EXTRACTION OF URANYLNITRATE BY TRIBUTYLPHOSPHATE SOLUTIONS IN MEDIUM OF LIQUID FREONS AND CARBON DIOXIDE

Vladislav KAMACHEV*, Andrew SHADRIN, Andrew MURZIN, Denis SHAFIKOV

Khlopin Radium Institute, St.-Petersburg, 194021, Russia

Tel. +7-812-247-5845, Fax. +7-812-247-8095, E-mail: kamachev@atom.nw.ru

ABSTRACT

The objective of the present work is to remove uranylnitrate from solid surfaces and to compare decontamination effectiveness in media of liquid carbon dioxide and liquid freons possessing the more technologically useful critical parameters than CO_2. Commercial freon-22 (CF_2ClH) and freon-134a (CF_3CFH_2) are applied in the study.

The performed experiments have revealed that the most recovery of uranium from uranylnitrate by TBP solutions in CO_2 per one operation is about 80 %; in the case of TBP solutions in freon-22 and freon-134a the highest recovery degree of uranium attains 95-98% in single operation.

INTRODUCTION

In recent years, in connection with the overfilling of most of existing liquid radioactive waste storage facilities and the more stringent standards of ecological protection, an active search is conducted for promising “dry” decontamination techniques to re-use or safely dispose-off contaminated equipment and work outfit. Traditional methods of surface decontamination involve the use of acidic and alkaline solutions of complexones for radionuclide wash-out. The majority of routine decontamination methods generate large volumes of secondary liquid radioactive wastes. The main advantage of non-aqueous (“dry”) decontamination techniques lies in the fact that they allow to reduce the volume of secondary liquid radioactive waste arising from decontamination considerably (20 times and more). One of such methods is decontamination in carbon dioxide medium [1, 2].

Decontamination in CO_2 is assigned to low-waste techniques and is being developed intensively. Its serious drawback is high working pressure. Previously, using hexafluoroacetylacetone (HFA) as an example, it was shown that [3] freons may be applied for metal extraction, instead of CO_2, and this may result in significant reduction of expenses on decontamination process due to decrease of working pressure. However, HFA is an expensive complexone and therefore preference is given to the more readily available and effective TBP. Besides, uranylnitrate frequently occurs on contaminated surfaces in combination with HNO_3, while HFA does not form complexes with uranylnitrate under these conditions.

The objective of the present work is the removal of uranylnitrate from solid surfaces as applied to decontamination process in media of liquid CO_2 and liquid freons having the more useful critical parameters from technological point of view. The commercially available

freon-22 (CF_2ClH) and freon-134a (CF_3CFH_2) were chosen to conduct the experiments on uranylnitrate extraction by TBP solutions.

MATERIALS AND REAGENTS

The main physico-chemical properties of freon-22 (CF_2ClH) and freon-134a (CF_3CFH_2) are given in Table 1[4]:

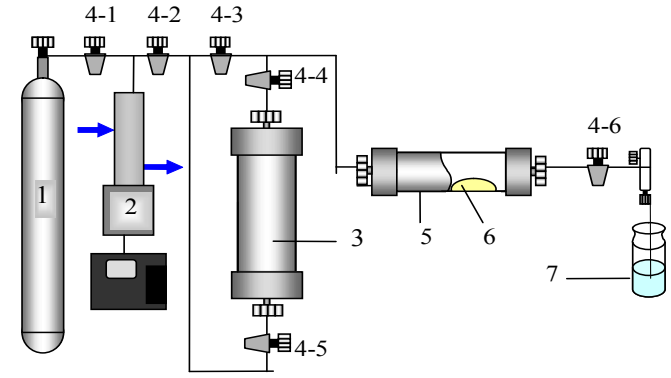
Table 1: Main physico-chemical properties of freons in use.

Freon	$T_{boil.}$, °C	$T_{crit.}$, °C	$P_{crit.}$, MPa	$\rho_{crit.}$, kg/m^3
freon-22	-40, 85	96,13	4, 986	512,8
freon-134a	-26,5	101,5	4,06	538,5

The freons were received from "Parus" Ltd (St.-Petersburg, Russia). TBP and other reagents were obtained from "Vekton" Ltd (St.-Petersburg, Russia). TBP was successively washed with soda solution, basic solution of potassium permanganate, nitric acid and water. The other reagents were applied without any additional purification.

EQUIPMENT

In this study the setup for supercritical fluid extraction was used; its diagram is shown in **Figure 1**.



1- cylinder with freon
2- high-pressure pump with control board
3- bubbler for dissolving of complexones in CO_2
4(1-6)- valves
5- extraction cell
6- sample to be decontaminated
7- adapter to restrictor
→ - cooling of pump

Figure 1: Block-diagram of setup equipped with syringe pump

EXPERIMENTAL PROCEDURE

Into temperature-controlled extraction cell of volume 3,5 ml a sample of $UO_2(NO_3)_2*6H_2O$ and a specified volume of HNO_3 were placed; TBP was poured into bubbler; then the cell and bubbler were hermetically sealed. After thermostatic control freon-22 (or freon-134a) was pumped into cell and then into bubbler up to pressure of 12 atm. at 20 ^{0}C. The system was kept for 20 min, next 50 ml of freon-22 were pumped through bubbler and cell at mean flowrate of ~ 1ml/min at the same pressure. Extract was collected into ethanol through restrictor of 35 μm in diameter. Uranium content in samples was determined by vanadatometric titration [5].

RESULTS OF EXPERIMENTS

The chief trend of our studies is concerned with the determination of uranium extraction from uranylnitrate in the presence of HNO_3. The data on dissolution of uranylnitrate versus HNO_3 concentration are given in **Table 3**. For the purposes of illustration, the dependence of uranium recovery and uranium concentration in solvents on HNO_3 concentration are presented in graphical form (**Figure 2, 3**).

Table 3: Extraction of uranylnitrate by TBP solutions in liquid CO_2, freon-22 and freon-134a at ratio of [U]:[TBP] equal to 1:7.

T, ^0C	P, MPa	Pumped medium	HNO_3 concentration in melt	Ratio of U:TBP in extract	Uranium concentration in freon, g/l	Uranium residue, %
30	7	CO_2+15% TBP	3 5	1:8,4 1:8,68	8 7,6	20 24
20	1,2	Freon-22 +15% TBP	3 5 8 12	1:7,42 1:7,14 1:9,03 1:9,52	9,4 9,8 7,1 6,4	6 2 29 36
20	1,2	Freon-134a +15% TBP	3 5 8 12	1:7,14 1:8,75 1:14 1:9,05	9,8 7,5 5 7,1	2 25 50 30

As follows from the data of **Table 3**, the recovery of uranylnitrate by TBP solutions in CO_2 moderately decreases with increase of HNO_3 concentration.

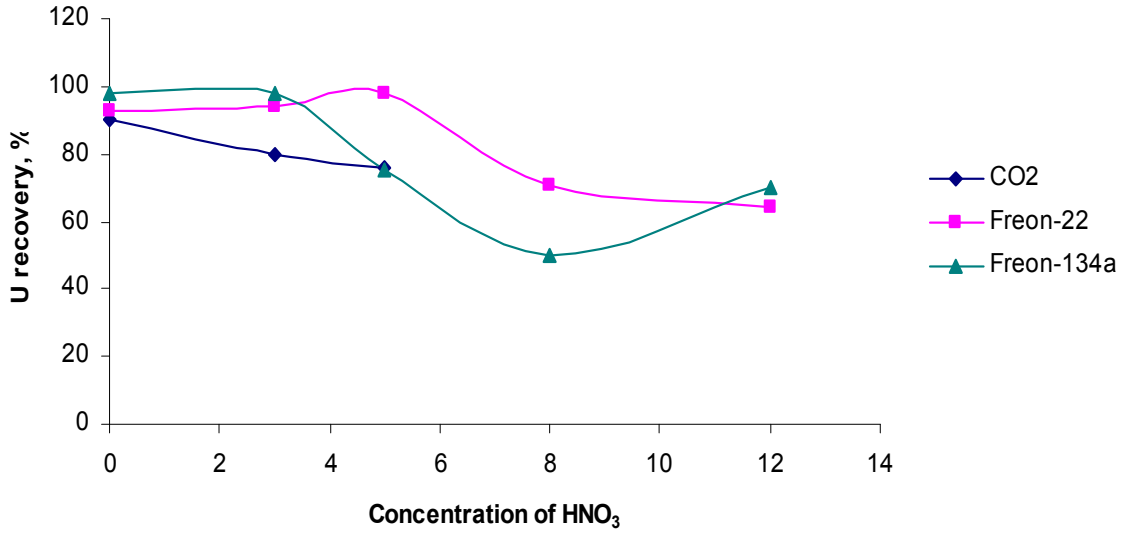


Figure 2: Dependence of uranylnitrate recovery on HNO_3 concentration

One can see from the plots that in the case of freon-22 and freon-134a the highest recovery and concentration of uranium in solvent are attained at 3-5 mole/L HNO_3, and with the further increase of acid concentration the extraction of U is deteriorated. This dependence is also observed during the traditional liquid-liquid extraction of uranylnitrate by TBP solutions [6].

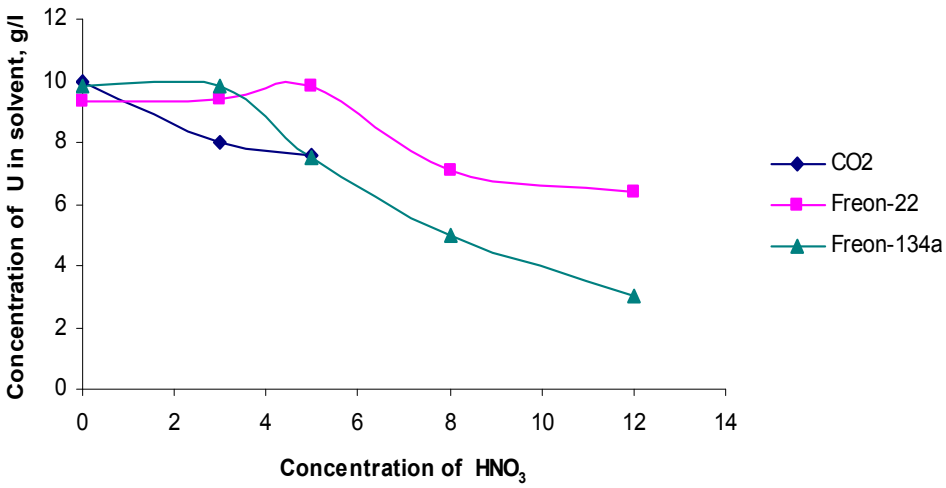


Figure 3: Dependence of uranium concentration in solvent on HNO_3 concentration in melt

CONCLUSIONS

As a result of the conducted experiments it has been found that the most recovery of uranylnitrate by TBP solution in CO_2 in one operation is ~ 80 %. As to freon-22 and freon-134a, the highest recovery of uranium attains 95-98% in a single operation. So, the decontamination efficiency in medium of liquid freons (at 12 atm.) is somewhat higher than in liquid CO_2 (at 70 atm).

Hence, the possibility for effective decontamination of solid surfaces by tributylphosphate in the medium of liquid freons at pressure of 12 atm has been demonstrated.

REFERENCES

[1] BONDIN, V., MURZIN, A., SHADRIN, A. et al., 9th Meeting on Supercritical Fluids, **2003**, Trieste, Italy, Proceedings, on CD.

[2] PARC, K. et al., Supergreen 2003, Nagoyya, Japan, Proceedings, **2003**, p. 55.

[3] BABAIN, V., KAMACHEV, V., MURZIN, A., SMIRNOV, I., SHADRIN, A. et al., Radiochemistry **2003**, p.543.

[4] MAXIMOV, B., BARABANOV, B., SERUSHKIN, I. et al., Commercial organofluoric products. Spb: Chemistry, **1996**. (In Russian)

[5] MARKOV, V., VINOGRADOV, A., ELINSON, S. et al., Uranium, methods of its determination. M., Gosatomizdat, **1960**, p.163. (In Russian)

[6] NIKOLOTOVA, Z., KARTASHOVA, N., Extraction by neutral organic compounds. M., Atomizdat, **1976**, p.396. (In Russian)