for drying concentrate (to 1 000°C)	2 000.00
Sub Total		40 000.00
4.	OTHER ITEMS	
4.1	Pipes and valves	30 000.00
4.2	Measuring instruments	20 000.00
4.3	Electrical circuits and panels	25 000.00
4.4	Distribution of utilities	5 000.00
4.5	Initial batch of reagents	10 000.00
4.6	Others	10 000.00
Sub total.		100 000.00
TOTAL OF EQUIPMENT, PIPES AND INSTRUMENTS (US \$)		423 000.00

test the complete process. The plant must be designed to be as flexible as possible. This way it is possible to study a large number of combinations of unit operations or to test any selected unit operation in isolation. Plant equipment can be supplied as "packages" in such a way that a minimum of connections must be done on site.

The aim of the pilot plant is to complete the information obtained from the laboratory tests, especially concerning aspects which the preliminary tests cannot elucidate, such as :

a) The complete process of acid conditioning, including the stages of:

- Temperature adjustment,
- Adjustment of the redox potential, if necessary;
- Reduction of the solids content, and
- Reduction of the content of organic matter.

Each of these stages can include several operations, especially for solids removal which can include ageing, flocculation, decantation and filtration of the fresh acid.

b) Continuous operation of both cycles of solvent extraction, in order to test:

- The process parameters as obtained in the laboratory;
- The cumulative effects of impurities in recycled streams;
- The physical behaviour of the system, especially regarding crud formation and solvent losses;

c) Materials testing, mainly in the acid conditioning stage, where conditions are the most aggressive. Different alternatives of process equipment can also be tested e.g. on the acid cooling system (flash cooling, spiral exchangers, graphite exchangers, and others).

d) Testing of the general system of plant control and control systems for particular pieces of equipment;

- e) Training of personnel and staff;
- f) Preparation of the process manual, which must include the necessary data to carry out the feasibility study and the engineering of the project for an industrial plant.

The size of the pilot plant is an important point to consider. This must be thought of as a scaled-down commercial plant rather than scaled-up laboratory equipment. Obviously, the results will be more trustworthy as the pilot plant grows in size, but then the investment costs will also be greater. For the present discussion, a plant capacity of 12 m<sup>3</sup> of acid/h has been chosen. This is considered to be the minimum capacity necessary to obtain adequate results which may be scaled-up to industrial scale without excessive risks.

### 3.2 Process Flowsheet

The main process features following the conventional D2EHPA-TOPO flowsheet are shown in the Figure 1 (40), and are discussed below:

- a) Acid conditioning, which includes the operations of:
  - Acid cooling by a flash evaporator system
  - Oxidation with H<sub>2</sub>O<sub>2</sub>
  - Acid ageing
  - Flocculation and decantation of solids
  - Filtration in a baryte bed
  - Absorption of organic matter with activated charcoal
- b) Recovery of uranium (First cycle of extraction), by:
  - Extraction with D2EHPA-TOPO (in 4 stages)
  - Reductive stripping with 7M phosphoric acid in (3 stages)
  - System for preparation of the organic phase
  - System for preparation of the stripping agent
  - System for crud treatment

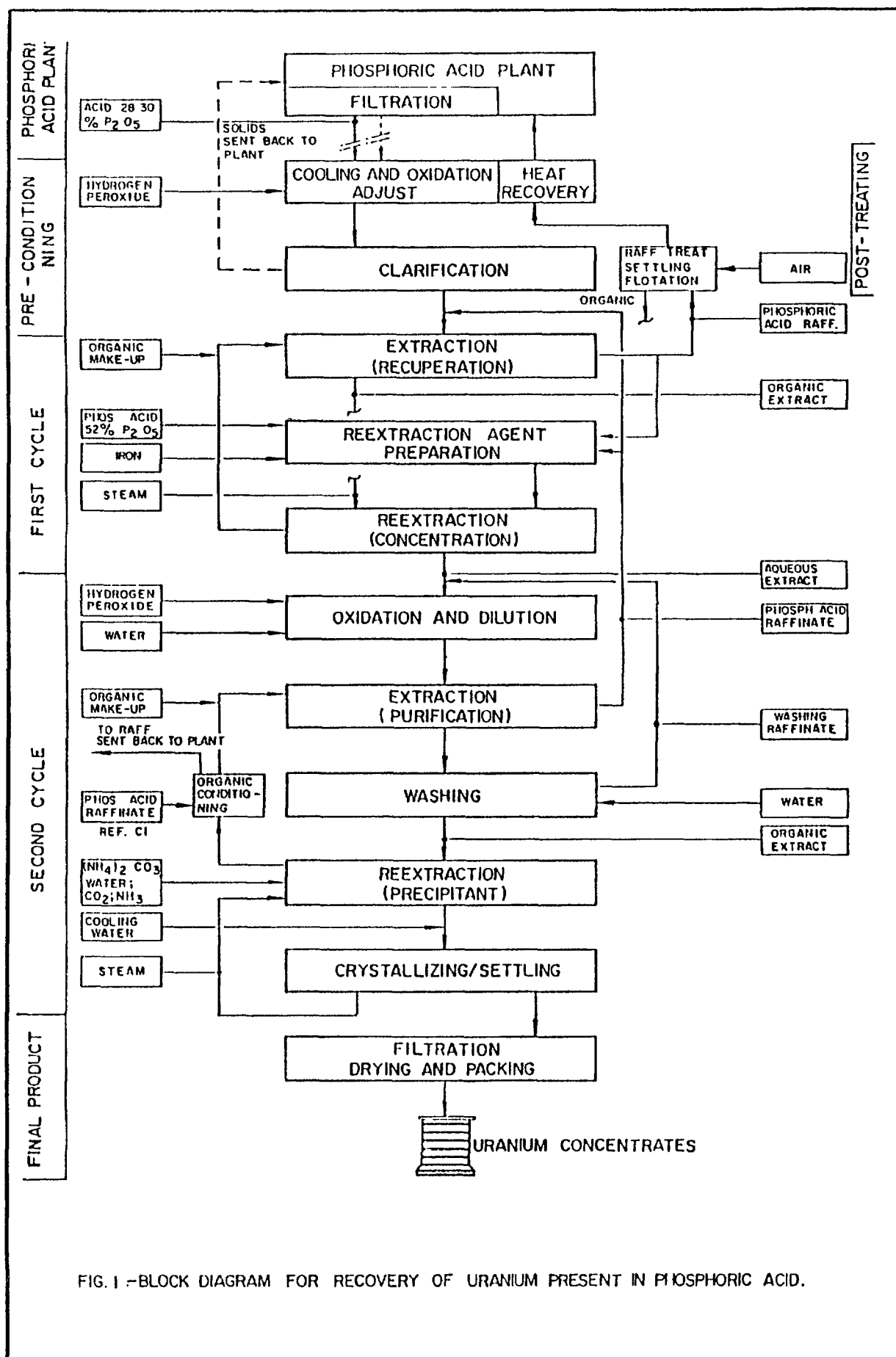


FIG. 1 - BLOCK DIAGRAM FOR RECOVERY OF URANIUM PRESENT IN PHOSPHORIC ACID.

- c) Uranium purification (Second cycle of extraction) and precipitation
  - Oxidation and dilution of the aqueous extract from Cycle I.
  - Extraction with D2EHPA-TOPO (in 4 stages)
  - Washing of the loaded organic phase (3 stages)
  - Stripping and precipitation of uranium with ammonium carbonate (2 stages)
  - Conditioning of the barren organic phase (1 stage)
  - Cooling system
  - Filtration and drying systems for the concentrate

#### 4. COSTS AND SCHEDULE OF OPERATIONS

The estimated costs of equipment, piping and instrumentation of the pilot plant are detailed in Table III. The main activities not included in these costs are those related to:

- Engineering and supervision
- Buildings
- Construction expenses
- Contingencies
- Start-up expenses

These can be valued at about US \$450 000. It is well known that in a pilot plant these last activities represent a higher proportion than in commercial plant. The overall investment costs are then about \$900 000 US dollars.

The costs of reagent and service consumptions are shown in Table IV, considering a continuous operation of 330 days per year. These costs represent the highest proportion of the annual operating costs, which have been estimated at about US \$20 000 (Table V). Amortization is not included because the investment of the pilot plant must be considered as part of the global investment necessary for the construction of a commercial plant. Operating labour requirements, including analytical services for continuous operation, may be estimated as:

- 5 engineers
- 12 operators

TABLE IV. CONSUMPTION OF CHEMICALS AND UTILITIES IN THE PILOT PLANT  
AND COST ESTIMATES FOR THESE ITEMS

Chemical	Consumption (kg per cubic meter of acid treated)	Unit price (US\$/kg)	Cost (US\$/year)
1. CHEMICALS			
H <sub>2</sub> O <sub>2</sub>	0.10	1.5	595
Flocculant	0.03	3.5	415
Activated coal	0.03	6.0	595
NaOH	0.12	0.3	145
D2EHPA	0.06	7	1 665
TOPO	0.02	20	1 585
Kerosene	0.90	0.65	2 320
Iron scrap	0.20	0.2	160
CO <sub>2</sub>	0.14	0.6	330
NH <sub>3</sub>	0.13	0.75	385
TOTAL			8 195
2. UTILITIES (Requirements per cubic meter of acid treated)			
Process water	0.01 m <sup>3</sup>	0.15	6
Cooling water	0.03 m <sup>3</sup>	0.02	3
Steam	6.0 kg	0.015	356
Electricity	6.0 kg	0.06	1 425
TOTAL			1 790
Acid throughput : 12 m <sup>3</sup> /d x 330 d/y = 3 960 m <sup>3</sup> /y			

TABLE V. OPERATING COSTS (US \$/YEAR)

	Estimated Cost
Reagents	3 195
Utilities	1 425
Maintenance	3 000
Laboratory charges	4 000
General expenses	2 000
Others	2 000
	<hr/>
TOTAL	20 620

NOTE : Amortization and operating labour costs are not included

The approximate time requirements for the various activities could be as follows:

Activity	Months
<hr/>	<hr/>
Engineering	5
Purchasing	6
Transportation	1
Construction and erection	4
Start-up	2
Tests	12
	<hr/>
Total	30

After obtaining the processing and operating data required for engineering a commercial plant, the continued operation of the pilot plant is no longer justified from a technical point of view.

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# **SUMMARY OF THE WORK OF THE PHOSPHATE RESEARCH CENTRE (CERPHOS) IN URANIUM EXTRACTION FROM PHOSPHORIC ACID**

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## **Abstract**

The Sherifian Phosphate Office (OCP) established its own research centre (CERPHOS) in 1975 to carry out the necessary work for its expansion plans. The capabilities of CERPHOS and the results obtained in the areas of ore characterization, ore processing, chemical upgrading of phosphates, corrosion and resistance of materials and project engineering are described.

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## **1. INTRODUCTION**

In 1975 the Sherifian Phosphate Office (OCP) Group acquired its own research centre which enabled it to carry out research work for projects forming part of its expansion plan.

As a result of the work carried out since then, CERPHOS has acquired human and material resources which have turned it into a real development tool for the phosphate industry in the following areas:

### **a) Characterization of ores and commercial products**

- Mineralogical composition (identification and quantitative phase analyses),
- Properties of the constituent minerals (chemical, thermochemical and physical),
- Chemical analysis of major and minor components and arbitrary analysis.

### **b) Ore processing**

- Preparation of ore processing systems,
- Study of ore processing techniques and procedures,
- Improvement or adaptation of the processes used in production units.

### **c) Chemical upgrading of phosphates**

- Acid treatment of ores,
- Phosphoric acid,
- Fertilizers,
- Valuable elements and wastes in the phosphate industry.

d) Industrial projects

-Basic studies on processing and chemical conversion procedures.

-Assistance in industrial facility acceptance tests.

e) Corrosion and resistance of materials

f) Analyses and abstracting of documents.

In the specific area of uranium extraction, CERPHOS has developed human and material resources and has also gained experience both through research in its own laboratories on various Moroccan phosphates and phosphoric acids and through close co-operation in research and development programmes with foreign companies specializing in this area.

2. MATERIAL AND HUMAN RESOURCES

2.1 Uranium analysis

The analytical services of CERPHOS comprise three engineers and 42 senior technicians. Our experience in the analysis of major and trace elements using modern methods developed in our laboratories is undoubtedly a great asset. We are now able to process efficiently large series of geological prospecting samples and to analyse commercial products using standardized methods (phosphates, phosphoric acid, fertilizers, various rocks, etc.).

In the specific area of uranium, the methods used by CERPHOS have been tested through interlaboratory trials arranged by international organizations specializing in this area.

The techniques used are fluorimetry and colorimetry. The latter method enables large series of samples to be analysed and can be easily automated.

2.2 Solubilization of uranium by acid treatment

CERPHOS has three pilot plants for the production of phosphoric acid by the dihydrate process and two pilot units for the concentration of the acid produced. Furthermore, CERPHOS has laboratory testing benches for sulphuric (using the dihydrate and semihydrate processes), nitric and hydrochloric treatment.

In the case of nitric treatment, CERPHOS also has methods of studying filtration treatment and other aspects of the process, namely crystallization of calcium nitrate and ammonization of phosphonitric solutions.

Consequently, CERPHOS is equipped to study all the parameters related to the various processes for the chemical upgrading of phosphates as well as the behaviour of these ores during the successive stages of these processes (study of balances, distribution of major and minor elements including uranium, etc.).

The research team working on phosphoric acid treatment is made up of three engineers and ten senior technicians.

### 2.3 Uranium extraction

The uranium extraction section comprises two engineers and three senior technicians.

The equipment available for the recovery of uranium consists of:

- Batch testing benches for carrying out different phosphoric acid preprocessing operations and for recovering uranium by means of solvents or ion exchange resins;
- A semi-industrial unit for preprocessing and a micropilot installation for solvent extraction.

## 3. WORK CARRIED OUT

### 3.1 Uranium analysis

Research to develop analytical methods using fluorimetry and colorimetry has led to the establishment of methods which can be implemented easily. We have continuously improved these methods in order to increase their accuracy, reliability and speed. The study of the colorimetric method has enabled us to introduce a procedure for determining the amount of uranium and thorium (which is often found with uranium) in the same solution.

Analyses in this area have led to interlaboratory test runs involving various organizations which employ different physical and chemical techniques for the analysis of uranium.

The samples analysed include all the products at different stages:

- a) Phosphate rock;
- b) Phosphoric acid solutions;
- c) Acid extraction phase.

### 3.2 Extraction of uranium from phosphoric acid

Research on the recovery of uranium has covered a wide range of studies, from the establishment of uranium balances during the production of phosphoric acid to the characterization of the uranium concentrates extracted.

Uranium balances have been established for each phosphoric workshop of the SAFI chemical complex.

Since the conditioning of the acid prior to uranium extraction is specific to each type of acid, CERPHOS has identified and set up a conditioning or pretreatment system for the different qualities of phosphoric acid produced in Morocco. For this purpose, tests have also been developed to assess the efficiency of the pretreatment system and to alter, if necessary, the nature or order of the pretreatment operations carried out.

Continuous tests on large batches of acids have been carried out in a semi-industrial pretreatment unit installed at SAFI.

Uranium was recovered principally with the various solvents on which industrialized uranium recovery processes are based nowadays.

#### 4. PROPOSALS FOR RESEARCH PROGRAMMES

##### 4.1 Uranium geochemistry

The CERPHOS laboratories are in a position to run analyses immediately on large series of samples.

The data gathered will make it possible to estimate the uranium reserves in phosphate deposits in Arab countries and their distribution, and to identify those ores which are richest and hence most promising in terms of subsequent uranium recovery.

##### 4.2 Basic research for the development of a uranium recovery process

Processes for the recovery of uranium from phosphoric acid use extraction reagents which are specific to each process (OPPA process, OPAP process, D2HPA/TOPO process, MOPA/DOPA process, etc.).

Basic research on the degree of uranium complexing in phosphoric acid, research on the adjustment of oxidation states and the determination of the diffusion coefficients of uranyl species should make it possible to identify and develop new extraction agents in order to study such properties as the chelating power, restitution power and stability. Thus new extractants may be adopted and used as a basis for the development of a new process.

CERPHOS may undertake some or all of this research. Additional resources would be necessary.

##### 4.3 Study and evaluation of existing processes

Processes used on an industrial or semi-industrial scale are based exclusively on extraction by solvents or by ion-exchange resins. Two levels of evaluation of these processes can be envisaged:

- (a) Laboratory-scale evaluation in batch or continuous process.  
The data that could be collected at this level basically cover:
- Number of extraction stages;
  - Extraction yields;
  - Specific consumption of certain reagents;
  - Quality of the products;
  - Necessary pretreatment and post-treatment operations;
  - Scaling-up for semi-industrial production.

CERPHOS is in a position to embark on all this research on phosphate ores immediately.

The pilot phosphoric acid production units at CERPHOS not only produce the necessary acids based on phosphate ores but also provide data on the distribution of uranium during the production of phosphoric acid.

(b) Semi-industrial-scale evaluation

Two pilot plants can be envisaged, one for extraction by solvents, the other for extraction by resins.

The data that could be gathered at this stage are:

- Extraction yields;
- Specific consumption of raw materials and reagents;
- Energy consumption;
- Quality of the products;
- Technical problems which were not detectable at the laboratory level and attempts to find suitable solutions;
- Choice of materials;
- Estimate of investment costs;
- Manufacturing costs;
- Recommendations regarding equipment needed to establish the process at industrial level.

In addition to providing information on scaling-up for industrial production, these pilot plants are used to train Arab technicians, engineers and research workers.

A phosphoric acid production unit based on phosphate ores will have to be established in order to supply phosphoric acid to these pilot plants. The output of this unit should correspond to the capacity of the pilot plants to be set up.



## PANEL 1

### CAPITAL AND OPERATING COST ESTIMATES FOR PLANTS FOR THE RECOVERY OF URANIUM FROM PHOSPHORIC ACID

*Chairman: T. Botella (Spain)*

Capital and operating costs for a uranium recovery plant depend strongly on the characteristics of the acid, the size of the plant, its location and other project-specific conditions. Nevertheless, cost estimates based on past experience can provide useful guidance when planning new projects.

#### 1. Reference conditions

The capital and operating cost estimates shown in this report are based on the following reference conditions:

##### 1.1. Phosphoric acid plant

Acid production	100 000 t P <sub>2</sub> O <sub>5</sub> /year
Acid composition:	
P <sub>2</sub> O <sub>5</sub> content	350 kg P <sub>2</sub> O <sub>5</sub> /m <sup>3</sup>
U content	0.09 kg U/m <sup>3</sup>

##### 1.2 Uranium recovery plant

Process used: Two-stage D2EHPA-TOPO process with a D2EHPA/TOPO ratio of 6/1.

Uranium recovery	90%
Working period	300 days/year

The volume of acid produced by the reference plant defined in Section 1.1 would be:

$$100\,000 \frac{\text{tP}_2\text{O}_5}{\text{y}} \times \frac{1 \text{ m}^3 \text{ acid}}{350 \text{ kg P}_2\text{O}_5} \times 1000 \frac{\text{Kg P}_2\text{O}_5}{\text{t P}_2\text{O}_5} =$$

$$= 285\,715 \text{ m}^3 \text{ acid/y}$$

This corresponds to an acid flow rate of:

$$285\,715 \frac{\text{m}^3 \text{ acid}}{\text{y}} \times \frac{1 \text{ y}}{300 \text{ d}} \times \frac{1 \text{ d}}{24 \text{ h}} = 39.7 \frac{\text{m}^3 \text{ acid}}{\text{h}}$$

The amount of uranium produced by the reference plant would then be:

$$285\,715 \frac{\text{m}^3 \text{ acid}}{\text{y}} \times \frac{0.09 \text{ KgU}}{\text{m}^3 \text{ acid}} \times 0.9 = 23\,143 \text{ kgU/y}$$

$$= 23.1 \text{ tU/y}$$

This would require the process to have a uranium throughput of:

$$\begin{aligned} & 23\,143 \frac{\text{KgU}}{\text{y}} \times \frac{1}{300} \frac{\text{y}}{\text{d}} = 77.1 \text{ KgU/d} \\ \text{or} \quad & 77.1 \frac{\text{KgU}}{\text{d}} \times \frac{1}{24} \frac{\text{d}}{\text{h}} = 3.21 \text{ KgU/h} \end{aligned}$$

## 2. Capital cost estimates

From historical data<sup>1/</sup> it is known that the capital cost for a uranium recovery plant treating an amount of acid equivalent to 750 000 t P<sub>2</sub>O<sub>5</sub>/year would be 45 MM US\$ (1985).

The capital cost of the reference uranium recovery plant would then be:

$$I = \frac{100.000}{750.000} 0,62^{2/} \times 45 = 13 \text{ MM US\$}$$

Approximate cost considered: 13 + 30% = 17 MM US\$

The distribution of the capital cost would be approximately as follows:

<u>Stage</u>	<u>Range (%)</u>
1. Pre treatment of acid	15-35
2. First cycle of extraction	30-40
3. Post-treatment of acid	5-10
4. Second cycle of extraction	5-15
5. Precipitation & Drying	15-25

\* Experimental rule:

Costs stages 1,2,3	65 - 80% of total
Costs stages 4,5	20 - 35% of total

<sup>1/</sup> Communication Dr. F. Hurst.

<sup>2/</sup> 0,62: Williams coefficient.

### 3. Operating cost estimates

Tables I and II summarize the estimated consumption of chemicals and utilities requirements for the reference uranium recovery plant.

Table III shows the estimated percent distribution of operating costs for five selected cases. This information is derived from actual plants which are not identified by name for reasons of confidentiality. Operating costs as shown in Table III range from 22 to 54 US\$/lb U<sub>3</sub>O<sub>8</sub> and are subject to strong variations depending on local conditions.

TABLE I. REFERENCE PLANT - ESTIMATED CONSUMPTION OF CHEMICALS

	kg/m <sup>3</sup> (L/m <sup>3</sup> )	t/year	kg/lb U <sub>3</sub> O <sub>8</sub>
H <sub>2</sub> O <sub>2</sub>	0,05	14,3	0,24
Flocculant	0,03	8,6	0,14
Activated Coal	0,03	8,6	0,14
Activated clay	0,6	171,4	2,85
NaOH	0,4	114,3	1,90
D2EHPA ( 1st Cycle: (0,06)		17,1	0,29
TOPO ( 2nd Cycle: (0,002)		0,6	0,01
(*)			
Kerosene ( 1st Cycle: (0,45)		28,6	2,14
( 2nd Cycle: (0,02)		4,6	0,08
Scrap iron	0,29	81,9	1,36
CO <sub>2</sub>	0,29	81,9	1,36
NH <sub>3</sub>	0,11	30,0	0,50

(\*) Ratio D2EHPA/TOPO = 6/1

TABLE II. REFERENCE PLANT - UTILITIES REQUIREMENTS

		per/m <sup>3</sup>	per/year	per/lbU <sub>3</sub> O <sub>8</sub>
Process-Water	I	0,1 m <sup>3</sup>	28.571 m <sup>3</sup>	0,48m <sup>3</sup>
	II	-	-	-
Steam	I	40 kg	11,4 x 10 <sup>6</sup> kg	190 kg
	II	11,5kg	3,3 x 10 <sup>6</sup> kg	54,5 kg
Electricity	I	10 kwh	2,8 x 10 <sup>6</sup> kwh	47,5kwh
	II	1,5 kwh	0,44 x 10 <sup>6</sup> kwh	7,3 kwh

I: Pre-treatment + 1st cycle

II: 2nd cycle + Final

Table III - OPERATING COST ESTIMATES FOR SELECTED CASES  
(Distribution in percent)

		Plant capacity (tP <sub>2</sub> O <sub>5</sub> /y)				
Costs		Case A 100.000	Case B 100.000	Case C 150.000	Case D 700.000	Case E 750.000
1. Direct						24
- Chemicals		15		25	37	-
- Utilities (1)		10	35	25	23	-
2. Fixed						38
- Labor		44(2)			24(2)	
- G & A		9	45	25	3	45
- Consumables		22	20	25	13	20
3. Financial		Not Incl	Not Incl	Not Incl	Not Incl	38
US\$/Lb U <sub>3</sub> O <sub>8</sub>		54	22-27	22	22	N.A.

Other - For 350.000 t P<sub>2</sub>O<sub>5</sub>/y : 38 US\$/lb U<sub>3</sub>O<sub>8</sub>Notes.- (1) Steam, water & electricity: (2) Based on 21 people.

## PANEL 2

### GUIDELINES FOR PRELIMINARY FEASIBILITY STUDIES FOR THE RECOVERY OF URANIUM FROM WET-PROCESS PHOSPHORIC ACID

*Chairman:* S. Ajuria (International Atomic Energy Agency)

The development of a project for the recovery of uranium from phosphoric acid is essentially the same as for other metallurgical projects (1). The main difference is that no mine is directly involved (since the phosphoric rock has already been mined for the acid plant). Work should begin with a project definition study with the objective of broadly defining the main characteristics of the project and to make an initial (order-of-magnitude) estimate of its feasibility.

#### 1. PROJECT DEFINITION STUDY

The project definition study should take into account the characteristics of the orebody, the phosphoric rock and the ore concentrate (if any), the phosphoric acid plant and the acid it produces.

##### 1.1. Orebody characteristics

The main characteristics of the orebody that have to be considered are:

- Location
- $P_2O_5$  reserves
- Grade and homogeneity of the deposit
- Chemical characteristics of the ore (including U/ $P_2O_5$  ratio)
- Mineralogical characteristics of the ore
- Physical and chemical characteristics of the constituent minerals
- Type of beneficiation process required (if any)
- Particle size distribution
- Chemical characteristics of ore concentrate

### 1.2. Characteristics of the phosphoric acid plant

The project depends strongly on the characteristics of the plant that will supply the phosphoric acid. It is important to know the plant's:

- Location
- Capacity
- Type of process
- Availability (on-stream time)
- Capacity of acid storage facilities
- Type of waste disposal

The characteristics of the phosphoric acid are crucial to the feasibility of the project.

#### b) Acid characteristics

- Chemical composition U,  $P_2O_5$ , CaO,  $H_2SO_4$ ,  $Fe_2O_3$  (and  $Fe^{2+}$ ),  $SiO_2$ ,  $Al_2O_3$ , MgO,  $Na_2O$ , HF, organic matter, solids content, trace impurities,  $H^+$  total, EMF
- Physical characteristics: temperature, density, viscosity, coloration

### 1.3. Uranium recovery process

Once the main characteristics of the orebody, the ore, the ore concentrate, the phosphoric acid plant and the phosphoric acid have been defined it is necessary to select a uranium recovery process, at least tentatively. Several processes are available, as discussed in the main body of this report (2). Each of them has advantages and disadvantages which should be carefully weighed taking into account the specific conditions of the project being considered.

All industrial plants for the recovery of uranium from phosphoric acid which are currently in operation use the DEAPA/TOPO process. This process is flexible and well-proven and should be given serious consideration.

Once a process has been selected it is necessary to show that it is compatible with the phosphoric acid that will be used as feed. This will require some laboratory tests, which, at this early stage, should be limited in scope.

#### 1.4. Production cost estimates

Estimates should be made of the capital investment required for the proposed plant, of the operating costs and, finally of the total production cost of the uranium concentrate.

#### 1.5. End uses of the uranium concentrate

The intended end use or uses of the uranium concentrate are an important factor in the project. There are two possibilities: either the uranium will be used in a national nuclear power programme or it will be exported.

If the uranium is intended for use within the country it is important to establish:

- The number and size of nuclear plants that the country has or expects to have,

The dates when these plants are expected to become operational

The uranium requirements of these plants (amounts and dates)

Alternate possibilities for meeting the expected uranium requirements including other national uranium resources (conventional mines and mills) and imported uranium.

#### 1.6. Legal aspects

The applicable legal requirements should be clearly established, including:

- The licensing procedure that has to be followed and
- The environmental restrictions that have to be observed

### 1.7. Financial aspects

The project definition studies shall provide an estimate of the capital investment and operating cost of the plant and an estimate of the total production cost of uranium concentrates. These estimates are usually accurate within 30 to 50%.

Due consideration should also be given to the method of financing the project. The main alternatives are:

- Self-financing
- Financing through bank loans
- Financing by international organizations, or
- Some combination of the above

The cost of the pre-feasibility and final feasibility studies and the method of financing these studies should also be taken into account (See Part 2 of this Panel Report).

### 1.8. Project evaluation

A preliminary evaluation of the feasibility of the project should be made upon completion of the project definition studies. If the result of this evaluation is positive the project should proceed to the next stage which is the pre-feasibility study.

## 2. PRELIMINARY FEASIBILITY STUDY

The preliminary feasibility study is more detailed and should result in cost estimates with an accuracy of plus or minus 20%. These studies usually entail substantive laboratory and pilot plant tests as detailed in the following sections.

The approximate cost of a pre-feasibility study of this type is 50 000 to 70 000 US dollars, and involves 2 to 3 man-months of expert services plus expenses.



## 2.1. Chemical Analyses

Detailed chemical analyses of the phosphate rock, the phosphoric acid and the residual gypsum should be performed. These analyses should include determinations of  $P_2O_5$ , CaO,  $H_2SO_4$ ,  $Fe_2O_3$ ,  $SiO_2$ ,  $Al_2O_3$ , MgO,  $Na_2O$ , F,  $U_3O_8$ , organic matter, EMF, density and viscosity (2,3).

Such analyses could be done in a period of about one month if performed by experienced analysts working in a well-equipped laboratory and should cost about \$4 000 U.S. dollars.

## 2.2. Laboratory tests for uranium extraction

The objective of the laboratory tests is to establish process conditions. Tests should be done around well-known values from technical references. The tests can be either batch or continuous.

Costs: 15.000 US \$ (Only tests)

Period: 2 months (assuming the tests are done by experienced engineers in a well-equipped installation)

## 2.3. Pre-treatment tests

Pre-treatment tests are very important and should be done for each acid. These tests should be done at the site of the phosphoric acid plant using fresh acid. There should be a flexible arrangement of the several unit operations involved in the treatment.

- Costs 100.000 - 200.000 US\$ (for the tests)

- Period 6 Months (if done by experienced personnel)

## 2.4. Pilot-plant tests

There are many reasons for its installation (process test, personnel training, and so on), but is rather expensive and may not always be required.

If it is installed, it is necessary to test the complete process until good results are obtained.

- Costs: 350.000 US\$ (Only for the tests)
- Period: 6 Months (if done by experienced personnel)

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