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Recovery of uranium from the filtrate of 'ammonium diuranate' prepared from uranium hexafluoride

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Abstract

The hydrolysis of uranium hexafluoride and its conversion to 'ammonium diuranate' yields an alkaline solution containing ammonium fluoride and low concentrations of uranium. The recovery of the uranium has the advantage of saving this valuable metal and the avoidance of unacceptable discarding the above mentioned solution to the environment. The recovery of uranium(VI) is based on its complex with the excess of fluoride in the solution and its adsorption on to an anionic ion-exchange resin. The 'ammonium diuranate' filtrate has an approximate concentration of 130 mg l^{-1} of uranium and 20 g l^{-1} of ammonium fluoride. An effective separation and recovery of the uranyl fluoride was achieved by choosing a suitable pH and flow rate of the uranium-bearing solution on to the resin column. The effluent ammonium fluoride will be recovered as well. Uranium fluoride adsorbed by the ion-exchanger is then transformed into the corresponding uranyl tricarbonate complex by percolation of a dilute ammonium carbonate solution. Finally, the free fluoride uranium carbonate is eluted from the resin with a more concentrate ammonium carbonate solution. The eluate now can be storage to be precipitated as ammonium uranyl carbonate (AUC). The loading and elution of uranium(VI) on to the ion-exchange column was followed up by a fluorescence test. A flux prepared using a mixture of sodium and potassium carbonate and ammonium fluoride was used for the uranium fluorescence test (ultraviolet lamp). Based on the successful recovery of the uranium on a laboratory scale this process is being considered for use with enriched uranium.

Keywords: Uranium; Ion exchange; Uranium recovery; Ammonium fluoride recovery; Effluent treatment

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1. Introduction

The Fuel Cycle Center of the Instituto de Pesquisas Energéticas e Nucleares (IPEN), S. Paulo, Brazil, is scheduling the expansion of the fuel element fabrication for its research reactor. One of the problems faced is to achieve a reliable technique for the treatment of the streams containing low concentration of enriched uranium.

Of the known techniques such as ion-exchange, solvent extraction and conventional precipitation, the first one was the one of choice.

1.1. From yellow cake to enriched uranium at IPEN

The nuclear fuel cycle involves several major steps. At IPEN the uranium operation starts with the purification of yellow cake to 'ammonium diuranate' (ADU) by solvent extraction using the uranyl nitrate–TBP–kerosene system and extraction with pulsed columns. In sequence ADU is converted into uranium dioxide (UO_2), uranium tetrafluoride (UF_4) and then to uranium hexafluoride (UF_6). The UF_6 is isotopically enriched, after which it is converted to ammonium uranyl carbonate (AUC) and then to uranium dioxide for the manufacture of the reactor fuel elements. Recently the IPEN pilot plant changed to the precipitation of ADU instead of obtaining the usual AUC.

A key step in the reactor fuel cycle is, of course, the enrichment process itself. In Brazil (S.Paulo) the process of choice is the centrifuge technique. The convertion UF_4 to UF_6 is done using elemental fluorine at IPEN. The first step in the uranium dioxide production process is to hydrolyze the uranium hexafluoride and to obtain a solution of uranyl fluoride. Ammonia gas is then added under controlled conditions to precipitate 'ammonium diuranate'. The precipitate is dried and reduced to uranium dioxide.

The uranium hexafluoride sent to the enrichment facility in S.Paulo was produced using very high purity 'ammonium diuranate' that was then converted to very pure UF_6. This material was processed further for use in the manufacture of fuel elements. For several years the product obtained from the hydrolyzed uranium hexafluoride was the ammonium uranyl carbonate. Very recently the pilot plant changed its operation to use 'ammonium diuranate'.

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The main feature described in this study is the residual enriched uranium that must be recovered from the ammonium fluoride as the ADU filtrate.

2. Experimental

2.1. Reagents and materials

All chemicals used were of analytical grade and solutions were prepared using deionized water.

For the ion-exchanger, Rohm and Haas IRA-458, 30–50 mesh anion-exchange commercial resin was initially used in the chloride form. The resin was washed only with deionized water to remove the fine grains. A portion of the resin in the chloride form as supplied was suspended in deionized water and allowed to settle, and the fines decanted. The resin slurry was added to the column. The first experimental run was made directly using the resin in the original chloride form and percolating NH_4OH 0.1 mol l^{-1} solution. A small amount of chloride remaining in the resin does not affect to the process. For the following cycles the resin was used in the carbonate-form.

The chromatographic column used was composed of a working column of 130 mm i.d. and 500 mm bed height, 20 g of resin, fed by gravity, using a reservoir of 5000 ml capacity and flow rate 2.1 ml min^{-1} cm^{-2}.

Apparatus

pH meter Procyon model AS 720. Electroanalyzer Metrohm 646 VA with electrode 647 VA HMDE (hanging mercury drop electrode). Ultraviolet lamp HGV, 125 W, 220 V, Philips. Electroanalyser Digimed DM21 with fluoride electrode selective model 409 and model 90.00.01(Ref.).

2.2. Procedure

2.2.1. Precipitation of ‘ammonium diuranate’

‘Ammonium diuranate’ was produced batchwise by precipitating uranyl solution with ammonia gas. The ADU was obtained from the uranyl fluoride solution prepared by the hydrolysis of the hexafluoride and bubbling NH_3 directly into the solution and maintaining the temperature in the range of 50–60°C and the final pH at 9.0–9.5 The ADU suspension was stirred for some hours. The precipitate was then separated by filtration after 12 h ageing. The ADU was washed using 0.01 mol l^{-1} ammonia solution. The resultant filtrate is an alkaline ammonium fluoride solution with very low concentration of residual soluble uranium. The filtrate was saved and used to study the separation and concentration of the uranyl ion by the anionic exchange technique.

The chemical composition of a representative sample of this ammonium fluoride after the separation by filtration has pH 9.2, 20 g l^{-1} NH_4F and about 130 mg l^{-1} U(VI).

2.2.2. Uptake of uranium from the ammonium fluoride solution

Chromatographic column investigations were performed for the recovery of uranium from aqueous uranyl fluoride solution using a bed of strong anionic ion-exchanger. Before each run the uranyl fluoride solution had its pH adjust to 9.5 using ammonium hydroxide. For each run of 5000 ml of filtrate was used. The parameters studied were the flow rate, from 2.1 to 4.3 ml min^{-1} cm^{-2} and pH from 8.0 to 10.5. After the loading operation, the resin was washed with 250 ml of deionized water.

2.2.3. Exchanging fluoride by carbonate in the uranyl complex inside the resin

After getting rid of the interstitial fluoride by washing the column with deionized water, the resin was treated with 500 ml of ammonium carbonate solution, and investigated in the range 0.1–0.5 mol l^{-1}. This treatment exchanges the fluoride adsorbed as $UO_2F_4^{-2}$ by the carbonate ion and forming the well retained $UO_2(CO_3)_3^{4-}$ complex. Thus the fluoride was completely removed from the resin by stepwise elution with water and then with dilute ammonium carbonate.

2.2.4. Elution of uranyl carbonate

Finally, the adsorbed uranyl tricarbonate ion was eluted from the resin with the aid of the same reagent, that is, ammonium carbonate, but at higher concentration. For desorption of the uranyl carbonate an ammonium carbonate solution of 2.0 mol l^{-1} was used. The eluted solution contains very pure fluoride-free uranyl carbonate that is ready for the final recovery and use of the uranium.

2.2.5. Follow-up of uranium in the process

During the operation uranium was detected by the fluorescence method. This test [11] uses a carbonate pearl prepared from a mixture of sodium and potassium carbonate and ammonium fluoride (4.55:4.55:0.9) g, using a platinum wire with one drop of the test solution placed on the flux and the pearl fused, cooled and examined under ultraviolet light. A green fluorescence confirms the presence of uranium.

Uranium was determined by eletroanalyser with hanging mercury drop electrode.

2.2.6. Follow-up of fluoride in the process

When necessary, fluoride was detected by the zirconium-alizarin test [11]. A quantitative filter paper strip was impregnated with the zirconium-alizarin reagent. The dried paper was moistened with a drop of 50% acetic acid and then a drop of neutral test solution was placed on the moist area. A yellow spot appears in the presence of fluorides.

Fluoride was determined by selective electrode, the detection limit being $0.02*10^{-6}$ g F^{-} ml^{-1} [12].

Table 1
Uptake of uranyl fluoride by the resin as a function of pH of the ammonium fluoride

pH	U uptake (%)	Flow-rate $ml*min^{-1}*cm^{-2}$
8.0	64.0	2.1
9.2	99.6	2.1
9.5	99.9	2.1
10.7	99.9	2.1

3. Results

For the loading of uranium the uptake of the anionic uranyl complex has enormous importance. Table 1 shows the results of the uptake of uranium from the ammonium fluoride solution as a function of the pH of the influent.

Based on the results depicted by Table 1 the recommended pH of the loading solution is in the 9.5–10.7 range. The working pH recommended is thus in the range 9.5–10.0. At pH values higher than 10 there is the possibility of partial precipitation of uranium inside the column.

The loading flow-rate is also important. Various runs for the uptake of uranyl fluoride with flow-rate in the range 2.1–4.3 ml min^{-1} cm^2 at pH 9.5 showed that at high flow-rates there is leakage of uranium. For instance, at the higher flow-rate used in this work (4.3 ml min^{-1} cm^2) the uptake of uranium was only 96.4%.

The exchange of fluoride by carbonate in the uranyl fluoride complex retained by the resin was achieved via percolation of a dilute ammonium carbonate solution. As before, the aim of this operation is to obtain a final uranium product completely free from fluoride. The investigation of this parameter was made at two concentration levels: 0.1 and 0.5 mol l^{-1} CO_3^{-2}. As expected, the higher carbonate concentration promoted the elution of the uranium; 30.3% of U(VI) was assayed in the washing solution. Based on these results a solution 0.1 mol l^{-1} ammonium carbonate that promoted the elution of 0.2% uranium, is recommended as the exchanger agent.

The uranium elution was accomplished using ammonium carbonate as the eluent, but at a higher concentration. Any ammonium carbonate concentration higher than 0.5 mol l^{-1} can remove completely the uranium from the resin. A set of experiments showed that an ammonium carbonate 2.0 mol l^{-1} was a convenient concentration. Such an eluent resulted in the removal of $>99\%$ of uranium, using approximately four column volumes.

4. Discussion

4.1. Nature of the fixed complex

The uranyl ion forms a stepwise series of complexes with fluoride ion, two being anionic in character: $UO_2F_4^{2-}$ and $UO_2F_3^-$ [1]. Both these complexes can be used to take up low levels of uranium(VI) by anionic ion-exchange.

The use of ion-exchangers in nuclear industry is well recognized. Several publications cover the different aspects of the use of ion-exchangers in the atomic energy industry [2–6]. MacCready and Sethington [4] reviewed hydrometallurgical aspects of ion-exchange and solvent extraction in the nuclear fuel cycle. More information is available in the literature on uranium uptake by various commercial exchangers from various media [7]. Many publications cover the system uranyl/carbonate, uranyl/sulfate, and uranyl/nitrate but for the system uranyl/fluoride only one paper exists [10].

In the present study special attention was given to recovering traces of uranium from a fairly concentrated ammonium fluoride solution. Although all experiments used natural uranium, the objective is to work with 20% enriched uranium.

The high capacity for uranium uptake obtained with the anionic exchanger indicates that the uranium species in solution are mainly in the anionic form. Using a white acrylic resin, as here, the uptake of uranium by the resin could be easily observed by a yellow zone in the upper part of the column, a very helpful visual observation. In this study uranium was removed effectively from the ammonium fluoride solution by the anionic resin.

4.2. The uranyl carbonate–anionic ion-exchange system

The absorption of uranium (VI) from alkaline carbonate solutions is marked by very favorable equilibrium loadings. The reaction is usually represented by

$$4\,RX + UO_2(CO_3)_3^{4-} = R_4UO_2(CO_3)_3 + 4X^-$$

Ammonium or sodium carbonate is the elution reagent used with strong-base ion-exchange resins.

Elution of uranium absorbed as a carbonate complex appears somewhat easier than the elution of uranium absorbed as a sulphate complex. Neutral or alkaline eluting reagents are used to avoid the evolution of CO_2 and the consumption of carbonate that would accompany treatment of carbonate-form resin with acid solutions. Strong alkaline carbonate solutions may be used to elute uranyl tricarbonate and this system should be considered for use whenever possible. Specifically, it is possible to retain the anionic uranyl–carbonate complex in an anionic ion-exchanger, using a moderate carbonate concentration, and using a more concentrated carbonate solution to elute the uranyl carbonate from the resin. This procedure is used at the IPEN.

The tetravalent anionic complex $UO_2(CO_3)_3^{4-}$ present in carbonate solution is strongly fixed by anionic cxchange resins. Carbonate forms a strong complex with the uranyl cation, facilitating its solubilization and uptake into an anionic resin. The next step is to recover the uranium as

$UO_2(CO_3)_3^{4-}$ or $UO_2(CO_3)_2{\cdot}(H_2O)_2]^{2-}$ on an ion-exchange bed. The uranyl carbonate complex has a large overall formation constant [8]:

$$UO_2^{2+} + 2CO_3^{2-} + 2H_2O = [UO_2(CO_3)_2 \cdot (H_2O)_2]^{2-}$$

$\beta_2 = 4 \times 10^{14}$ and

$$UO_2^{2+} + 3CO_3^{2-} = UO_2(CO_3)_3^{4-} \quad \beta_3 = 2 \times 10^{18}$$

In this study the practice of combining the fluoride solution with the carbonate solution to recover fluoride free uranium from the filtrate ammonium fluoride was introduced.. The task was to develop a chromatographic procedure technologically feasible for the separation of the low concentration of uranium from the bulk of ammonium fluoride by anionic ion-exchange. The behaviour of the uranyl carbonate complex with different anion-exchangers has been investigated for pure substances by Haag [9].

4.3. What to do with the uranium-free ammonium fluoride stream?

Many fluorine compounds are useful substances. Significant quantities of fluoride are used in the aluminum industry and in making fluoropolymers. Another fluoride recovery process uses calcium carbonate or magnesium hydroxide, which react with aqueous hydrofluoric acid or ammonium fluoride to produce calcium fluoride. This process removes fluoride from solution that might otherwise cause disposal problems. For small amounts there are some applications at the Institute, for example, in the preparation of aqueous uranium(IV) fluoride. But for the future, with greater amounts of ammonium generated inside the uranium cycle an economical application must be found.

5. Conclusion

In this paper, a technologically feasible procedure is proposed for separating and concentrating uranium from ammonium fluoride solution, by retaining a uranyl fluoride anionic complex in a resin, cleaning the fluoride from the system by the use of dilute ammonium carbonate solution and eluting the uranium with a more concentrated ammonium carbonate solution. Fluoride is desorbed effectively and the uranyl carbonate solution as final product is fluoride-free. Although in this studynatural UF_6 was used, the process here described can be applied to enriched uranium.

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