

PM

**EXPERIENCE IN YELLOWCAKE REFINING AND ITS
CONVERSION TO URANIUM TETRAFLUORIDE AT
IPEN-CNEN/SP**

A. ABRAO

Instituto de Pesquisas Energéticas e Nucleares,
Comissão Nacional de Energia Nuclear,
Sao Paulo, Brazil



Abstract

This paper will focus the experience acquired during the operation of a pulsed columns solvent extraction pilot plant in the purification of a yellowcake produced from the industrial treatment of monazite sand. Special care was devoted to the rare earths elements, thorium and zirconium decontamination. Intermediate product is an uranium trioxide obtained by dewatering and thermal decomposition of diuranate and its conversion to uranium tetrafluoride.

The experience developed and the establishment of the quality control procedures to follow up all steps on both pilot units as an important support to the technical work is emphasised.

1. INTRODUCTION

As contribution to the national program for developing atomic energy for peaceful uses, headed by the Brazilian Nuclear Energy Commission (CNEN), the Instituto de Pesquisas Energéticas e Nucleares (IPEN), S. Paulo, has given a great deal of effort concerning a systematic development of research for the establishment of the technology of uranium and thorium. The program is very much dedicated to the education and training of chemists and engineers, and to the production of some nuclear material for further metallurgical work and fabrication of fuel elements for research reactors.

In this paper we summarize the main activities on the purification of uranium raw concentrates and their conversion into nuclear grade compounds. The design and assemblage of pilot facilities for pure ammonium diuranate (ADU), uranium tetrafluoride and uranyl nitrate (UN) and its further denitration to trioxide are discussed.

The development and adaptation of analytical procedures and their applicability as an important support to the technical work and the quality control of the abovementioned nuclear grade materials is emphasised as well.

IAEA - TECDOC - 420
ADVANCES IN URANIUM REFINING AND CONVERSION
I.A.E.A., VIENNA, 1987.

2. THE FIRST YELLOWCAKE

The first yellowcake that we work with since several years is a sodium diuranate (SDU) produced from the industrial processing of monazite sand [1]. The chemical treatment for breaking up monazite sand by alkaline process has been in practice in Brazil (S.Paulo) since 1948 on an industrial scale [2]. The production capacity is about 3000 metric tons of monazite per year for the production of thorium, rare earth chlorides (2000 tons) and phosphate as the main products. After decontaminated from radium and its descendents by coprecipitation with barium sulphate the rare earth chlorides are commercialized. Thorium is stocked mainly as a crude hydroxide (thorium sludge). Uranium is recovered as a by-product in the form of sodium diuranate.

The main impurities considered in this yellow cake are sodium, phosphate, silica, iron and, of course, thorium and rare earth elements (RE). Great concern was given to the decontamination of thorium and rare earths. In Table I is presented a representative composition of this SDU.

TABLE I - CHEMICAL COMPOSITION OF SODIUM DIURANATE

ELEMENT	%
U as U_3O_8	79.5
B	0.0002
Cu	0.001
V	0.004
Mo	0.0005
As	0.01
P as PO_4	0.3
S as SO_4	1.5
F	0.02
Halogens	0.015
Th as ThO_2	3.0*
Rare Earths	0.2
Sm + Eu + Gd + Dy	0.02 max.
Fe	0.1
Cd	0.007
Pb	0.0015
Ti	0.0015
Si as SiO_2	1.4
Na as Na_2O	9.2

* Variable from 0.3 to 8.0%

As the abovementioned SDU at the monazite plant is only dewatered at 110-120°C and usually contains some organic mater, as a not controlled impurity, before its dissolution the yellowcake is calcined at 450°C during two hours. This treatment was introduced in the flow-sheet to avoid evolution of NO_x gases. We worked with this uranium concentrate for several years, as it was the unique raw material at hand.

3. A NEW YELLOWCAKE

Recently a second yellowcake could be used. It came from the Poços de Caldas Industrial Complex, at Poços de Caldas, Minas Gerais State. This industrial plant is owned and operated by NUCLEBRAS. The yellowcake is an ammonium diuranate of very good quality. The unique difficulty we had to cope with is the presence of zirconium contamination. After its dissolution with nitric acid, the clear uranyl nitrate solution was treated for the removal of the great majority of zirconium. It is clear that this yellowcake could not be calcined, otherwise it will be converted into uranium oxide which solubilization will generate high evolution of NO_x gases and the installation is not ready to absorb them.

4. DISSOLUTION OF YELLOWCAKE

The initial step is the dissolution of the concentrate with nitric acid for the obtaintion of a clear uranyl nitrate. During the dissolution the gross amount of silica is removed by dehydration of silicious acid. The dissolution is accomplished into a stainless steel reactor of 300 L capacity in a batchwise fashion. The yellowcake is poured direct and slowly into the nitric acid. After all the yellow cake was introduced its digestion is made with 2M HNO_3 at $90-100^\circ\text{C}$ for the complete flocculation of silica.

If zirconium is present, the uranyl nitrate is treated with controlled amount of phosphoric acid. Both silica and zirconyl phosphate are separated together. The hot pulp is filtered into a canvas filter and the residue thoroughly washed for the removal of soluble uranyl nitrate. The filtered uranyl nitrate solution has a concentration of 475 g U/L and after cooled is adjusted to 300 g U/L and 1M HNO_3 previously to the solvent extraction. Sodium or ammonium nitrate, not less than 1M used as salting out agent is formed during the dissolution. In the case of the SDU produced from the monazite sand the trouble some presence of Th and RE is minimized by the controlled addition of sodium sulfate [3,4].

5. TBP 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 the extraction, scrubbing and stripping, respectively. The facility and its equipment, operational flow-sheet, performance and gained experience were published [5,6]. The facility comprises a section for the safety opening of the drums and for the dissolution of the yellowcake. The organic phase is a (v/v) 35% TBP-varsol. The three columns have perforated plates of about 23% area. The extraction is accomplished in countercurrent using an organic to aqueous ration of 2.2 to 1. The loaded organic phase containing 135 g U/L leaves the extraction column and is admitted to the scrubbing column where it is scrubbed with 0.2M HNO_3 in an organic/aqueous phases ratio of 1:1. The washed organic phase

(110-115 g U/L) is stripped with water using an aqueous/organic ratio of 1.6 to 1, resulting in a uranyl nitrate solution of 70-105 g U/L. The third column can be steam heated and operated at 40-60°C resulting in a uranyl solution of mean 100 g U/L value. This solution is filtered through a celite layer for the coalescence of small droplets of TBP and then forced into a layer of pure diluent to remove the last traces of TBP.

6. PRECIPITATION OF AMMONIUM DIURANATE (ADU)

The pilot plant is equipped to perform the precipitation in a batchwise way, into a 500 L reactor, and as continuous operation as well. The pure uranyl nitrate solution (100 g U/L) is heated to about 60°C and the ADU is obtained by bubbling undiluted anhydrous NH_3 gas. The final pH can be controlled to values ranging from 4.0 to 7.5 for ADU to be sent to the UF_4 unit or to pH about 10 (excess NH_3), if the ADU is directed to ceramic grade UO_2 pellets. For the batchwise precipitation the ADU is dewatered into a vacuum canvas filter and has a humidity ranging from 45 to 50%.

In the continuous precipitation using one step reaction the reactor ($\varnothing 27$ cm x 100 cm, 56L) is fed with uranyl nitrate at a rate of 1.2-2.0 L/min, heated at 60°C, and NH_3 bubbled at a rate of 60-80 L/min. The final pH is usually about 10 (excess NH_3). The slurry of ADU is deposited in the bottom of the continuous filter and is sucked by vacuum into the rotating drum. The cake leaves the drum with about 50% humidity, the thickness of the layer ranging from 2.5 to 3.5 mm.

7. TRIOXIDE FACILITY

A facility for the conversion of ADU to UO_3 comprises a continuous, electrically heated, belt furnace. The ADU is fed directly from the rotating filter to the stainless steel conveyor belt moving inside the furnace with zones having different temperatures, the gradient ranging from 110° to 500°C. The final product is an UO_3 oxide used as feeding material for the tetrafluoride plant or sent to further conversion to ceramic grade dioxide. The residence time during the dewatering is 2-3 hours.

8. TREATMENT OF AQUEOUS EFFLUENTS

The uranium purification pilot plant gives rise to some solutions containing uranium, thorium, rare earths, iron and titanium, the main stream coming from the extraction column. All effluents are collected and treated with sodium hydroxide. The precipitate is filtered out and returned to the dissolution section with nitric acid and sent to the extraction again.

9. TETRAFLUORIDE PILOT PLANT

After some previous work [7,8] a pilot plant facility to acquire the necessary technology on the UF_4 production for further uses in the reduction to U metal and preparation of UF_6 was set up [9]. The establishment of this unit had the collaboration and technical assistance from the International Atomic Energy Agency (IAEA).

The starting material is UO_3 , reduced to UO_2 by cracked NH_3 and the use of anhydrous hydrogen fluoride for the conversion to UF_4 . During some operation of this pilot the process of obtaintion of UO_3 was changed in the sense that the ADU precipitate at pH 7.5 for ceramic grade was calcined to UO_3 in the continuous belt furnace and then pelletized in spheres of about 4-6 mm, dried again and used as feed material in the L reactor. This new type of UO_3 exhibited excellent mechanical properties. Nowa days we changed once more to the use of directly UO_3 produced as flakes of 3-4 mm thickness by filtration of ADU in the vacuum rotating filter and dried and calcined in the moving belt conveyor. This type of UO_3 exhibited excellent mechanical properties. This trioxide is contacted with anhydrous hydrogen fluoride for the conversion to UF_4 . The green salt produced is of good quality, assessing a minimum of 95% UF_4 .

10. WET WAY UF_4 PREPARATION

A bench scale facility for preparation of uranium tetra fluoride via aqueous conversion of UO_2 powder with hydrofluoric acid is under experimental test. The dioxide is obtained in the dry moving bed reactor that has been in operation also for the UO_2 production as well. The UO_3 is reduced again by hydrogen generated by ammonia cracking. A second UO_2 type is produced by direct reduction of ADU in a moving belt furnace with hydrogen.

The conversion of both type of UO_2 with hydrofluoric acid is quite simple and effective, the tetrafluoride being filtered using a vacuum canvas filter and dried stepwise, first at 110-120°C and then at higher temperature. The quality of this green salt for uranium reduction or hexafluoride preparation is under investigation, the first results being promissor.

11. DENITRATION OF URANYL NITRATE

Development studies on a fluidized bed process for conversion of uranyl nitrate solution to uranium trioxide and recovery of nitric acid is under investigation. A pilot plant is being set up comprising an unity for concentration of uranyl nitrate solution from 100 g U/L to about 900 g U/L, followed by denitration of the melted uranyl nitrate to UO_3 . This new unity has the first test scheduled for second semester 1986.

12. QUALITY CONTROL

Mention will be made for some procedures specially developed to assist the pilot plant work. A rapid routine determination of uranium content in uranyl solution is done by gamma-ray spectrometry [10], using the ^{235}U 185 Kev photopeak. A procedure was outlined for the direct determination of U content of uranyl nitrate-TBP-organic phase [11]. The thermogravimetric behavior of ADU samples, and specially the pyrophoricity grade of UO_2 powders and their O/U ratio in UO_2 - powder and pellets was developed [12]. The analytical control of UF_4 was made by sequential analysis of the most probable products existing with the tetrafluoride [13]. The determination of microquantities of

B in highly pure uranium and thorium compounds is done through the extraction of the colored complex of BF_4^- -monomethyl thionine [14,15].

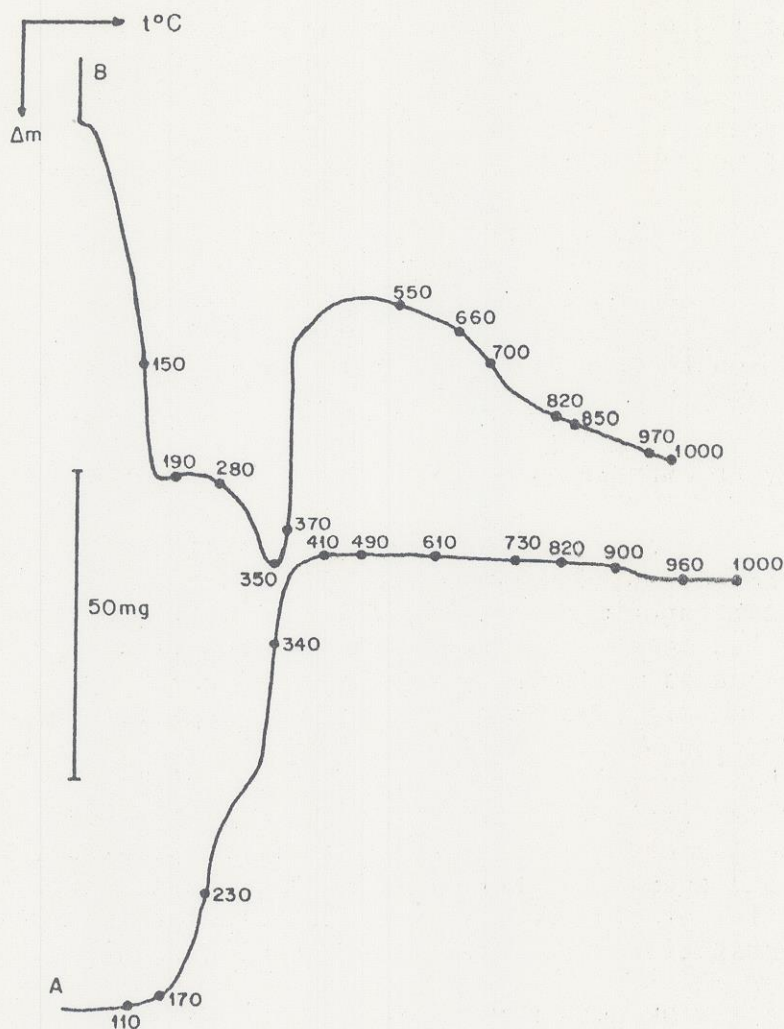


FIG. 1 THERMOGRAVIMETRIC CURVES OF URANIUM DIOXIDE [12]

(A) UO_2 (normal) obtained by reduction of U_3O_8 in H_2 at 770°C .

(B) UO_2 (pyrophoric) obtained by direct reduction of ADU in H_2 at 770°C .

A procedure for the separation and concentration of extremely low amounts of thorium and rare earths from uranyl solutions was developed based upon the sorption of those elements from solutions containing 0,3M HF into a small column of alumina [16]. Using this technique the individual RE have been analysed by emission spectrography [17]. A semiquantitative routine spectrometric method was outlined for the direct determination of 18 elements in uranium compounds, including UF_6 , using gallium oxide and sodium fluoride. Vanishing small amounts of RE in uranium are determined by fluorescence spectrometry after separation into an alumina column [18]. Zirconium is analysed by direct spectrofluorimetric determination in uranyl chloride using morin [19] and spectrophotometrically with chloroanilic acid [20].

Procedures for the determination of the composition of the cell 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. The presence of residual HF in uranium hexafluoride is determined after its hydrolysis and measurement of total uranium and total hydrofluoric acid.

REFERENCES

- [1] BRIL & KRUMHOLZ P. Produção de óxido de tório nuclearmente puro. São Paulo, Instituto de Energia Atômica, dez. 1965. (IEA-115).
- [2] KRUMHOLZ, P. and GOTTENKER, F. The extraction of thorium and uranium from monazite. In: United Nations, New York, Proceedings of the international conference on the Peaceful Uses of Atomic Energy, held in Geneva 8 August 20 August 1955, 4-8: Production technology of the material used for nuclear energy. New York, 1956, p.126-8.
- [3] BRIL, K.J. & KRUMHOLZ, P. Production of nuclearly pure uranium study on the decontamination of uranium from thorium and rare earths by extraction with tributylphosphate in: INTERAMERICAN NUCLEAR ENERGY COMMISSION. Proceedings of the 3rd Interamerican symposium on the peaceful applications of nuclear energy, Rio de Janeiro, 1960. Washington, D.C., Pan American Union, 1961. p.37-59.
- [4] BRIL & KRUMHOLZ, P. Um processo industrial de produção de urânio nuclearmente puro. São Paulo, ORQUIMA, Lab. Pesquisas, 1960. (LPO-9).
- [5] FRANÇA JR., J.M. Usina piloto de purificação de urânio pelo processo de colunas pulsadas em operação no Instituto de Energia Atômica, São Paulo, Instituto de Energia Atômica, out. 1972, (IEA-277).
- [6] FRANÇA JR., J.M. & MESSANO, J. Dimensionamento de colunas pulsadas industriais na purificação de urânio para fins nucleares, pelo método do HTU indireto. São Paulo, Instituto de Energia Atômica, maio 1974. (IEA-343).
- [7] CUSSIOL FILHO, A. & ABRÃO, A. Tecnologia para a preparação de tetrafluoreto de urânio por fluoridretação de UO_2 obtido de diuranato de amônio. São Paulo, Instituto de Energia Atômica, ja. 1975. (IEA-379).
- [8] RIBAS, A.G.S. and ABRÃO, A. Preparação de UO_2 apropriado para obtenção de UF_4 . S.Paulo, Instituto de Energia Atômica, nov. 1973 (IEA-318).
- [9] FRANÇA JR. J.M. Unidade piloto de tetrafluoreto de urânio pelo processo de leito móvel em operação no IEA, São Paulo, Instituto de Energia Atômica, jan. 1975. (IEA-381).

- [10] ABRÃO, A. & TAMURA, H. Routine radiometric determination of uranium by gamma-ray spectrometry. São Paulo, Instituto de Energia Atômica, ago. 1968. (IEA-170).
- [11] FEDERGRÜN, L. & ABRÃO, A. Determinação espectrofotométrica direta de urânio na fase orgânica fosfato de n-tributílo-nitrato de urânio. São Paulo, Instituto de Energia Atômica, jul. 1971. (IEA-242).
- [12] ABRÃO, A. Thermogravimetric behavior of some uranium compounds; application to O/U ratio determination. São Paulo, Instituto de Energia Atômica, ago. 1965. (IEA-105).
- [13] FEDERGRÜN, L. & ABRÃO, A. Determinação dos conteúdos de UO_2F_2 de UO_2 e de UF_4 em tetrafluoreto de urânio. São Paulo, Instituto de Energia Atômica, maio 1974. (IEA-341).
- [14] FEDERGRÜN, L. & ABRÃO, A. Determinação espectrofotométrica de boro em sulfato de tório. São Paulo, Instituto de Energia Atômica, jun. 1976. (IEA-420).
- [15] FEDERGRÜN, L. & ABRÃO, A. Determinação espectrofotométrica de boro em urânio, alumínio e magnésio: extração de tetrafluoreto de monometiltionina. São Paulo, Instituto de Energia Atômica, jun. 1968. (IEA-165).
- [16] ABRÃO, A. Chromatographic separation and concentration of thorium and rare earths from uranium using alumina-hydrofluoric acid. Preparation of carrier-free radiothorium and contribution to the fission rare earths. São Paulo, Instituto de Energia Atômica, jun. 1970. (IEA-217).
- [17] LORDELLO, A.R. Determinação espectroquímica dos elementos lantanídeos em compostos de urânio, via separação cromatográfica em coluna de alumina-ácido fluorídrico. São Paulo, 1972. [Master Thesis].
- [18] CAZOTTI, R.I. & ABRÃO, A. Spectrofluorimetric determination of rare earths in U after separation and concentration of total lanthanides onto an alumina column. São Paulo, Instituto de Energia Atômica, jun. 1973. (IEA-295).
- [19] CAZOTTI, R.I. et alii. Determinação espectrofluorimétrica direta de microquantidades de zircônio em urânio. São Paulo, Instituto de Energia Atômica, fev. 1976. (IEA-401).
- [20] FLOH, B. et alii. Separação de zircônio por extração em meio clorídrico com tri-n-octilamina e sua determinação espectrofotométrica com ácido cloroanílico. São Paulo, Instituto de Energia Atômica, ago. 1976. (IEA-427).