



# Uranium stripping from tri-*n*-butyl phosphate by hydrofluoric acid solutions with hydrazine addition



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## ARTICLE INFO

### Article history:

Received 21 February 2015  
Received in revised form 1 August 2015  
Accepted 19 August 2015  
Available online 25 August 2015

### Keywords:

Solvent extraction  
Uranium stripping  
Tri-*n*-butyl phosphate  
Hydrazine hydrate  
Uranium tetrafluoride  
Hydrofluoric acid

## ABSTRACT

The process of uranium stripping from tri-*n*-butyl phosphate by hydrofluoric acid solutions with the addition of hydrazine was investigated in the temperature range of 20 to 60 °C. Uranium was selectively precipitated in the form of a hydrazine uranyl fluoride complex when stripped from TBP by HF solutions with the addition of hydrazine. The uranium precipitation increased with increasing N<sub>2</sub>H<sub>4</sub>/U molar ratio in the range of 1 to 3 and with increasing holding time. Uranium tetrafluoride was obtained by the thermal decomposition of the hydrazine uranyl fluoride complex in a hydrogen stream. The uranium content in UF<sub>4</sub> is 76%. The obtained uranium tetrafluoride is a high-purity product and meets all requirements imposed on UF<sub>4</sub> at conversion plants. Thus, the stripping method provides a reduction of uranium processing operations to uranium tetrafluoride.

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## 1. Introduction

The aim of any uranium-refining method is to obtain nuclear grade material, which could be used as a reactor fuel. The decrease in the content of elemental impurities to acceptable values by a single operation at the present stage of refining technology development is not feasible. The problem of obtaining a nuclear grade product is achieved by combining two or more refining methods. Mainly, the flowsheets use a combination of solvent extraction and preparation of uranium tetrafluoride.

Solvent extraction consists of the dissolution of yellow cake in nitric acid and the selective extraction of uranium using tri-*n*-butyl phosphate (TBP). The purified uranium is usually stripped from the organic phase into the aqueous phase by water or dilute nitric acid. The resulting uranyl nitrate solution is converted to UO<sub>3</sub> in two steps, evaporation and denitration. UO<sub>3</sub> is subsequently reduced with hydrogen to UO<sub>2</sub>, then converted to UF<sub>4</sub> with hydrogen fluoride at elevated temperatures (Benedict et al., 1981; Edwards and Oliver, 2000; Morss et al., 2010; Wilson, 1996).

The main disadvantage of this approach is the multi-step process of producing uranium tetrafluoride and the use of complicated, expensive and highly energy-consuming operations, such as evaporation, denitration, and the reduction of UO<sub>3</sub> to UO<sub>2</sub>.

Reducing the number of operations is possible through the use of hydrogen peroxide or ammonium carbonate as stripping agent. The application of hydrogen peroxide or ammonium carbonate solutions for

stripping from loaded TBP results in the precipitation of uranium in the form of uranium peroxide or ammonium uranyl tricarbonate, respectively, which can readily be converted to UO<sub>3</sub> (Chegrouche and Kebir, 1992; Singh and Gupta, 2000; Smirnov et al., 2013). The operations of evaporation and denitration can be also eliminated by the use of the precipitation method. The introduction of ammonia, hydrogen peroxide or ammonium carbonate into the uranyl nitrate solution from solvent extraction causes the precipitation of uranium in the form of ammonium diuranate, uranium peroxide or ammonium uranyl tricarbonate, respectively. These products are then calcined to form UO<sub>3</sub>. Ammonium uranyl tricarbonate can also be converted to UO<sub>2</sub> in an inert or reducing atmosphere (Benedict et al., 1981; Gupta and Singh, 2003; Mishra et al., 2013).

However, the number of operations could be significantly reduced by obtaining uranium fluorides directly from the stripping stage. High-purity uranium tetrafluoride is precipitated from loaded TBP by the use of hydrofluoric acid stripping solutions if the organic phase contains the uranium as a tetravalent uranium compound. In this case, the prior reduction of U(VI) to U(IV) in feed process solutions using aluminum (or electrolysis) is required (Ellis et al., 1962).

This paper describes the application of a hydrofluoric acid solution with hydrazine addition as an agent for the stripping of uranium from loaded TBP. This method differs from traditional stripping methods and has several advantages. Uranium is stripped from the loaded organic phase through direct precipitation in the form of the hydrazine uranyl fluoride complex. This product is readily converted to uranium tetrafluoride by thermal decomposition in a reducing atmosphere. The final product meets all requirements imposed on UF<sub>4</sub> at conversion plants.

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**Table 1**  
Elemental impurities in ammonium polyuranate,  $\mu\text{g/g U}$ .

B	136	P	1390	Li	1.5	Ti	196
Ca	1435	S	19714	Sn	<10	W	3.2
Fe	118	Si	1775	Mn	18	Sb	1.5
K	50	Th	45	Ni	22	Ta	0.3
Mg	364	V	71	Cu	3.2	Bi	2.4
Mo	1731	Al	648	Cl	133	Nb	1.4
Na	3414	Pb	<10	Cr	37	Sr	2.5

The use of this stripping method eliminates certain processing steps from uranium refinement, including evaporation, the denitration stage and the reduction of  $\text{UO}_3$  to  $\text{UO}_2$ .

## 2. Experimental

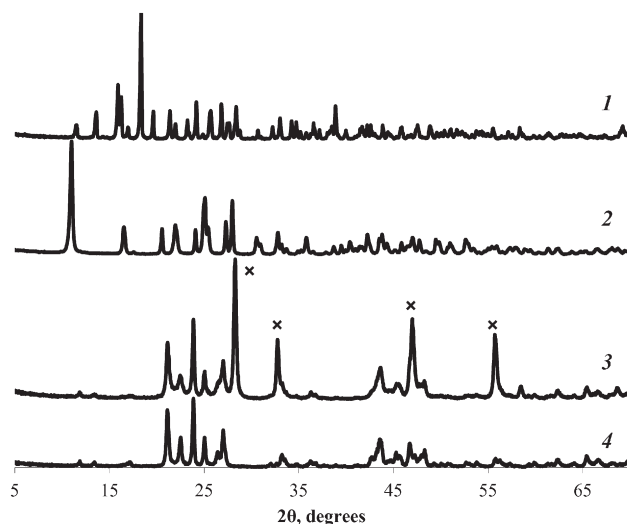
The loaded organic phase containing 84 g/L U(VI) and 0.27 mol/L  $\text{HNO}_3$  was prepared through the selective extraction of uranium from uranyl nitrate solution (100 g/L U(VI), 1.59 mol/L  $\text{HNO}_3$ ) using 30% (by volume) tri-*n*-butyl phosphate in kerosene (ShellSol D90). The extraction was conducted in a separatory funnel at room temperature (20–25 °C). The volumetric ratio between the organic and aqueous phases (O/A) was 1. The uranyl nitrate solution was prepared by the dissolution of ammonium polyuranate in nitric acid solution. The process was continued until the complete dissolution of uranium concentrate. Ammonium polyuranate was obtained from uranium ore at the JSC Dalur (Kurgan region, Russia). JSC Dalur produces uranium using the acid in-situ leaching (ISL) method. The recovery of uranium from ISL solutions includes the following process steps: uranium sorption on strong base anionic resins, uranium desorption using ammonium nitrate as eluting reagent, and ammonium polyuranate precipitation by ammonium bicarbonate. The X-ray phase analysis revealed that the ammonium polyuranate used in this study contains the following phases:  $2\text{UO}_3 \cdot \text{NH}_3 \cdot 3\text{H}_2\text{O}$  and  $(\text{NH}_4)_4(\text{H}_2\text{O})[(\text{UO}_2)_2(\text{SO}_4)\text{O}_2]_2$ . The predominant phase is  $2\text{UO}_3 \cdot \text{NH}_3 \cdot 3\text{H}_2\text{O}$  (97.25%). The humidity of the ammonium polyuranate was 31.2%; the uranium content in the dry product was 70.94%. The elemental impurity contents in the ammonium polyuranate are presented in Table 1.

The stripping procedures were performed in a polypropylene tube (50 mL) at 20–60 °C. In all the experiments, the volumetric ratio between the organic and aqueous phases (O/A) was 1. The uranium was stripped from the loaded organic phase by hydrofluoric acid solutions both with and without hydrazine. The stripping solutions were prepared using distilled water, concentrated hydrofluoric acid, and hydrazine hydrate shortly prior to the experiments. All chemicals used in the study were reagents of chemically pure grade.

The stripping experiments were performed using the following procedure. Equal volumes (20 mL) of loaded organic phase and stripping solution were placed in a polypropylene tube and stirred using a rotary mixer (ELMI Intelli Mixer RM-2) at 90 rpm. All three phases were then separated. First, the organic phase was separated using a separatory funnel. The uranium precipitate was then collected from the aqueous

**Table 2**  
The effect of HF concentration on uranium distribution during stripping from loaded organic phase.

HF concentration, mol/L	Uranium distribution, %	
	Organic phase	Aqueous phase
0.5	27.2	72.8
1.0	11.4	88.6
1.3	4.1	95.9
1.5	1.2	98.8
2.0	0.8	99.2
4.0	0.5	99.5
6.0	0.3	99.7

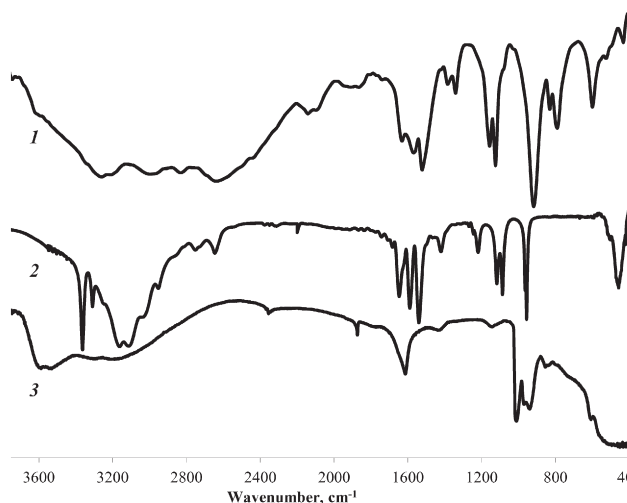


**Fig. 1.** X-ray powder diffraction pattern of uranium compounds: 1 –  $\text{UO}_2\text{F}_2 \cdot \text{N}_2\text{H}_4 \cdot 2\text{HF} \cdot 1.25\text{H}_2\text{O}$ ; 2 –  $\text{UF}_4 \cdot 2.5\text{H}_2\text{O}$ ; 3 – mixture of  $\text{UF}_4$  and  $\text{UO}_2$  (x); 4 –  $\text{UF}_4$ .

phase by vacuum filtration, washed with ethanol and dried at room temperature.

The thermal decomposition of uranium compounds was performed in a pipe furnace at a temperature of 450–600 °C in vacuum and in a hydrogen stream.

The uranium concentration in the aqueous phase was determined using ICP-AES (Optima 4300 DV Perkin Elmer). The uranium compounds obtained by stripping were analyzed using ICP-AES. The uranium concentration in the organic phases was calculated based on the mass balance. X-ray diffraction patterns of uranium compound powders were obtained on a STADI-P (STOE, Germany). Qualitative phase analysis of the diffraction patterns was conducted by search/match techniques using a powder diffraction database (ICDD PDF-2, 2009). Quantitative phase analysis of uranium compounds was performed by the Rietveld method using X-ray powder diffraction data. The particle size distribution of uranium tetrafluoride was determined using an Analysette 22 laser particle sizer. All infrared spectra of the uranium compounds were measured in the range of 400–4000  $\text{cm}^{-1}$  using a Bruker VERTEX 70 spectrometer. The measurements of IR spectra of uranium compounds were performed on solid-phase samples using the KBr pellet technique. Mixtures of KBr and the samples were pressed into transparent pellets ( $d = 13 \text{ mm}$ ) at 600 MPa.



**Fig. 2.** Infrared spectra for uranium compounds: 1 –  $\text{UO}_2\text{F}_2 \cdot \text{N}_2\text{H}_4 \cdot 2\text{HF} \cdot 1.25\text{H}_2\text{O}$ ; 2 –  $\text{UF}_4 \cdot 2.5\text{H}_2\text{O}$ ; 3 –  $\text{UF}_4$ .

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