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Hexafluoride and the Experimental Production of Nuclear Grade  
Thorium Compounds.

*Fuel Cycle at the IPEN: From the Uranium Concentrate to the*

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### INTRODUCTION

A great deal of effort has been done by the Instituto de Pesquisas Energéticas e Nucleares (IPEN), São Paulo, concerning a systematic development of research for the establishment of the technology of uranium and thorium, personal training of chemists and engineers, production of nuclear grade materials for further metallurgic work and fabrication of fuel elements for nuclear research reactors.

This paper summarizes the main work on the purification of uranium concentrates and their transformation in nuclear grade compounds. The upmost important products are ammonium diuranate (ADU), uranium tetrafluoride, uranium trioxide, uranium oxide microspheres, uranyl nitrate, uranium hexafluoride, thorium nitrate, thorium oxalate and thorium oxide.

The development and adaptation of analytical procedures for the quality control of the several abovementioned produced nuclear grade materials is emphasized.

### THE FIRST BRAZILIAN YELLOW-CAKE

The first and until now the unique uranium concentrate worked out aiming the experimental production of nuclear grade uranium compounds is a sodium diuranate (SDU). This salt is produced from the industrial processing of monazite. The main impurities considered in the concentrate are sodium, phosphate, silicium, iron and, of course, thorium and rare earth (RE). The first step is the dissolution of the concentrate with nitric acid for the obtaining of a clear uranyl nitrate. During this dissolution the gross amount of silicium is removed by dehydration of silicic acid. The main characteristics of this concentrate were previously described<sup>(6)</sup>.

SOLVENT EXTRACTION PILOT PLANT FOR  
PURIFICATION OF URANIUM

A pilot plant facility set up for the purification of uranyl nitrate is based on the conventional liquid-liquid extraction technique using three pulsed columns for extraction, scrubbing and stripping, respectively. The facility and its equipment, operational flow-sheet, performance and gained experience were published <sup>(28, 29)</sup>. The facility comprises a section for the opening of the drums and for the dissolution of the yellow cake. The organic phase is a (v/v) 35% TBP-varsol. Details are given <sup>(28)</sup> for the precipitation of pure ADU with ammonia gas by discontinuous and continuous processes and the instrumentation control panel.

URANYL NITRATE PREPARATION AND ITS  
PURIFICATION

The clear uranyl nitrate solution is prepared by dissolution of the yellow-cake (SDU) in a batchwise fashion into a reactor of 300 ℓ capacity. The digestion of SDU is made with 2M HNO<sub>3</sub> at 90-100°C for the complete flocculation of silica. The hot product is filtered into a canvas filter and the residue thoroughly washed for the removal of soluble uranyl nitrate. The filtered uranyl nitrate has a concentration of 475 g U/ℓ and is adjusted to 300 g U/ℓ and 1M HNO<sub>3</sub> (NaNO<sub>3</sub> as salting out agent is formed during the dissolution) before the extraction.

Great concern was given to the decontamination of thorium and rare earths, specially for this concentrate obtained from the monazite sand. To overcome the troublesome presence of thorium and rare earths, controlled addition of sodium sulfate is introduced <sup>(11, 12)</sup>.

The purification of the crude uranyl nitrate solution is done by countercurrent extraction with 35% TBP (v/v)-varsol using pulsed columns with perforated plates of about 23% area. The pulsed columns were dimensioned according to experience gained in theoretical and practical work <sup>(8, 9)</sup>. The extraction is accomplished in countercurrent using an organic to aqueous ratio of : 2.2. The loaded organic phase containing 135 g U/ℓ, lea

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ves the extraction column and is admitted to the scrubbing column where it is treated with 0.2M  $\text{HNO}_3$  in a organic/aqueous phase ratio of 10:1. The washed organic phase (110-115 g U/l) is stripped with water using an aqueous/organic ratio of 1.6, resulting an uranyl nitrate solution of 70 - 105 g U/l. The third column (stripping) can be operated at 40 - 60°C resulting in an aqueous uranyl nitrate of 100 g U/l<sup>(28)</sup>. This solution is filtered through a celite layer for the coalescence and removal of small amounts of TBP and finally sent to the precipitation unit.

#### PRECIPITATION OF AMMONIUM DIURANATE (ADU)

The pure uranyl nitrate solution (100 g U/l) is heated to about 60°C and the ADU is obtained by bubbling undiluted anhydrous  $\text{NH}_3$  gas and the final pH ascertained to 7.0 - 7.5 or to maximum value of about 10 (excess  $\text{NH}_3$ ). The pilot plant is equipped to perform the precipitation in a batchwise way and in a continuous operation as well. For the batch precipitation the ADU is dewatered into a vacuum canvas filter and has a umidity / ranging from 45 to 50%<sup>(28)</sup>.

Starting last 1979 the ADU is being precipitated in a continuous reactor and the filtration is done in a continuous filter. The reactor (Ø 27cm x 100cm; 56 liters) is fed with uranyl nitrate at a rate of 1.2-2.0 litter/min, heated at 60°C, and  $\text{NH}_3$  bubbled at a rate of 60 - 80 l/min. The final pH is about 10 (excess  $\text{NH}_3$ ). The slurry of ADU is deposited in the bottom of the continuous filter and is sucked by vacuum into the rotated drum. The filtered ADU leaves the drum with about 50 % umidity, the thickness of the layer ranging from 2.5 to 3.5 mm.

#### UO<sub>3</sub> Facility

A facility<sup>(28)</sup> for the conversion of ammonium diuranate to  $\text{UO}_3$  comprises a continuous, electrically heated, belt furnace. The ADU is fed directly to the stainless steel conveyor belt moving inside the furnace with zones having different temperatures, ranging from 110 to 50°C. The final product is an  $\text{UO}_3$  oxide used as feeding material for the  $\text{UF}_4$  plant or sent to the Metallurgical Division for further transformation to ceramic grade  $\text{UO}_2$ . The capacity of the filter and furnace is about 10kg U/hour. The residence time during the dewatering is 2-3 hours.

The uranium purification pilot plants give rise to some solutions containing uranium, thorium, rare earths, iron, titanium. The main stream comes from the first pulsed column (extraction). All effluents are collected and treated with sodium hydroxide. The precipitate is filtered out and returned to the dissolution reactor where it is dissolved with nitric acid and sent to the extraction column. The dried precipitate assessed about 25% U and 14% Th, titanium, iron and rare earths being the sterile materials.

UF<sub>4</sub> PILOT PLANT

Previous experience on preparation of UO<sub>2</sub> appropriate for the conversion to UF<sub>4</sub> starting from ADU and using NH<sub>3</sub> as reducing agent was published<sup>(38)</sup>. After those preliminary studies, a pilot plant facility to acquire the necessary technology on the green salt production for further uses in the reduction to U metal / and preparation of UF<sub>6</sub> was set up<sup>(27)</sup>. The starting material used in this unit is UO<sub>3</sub>. For the first experiments the UO<sub>3</sub> used was prepared from powder ADU that was previously pelletized and calcined to UO<sub>3</sub> and then (spheres of about 4-6mm) dried again. This operation was necessary when the ADU was batchwise obtained. At the moment, with the continuous precipitation reactor and the continuous filter in operation, the ADU is obtained as plates 2.5 - 3.5 mm thickness, dried and calcined to UO<sub>3</sub> in the moving belt conveyor. This new type of UO<sub>3</sub> exhibited excellent mechanical properties. This trioxide is fed to the moving bed reactor, reduced to UO<sub>2</sub> by cracked NH<sub>3</sub> and contacted with anhydrous hydrogen fluoride for the conversion to UF<sub>4</sub>. The UF<sub>4</sub> unit has been in operation serving only for the UO<sub>2</sub> production as well.

PREPARATION OF UF<sub>6</sub> BY OXIDATIVEDECOMPOSITION OF UF<sub>4</sub>

Solely as part of personal training program the first gram-amounts of UF<sub>6</sub> were prepared by oxidative decomposition of UF<sub>4</sub> with dry oxygen. These preparative experiments were carried out using a quartz tube inserted into a tubular furnace. / Besides the training it has interest in getting some UF<sub>6</sub> of high purity, containing no elemental fluorine or residual anhydrous HF, for use as standard hexafluoride.

## 178) ELECTROLYTIC GENERATION OF FLUORINE

Since 1975 considerable efforts were / expended by the IPE N in personal training in handling of HF, F<sub>2</sub> and UF<sub>6</sub>, and to set up facilities for electrolytic generation of elemental fluorine. First experiments were runned using a high-temperature / (240-280°C), V-shape cell with two carbon electrodes and KF.HF as electrolyte. Elemental fluorine was then cooled down using dry ice-acetone for the removal of residual HF before reacting with UF<sub>4</sub> into a heated tubular UF<sub>6</sub> reactor.

The monel-400 electrolytic cell was designed for medium-temperature electrolyte (80-100°C) and has the following dimensions: 8" x 22" and 16" height and has a total volume 46 liters and a capacity of accomodation for 38 liters melted electrolyte. The cell is heated by a water jacket and the electrolyte maintained at 95°C. The electrolyte is prepared by the introduction of gaseous anhydrous HF over the heated anhydrous KF untill the melted mixture / reached the KF.1.90-1.95 HF composition. During the first experiments the cell operated at 60-200 A current. Further modification of the electrodes disposition allowed to operate the cell at 200-300A and the cell is being prepared for use at its maximum 484A' (9-12V theoretically at 90% current yield). The electrolyte level is maintained at a minimum value through a gamma-ray source and a detector on the opposite wall; a sound alarm is switch on when the level is reaching the minimum position or when cell pressure is over the previously established / value.

The current source is a PRODELEC model 1-18, 220 volts triphasic, 60 HZ, Output of 3,6-18 volts, 1000A; the ripple is 4.2%.

### PURIFICATION OF FLUORINE

The elemental fluorine generated leaving the electrolytic cell is admitted into a cold trap (-80°C) where the most part accompanying HF is liquefied; this previously purified fluorine is then introduced into a heated (100°C) anhydrous NaF tower, from where fluorine containing only about 0.05 moles % HF is obtained. After saturated, the NaF tower is regenerated by heating at 250-350°C.

Purified fluorine is then compressed by a pulsafeeder diaphragm pump into monel cylinder at a maximum pressure of 45 psig for further use.

UF<sub>6</sub> PILOT PLANT

Uranium hexafluoride is obtained by the exothermic reaction of F<sub>2</sub> with UF<sub>4</sub> inside a moving bed reactor. / This experimental set up uses UF<sub>4</sub> flakes or spheres. The reactor is made of monel and heated at 400-500°C. The hot UF<sub>6</sub> is filtered through a sintered monel plate and then sent to the cold traps (-15° and -40°C). From these cold traps the UF<sub>6</sub> is transferred to the storage cylinder by conventional technique after being melted by heating and pressure raising. This small prototype / reactor can accommodate about 3Kg of UF<sub>4</sub> and has a capacity of 300-700 kg UF<sub>6</sub>/hour. Hot fluorine gas is distributed from the bottom and contact the UF<sub>4</sub> in a countercurrent fashion, maintaining always a considerable excess of UF<sub>4</sub>.

The pilot plant is equipped with scrubbing columns for the removal of HF and F<sub>2</sub> from H<sub>2</sub> and N<sub>2</sub> residual and purging streams, where the reactive gases are removed by contact with a spray of potassium hydroxide solution.

SPHERICAL NUCLEAR FUEL PARTICLES

The experimental production of UO<sub>2</sub>, ThO<sub>2</sub>, (U,Th)O<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> microspheres is being carried out at a large laboratory scale, by the known internal gelation process (26). / Particles in a wide diameter range (50-800 μm) are obtained.

Although not used as nuclear fuel the alumina microspheres has special interest as chromatographic bed columns (inorganic ion-exchanger), as support for some radioisotopes and as catalysts .

NUCLEAR GRADE THORIUM TECHNOLOGY

The alkaline process for breaking up monazite sand is being practiced in Brazil since 1948 on an industrial scale. A thorium concentrate is obtained in a form very suitable for solvent extraction purification (10).

Supported by several years work at large laboratory scale in the purification of thorium nitrate, a pilot plant was erected based on solvent extraction of thorium nitrate using 50% (v/v) TBP-varsol (31). The obtained thorium nitrate solution of high purity is designed to be converted into thorium oxide via thorium oxide pellets. The thorium pilot plant is equipped to be able to supply crystallised, Th(NO<sub>3</sub>)<sub>4</sub>·4H<sub>2</sub>O, thorium oxalate and a highly concentrated thorium nitrate solution (about 900 g ThO<sub>2</sub>/ℓ).

The purification step is accomplished with a compound extraction-scrubbing pulsed column. The thorium concentrate / is a crude thorium hydroxide containing uranium and chloride ions. For this reason the pilot plants is equipped with a section for preparation of a slurry of thorium hydroxide that is further filtered to get rid / of chloride ions before the dissolution with nitric acid. The thorium nitrate is extracted with TBP-varsol after addition of sodium nitrate (2.2M) and free nitric acid (0.8M). The organic phase rich in thorium nitrate can be scrubbed with 2.2M  $\text{NaNO}_3$  - 0.8M  $\text{HNO}_3$  or with pure /  $\text{Th}(\text{NO}_3)_4$  solution. Finally thorium nitrate is stripped from the organic phase with demineralized water. As an alternative a highly efficient thorium-uranium separation can be applied by using an extractive-precipitation of the thorium sulfate <sup>(10)</sup>.

#### ANALYTICAL QUALITY CONTROL

A rapid routine determination of natural U content in uranyl solution is done by gamma-ray spectrometry <sup>(7)</sup> / ( $^{235}\text{U}$  185 KeV). A procedure was outlined for the direct determination of the U content of uranyl-nitrate - TBP - organic phase <sup>(23)</sup>. The thermogravimetric behavior of ADU samples, the pyrophoricity grade of  $\text{UO}_2$  powders and their O/U ratio in  $\text{UO}_{2+x}$  and  $\text{UO}_{2-x}$ .  $\text{ThO}_2$  sintered pellets was developed <sup>(24)</sup>. The analytical control of  $\text{UF}_4$  was made by sequential analysis of the most probable products existing with the tetrafluoride <sup>(20)</sup>. A colorimetric method for the determination of calcium in nuclear grade uranyl salts and uranium oxides was / established <sup>(3)</sup>. The determination of microquantities of B in highly pure U and thorium compounds is done through the extraction of the colored complex of  $\text{BF}_4^-$  - monomethylthionime <sup>(21,22)</sup>. A procedure for the separation and concentration of extremely low amounts of Th and RE from uranyl solutions was developed based upon the sorption of those elements from solutions containing 0.3M HF into a small column of alumina <sup>(1)</sup>. Using this technique the individual RE have been / analysed by emission spectrography <sup>(34)</sup>. A semiquantitative routine spectrometric method was outlined for the direct determination of 18 elements in uranium compounds, using gallium oxide and sodium fluoride as carriers <sup>(19)</sup>. Traces of RE were spectrographically determined / after separation of uranyl chloride with TBP <sup>(2)</sup>. A comparative study of the efficiency of some spectrochemical carriers was established / for the quantitative spectrographic analysis as trace impurities in uranium <sup>(30)</sup>.

Vanishing small amounts of RE in U are determined by fluorescence spectrometry after separation into an alumina column<sup>(15)</sup>. Zirconium was analysed by direct spectrofluorimetric / determination in uranyl chloride using morin<sup>(16)</sup> and spectrophotometrically with chloroanilic acid<sup>(25)</sup>.

The separation of contaminants in U is achieved by extraction chromatography and the impurities determined by atomic absorption spectrophotometry (AAS)<sup>(33)</sup>. The extraction of Zn and Pd<sup>(37)</sup> and of Bi, Cd, Pb, Hg, Au and Ag<sup>(35)</sup> in nuclear grade uranium and their determination by AAS was investigated, burning directly the organic phase. Preconcentration and determination of Cd, Pb, Tl, Bi and Cu in highly pure U salts was accomplished by anodic stripping polarography<sup>(13)</sup>.

The determination of uranyl nitrate diffusion coefficients for the calculation of the height of transfer unit was studied<sup>(17)</sup>. A routine method for mean crystallite size determination of  $U_3O_8$  microspheres was established by X-ray diffraction line broadening technique<sup>(32)</sup>.

Procedures for the determination of the composition of the electrolyte were developed based on the alkalimetric determination of HF and the total determination of free hydrofluoric acid liberated after percolation on a strong cationic ion-exchange resin / (H-form) and on the determination of melting point of the mixture.

A procedure was adapted for the determination of uranium (150-700  $\mu$ g U) in several uranyl solutions and in solid compounds by the constant potential coulometric technique with mercury / pool as cathode<sup>(39)</sup>.

The rapid determination of thorium in monazite samples was made directly by measurement of the height of the  $^{212}\text{Pb}$  / photopeak (240 KeV)<sup>(40)</sup>. A procedure for direct fluorimetric determination of rare earth elements in thorium compounds was established<sup>(14)</sup>. The separation of several metal traces by solvent extraction from pure thorium and their determination by atomic absorption from pure thorium and their determination by atomic absorption spectrophotometry was also carried out<sup>(36)</sup>. The determination of extremely low amounts of uranium in nuclear grade thorium (0.1 to 10 ppm U/Th) until now is not well / established but the work is on progress.



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