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URANIUM RECOVERY FROM WASTE OF THE NUCLEAR FUEL CYCLE PLANTS AT IPEN-CNEN/SP

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ABSTRACT

Sodium diuranate (DUS) is a uranium concentrate produced in monazite industry with 80% typical average grade of U_3O_8, containing sodium, silicon, phosphorus, thorium and rare earths as main impurities. Purification of such concentrate was achieved at the nuclear fuel cycle pilot plants of uranium at IPEN by nitric dissolution and uranium extraction into an organic phase using TBP/Varsol™, while the aqueous phase retains impurities and a small quantity of non extracted uranium; both can be recovered later by precipitation with sodium hydroxide. Then the residual sodium diuranate goes to a long term storage at a safeguards deposit currently reaching 20 tonnes. This work shows how uranium separation and purification from such bulk waste can be achieved by ion exchange chromatography, aiming at decreased volume and cost of storage, minimization of environmental impacts and reduction of occupational doses. Additionally, the resulting purified uranium can be reused in nuclear fuel cycle.

1. INTRODUCTION

The uranium purification has been made for many years and the processes commonly used are solvent extraction and ion exchange. The solution is uranyl nitrate, sulfate or chloride, depending on the method to be adopted. The high purity solution is processed to obtain the desired uranium compound.

The first studies performed in Brazil for the installation and operation of a uranium purification pilot plant based on the phenomenon of ion exchange were initiated in radiochemistry division (CDRQ) in former IEA (Atomic Energy Institute), now IPEN. In 1960, came into operation at the Chemical Engineering Center of IEA a pilot plant which produced 04 (four) tons of high purity ammonium diuranate, being closed in 1963.

The nuclear purity ammonium diuranate obtained from the solutions of this purification was converted into uranium dioxide and used in the manufacture of fuel plates. Due the success of this separation and purification process, a new plant went in operation in 1969 at the same center, in order to complement the studies of purifying uranium compounds by ion exchange process [1, 2]. The techniques of separation and concentration of uranium using ionic resins are known. They are simple and can be achieved good separations and have the advantage of a large number of theoretical stages per unit length. With the cationic resin occurs UO_2^{2+} retention and with the anionic resin occurs the retention of the complex ions $[UO_2Cl_3]^-$, $[UO_2Cl_4]^{2-}$, $[UO_2(SO_4)_3]^{4-}$ or $[UO_2(SO_4)_2]^-$.

Impurities such thorium and iron are serious problems with regard to the uranium separation. This is because anionic or cationic complexes of these elements are formed with the same groups that are generally used for formation of anionic or cationic uranium complexes as well. When these interferences are present in the solution to be purified, the choice should be cationic resin, because it can use ethylenediaminetetracetic acid (EDTA) as complexing agent which forms anionic or no ionic complexes with most metals [3].

The cationic resin also offers other advantages over the anionic. The anionic resin are very unstable and loose its ability to absorb faster than cationic. Therefore, in a comparative process based on both of the resins it would require twice the amount of anionic resin for the same efficiency of the process. Besides this, anionic resins are much expensive per unit weight than the cationic [3].

1.1. Purification of uranium at IPEN

In the industrial processing of monazite by the Administration of Production of Monazite (APM), São Paulo, was produced the sodium diuranate (DUS), with 80% average grade of U_3O_8 containing sodium, silicon, phosphorus thorium and rare earths as main impurities [4].

Purification of such concentrate was achieved at the nuclear fuel cycle pilot plants of uranium at IPEN. In the first stage, the sodium diuranate was dissolved by nitric acid and then filtered, achieving impure uranyl nitrate. The second step was the uranium extraction into an organic phase in pulsed columns. The uranium was extracted by TBP/varsol^{TM} solution, remaining in

the aqueous phase the impurities and a small amount of uranium that was not extracted. This solution containing uranium and others impurities was precipitated by sodium hydroxide solution on pH = 7,5, at a temperature between 85-90^{o}C. The precipitate was filtered and washed generating a residue of impure sodium diuranate (DUS) [5].

This residue goes to a long term storage at a IPEN-CNEN/SP safeguards deposit currently reaching 20 tonnes [6]. The amount of uranium in this material shows the feasibility of this process and a treatment of this waste will decrease volume and cost storage, reducing the occupational dose, minimizing environmental impacts. The purified uranium can be reused in nuclear fuel cycle [7].

2. METHODOLOGY

2.1. Removal of DUS samples from Safeguards deposit

It was removed about 1,5kg of impure DUS from 04 (four) of the containers containing the waste. Each of these contains 30-80 kg of this material.

2.2. Chemical characterization

DUS samples were homogenized with a mechanical stirrer about 1 hour. Aliquots of this material were dryed at 130^{o}C until constant weight for humidity analysis and characterization by X-ray fluorescence analysis [8].

2.3. Nitric dissolution

DUS aliquots were dissolved by nitric acid solution in 1:5 ratio (weight:volume), under stirring and heating at 70^{o}C. It was used 3, 5 and 7 mol.L^{-1} nitric acid concentrations. After digestion, the mixture was filtered, achieving a clear nitrate filtrate. The residue was washed by warm water and collected separately.

2.4. Ion exchange chromatography

A cationic exchange resin Dowex50W-X12, 50-100mesh, was used for uranium retention from the nitrate solution at 0.2 $mol.L^{-1}$ on a chromatographic column. EDTA was added as a complexing agent for thorium, rare earths, iron and other impurities. Under these conditions it achieves separation of any phosphate, leaving the uranium retained in the column. The elution was performed with 2$mol.L^{-1}$ HNO_3. The column washing was performed by deionized water, adding the washing water to the eluate. The percolation and elution speeds were 1-3 $mL.min^{-1}$.

3. RESULTS AND DISCUSSION

3.1. Collected samples

The total weigh of material collected was 1.438kg

3.2. Humidity analysis

Aliquots of this material were dried at 130^{o}C to constant weight. The water content found was 45.3%, yielding 0.748g of dry waste containing uranium

3.3. X-ray fluorescence spectrometry analysis

Table 1 shows the constituents of the waste from the dried sample by X-ray fluorescence spectrometry analysis

Table 1 – Chemical characterization of residual DUS by X-ray fluorescence spectrometry analysis

Elements	Teor (%)
U	86,4±0,6
Na	9,6± 0,5
F	3,35±0,05
Fe	0,33±0,03
Si	0,11±0,01
Ni	0,10±0,01
Cl	0,09±0,02
Cu	0,04±0,01
Mo	0,010±0,004
S	0,010±0,006
Zr	ND

3.4. DUS Dissolution

DUS samples aliquots were added to nitric acid solutions and slowly stirred at room temperature. After this the solution was maintained at 70^{o}C for approximately 2 hours. At the end of digestion, the solution was filtered yielding a clear filtrate of uranyl nitrate. The residue was washed with boiling water that was added to the filtrate. Table 2 presents the results of the dissolution.

Table 2 – Percentage of final residue after nitric dissolution

HNO_3 (mol. L^{-1})	DUS waste (g)	Residue after dissolution (g)	Residue (%)
3	5,488	0,118	2,15
5	5,479	0,120	2,19
7	5,493	0,039	0,71

The 7 mol.L^{-1} HNO_3 dissolution showed a lower amount of residue after filtration. This residue showed gelatinous aspect showing silica presence.

3.5. Retention and elution of uranium on cationic resin

The solution acidity was set to 0.2mol.L^{-1} and EDTA was added as complexing agent. The total volume of impure uranyl nitrate solution was 150 mL. The percolation rate of the solution on cationic exchange resin was approximately 2mL.min^{-1}. The column was washed with deionized water. The elution was performed by 2mol.L^{-1} nitric acid solution. The eluate was precipitated with ammonium hydroxide and the ammonium diuranate was burned at 950^{o}C. The U_3O_8 purity achieved was 98% approximately, containing a few quantities of copper, iron, siliceous and aluminum.

4. CONCLUSION

The DUS waste dissolution by nitric acid is viable and its filtration is easy. The filtrate was clear and the residue ranged approximately 0.7 to 2.2% to the dissolved amount. The retention and elution of the uranium in the cationic resin was efficient, resulting a 98% purity uranium concentrate.

The monazite sand used in IPEN pilot plants comes from coastal regions of Bahia and Espírito Santo, Brazil. The concentration was approximately 60% rare earths, 5- 7% thorium and 0,1 to 0,4% uranium. As the residue used in this work contains about 86% of uranium, on a dry sample, it is justified the treatment of this uranium rich waste using this simple and low cost technology.

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