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Study the Influence of Process Variables on the Efficiency of Uranium Extraction

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Abstract: This paper presents a study on the statistical modelling of the results obtained at uranium purification by liquid-liquid extraction. The main purpose of this work consists of establishing a optimal domain for process variables (content of uranium in aqueous phase, the acidity of the aqueous phase, the aqueous: organic phase's ratio (A:O), the TBP concentration in kerosene, number of the extraction steps etc.), in order to obtain a maximum yield of extraction. To study the influence of process variables on the uranium extraction efficiency we used the method of planning experiments, that allows to obtain completely information and significant enough in a small number of experiments. At the same time, by this method are obtained mathematical relationships and data processing for complete characterization of the statistical model. The general effect of the optimization consists in the decreasing of the uranium technological losses (by avoiding the third phase formation) and, as a result it is obtained the increasing of the process efficiency up to 5%.

Keywords: uranium, solvent extraction, process variable, statistical modelling

1. Introduction

Technology manufacturing sintered powder of uranium dioxide - UO_2 in Romania is similar to other factories abroad. The first phase is done processing ore until the uranium salt - sodium diuranate ($Na_2U_2O_7$), and the second phase are nuclear uranium purification with obtaining sintered. uranium dioxide (UO_2)[1].

In combustible obtain based of natural uranium, for nuclear-electric power-plants - CANDU, a obligatory technological operation is the purification of uranium until the product specificity for nuclear combustible. The optima process to purification, the only applied at industry scale, is liquid – liquid extraction, using like extractor a solution of tributyl – n – phosphate (TBP) in kerosene [2, 3]. The purification of uranium by extracting from aqueous phase in organic phase is realized by the selective transfer of $UO_2(NO_3)_2$ from aqueous phase in organic phase under the form of solvating complex with TBP, $UO_2(NO_3)_2 \cdot 2TBP$, during the others inorganic nitrates remain in aqueous phase Specialized literature reports numerous cases of TBP-based uranium extraction from nitric acid solutions [4].

It was found that the $UO_2 (NO_3)_2$ extracted in organic phase as solvation complex with TBP, $UO_2 (NO_3)_2 \cdot 2TBP$ has depressant action on impurities, which is even more powerful, as the degree of saturation of organic phase in uranium is approaching the limit.

The success of TBP solvent extraction compared to other processes for purification of uranium is due to:

1) TBP is highly selective for uranium, and provides excellent decontamination from most impurities.
2) TBP is relatively stable against degradation under conditions normally used to purify uranium. Simple washing techniques are available to remove solvent degradation products.
3) TBP/kerosene solutions have low vapour pressure and can be stored and handled without elaborating precautions against fires [5,6].

Third phase formation in nuclear solvent extraction system is observed at high metal and / or mineral acid loading of the organic phase. Under certain conditions, the organic phase splits into two layers, the light layer containing most of the diluent, little extractant and metal; and a heavy or third phase containing high concentration of extractant, metal and little diluent. The phenomenon of third phase formation is mainly caused by the limited solubility of the metal-ligand complex in the non-polar organic phase [7, 8, 9].

The general effect of the optimization consists in diminishing the uranium technological losses (by avoiding the third phase formation) and, as a result, in increasing the efficiency of this processing operation by 5 %.

The paper presents a statistical modeling of uranium purification by liquid-liquid extraction in terms of achieving optimum process parameters.

2. Experimental

Tri-butylphosphate used as an extractant was from FLUCKA , with purity 99%. The diluent used was the Kerosene from Acros Organics, which has a density of 790–800 kg /m^3 at 15 °C, its boiling point range is 200 − 250 °C, and aromatic content of max 0.2 % (v/v) Nitric acid was obtained from (MERCK, 65 %).

Organic extraction phases were prepared using 30 vol. % tri-n-butylphosphate in kerosene. Stock solutions of uranyl nitrate were prepared at constant nitric acid concentration by dissolution of known quantities of sodium diuranate ($Na_2U_2O_7$) obtained from a pilot plant of PUREX process.

The extraction was carried out in 250 mL separating funnel by stirring 2 min. different volumes (25 mL) of aqueous and organic phases (75 mL), corresponding an 1:3 aqueous – organic ratio. To make contact we use a IKA HS 501 digital shaker. The mixtures were separated after 6 min. by decantation. It is very important to note that no third phase or any precipitation was observed during the extraction process.

Uranium was determined in the aqueous phase by HPG γ –spectral method using an ORTEC multi-channel analyser with Ge detector for γ radiations (0-3 MeV). The concentration of nitric acid in the aqueous phase solutions was calculated using an potentiometer titrator. The amount of uranium extracted by the TBP was determined from the difference between the initial and final concentrations of uranium in aqueous solutions.

3. Results and discussion

To make modeling uranium purification by liquid-liquid extraction in terms of achieving optimum process parameters, it will use the method of planning experiments [10, 11], which allows obtaining significant and sufficient information from a small number of experiments.

The studied process factors are: the uranium content in aqueous phase (x1), the free acidity (x2) and, the number of extraction steps (x3), presented in Table 1.

TABLE 1. The factors used in the factorial model

Factors	code	Range $x_{jmin} \rightarrow x_{jmax}$	The exp. centre X_{jo}	Δx_j	Level	
					inf -	sup +
U content in aq. phase, g/l	x1	280→320	300	20	40	80
Free acidity, M	x2	2.8 → 3.2	3	0.2	2.8	3.2
No. of extr. steps	x3	6→10	8	2	6	10

A 2^3 fractional factorial calculus was used in order to develop the first order model with the interaction terms (x1, x2, x3).

The experiments were randomly performed in order to avoid a systematic error. Furthermore, it was performed 3 central reproductions (1^0, 2^0 3^0) for experimental error calculation, presented in Table 2.

The considered regression models for the selected factors are first order polynomial models that are obtained by variation analysis using Design Expert v.6 program.

TABLE 2. Value for extraction efficiency in the central point of the domain

y_k^0	y_1^0	y_2^0	y_3^0
η	98,75	97,63	99,54

The regression equation o expressed depending on the codified terms (-1/+1):

$$Y = 101{,}146 + 7{,}643 \cdot x_1 - 1{,}512 \cdot x_2 - 2{,}342 \cdot x_3 - 6{,}652 \cdot x_1^2 - 0{,}872 \cdot x_2^2 - 3{,}376 \cdot x_3^2 + 2{,}212 \cdot x_1 \cdot x_2 + 2{,}835 \cdot x_1 \cdot x_3 - 0{,}527 \cdot x_2 \cdot x_3 + 0{,}614 \cdot x_1 \cdot x_2 \cdot x_3 \quad (1)$$

Hence, after the elimination of the insignificant interactions, the following regression equations were obtained:

$$Y = 101{,}146 + 7{,}643 \cdot x_1 - 1{,}512 \cdot x_2 - 2{,}342 \cdot x_3 - 6{,}652 \cdot x_1^2 - 3{,}376 \cdot x_3^2 + 2{,}212 \cdot x_1 \cdot x_2 + 2{,}835 \cdot x_1 \cdot x_3 \quad (2)$$

The accuracy of mathematic model is tested through ANOVA variance of analysis and with Fisher's test. The value of the Fisher's test (F = 217) of the model emphasizes that this is adequate for the experimental data, existing a 4.32 % probability that this value to be a simple occurrence.

Were calculated partial derivatives of first order in relation to each variable. The best looking is (0,68; 0,70; -0,06) in the a-dimensional coordinated. Note that the optimal values for x1, x2 and x3 are included in the scope of permissible limits (-1, 1) fixed: X_1 = 313.6 gU/L , X_2 = 3.14 M HNO_3, X_3=8.

The models will be obtained based plot of two parameters, the other parameters remaining constant at 0 representing the scope of variation

For extraction yield (Y) will get three response surfaces characterized by the following mathematical models:

For x_1=0

$$Y = 101{,}146 - 1{,}512 \cdot x_2 - 2{,}342 \cdot x_3 - 3{,}376 \cdot x_3^2 \quad (3)$$

For x_2=0

$$Y = 101{,}146 + 7{,}643 \cdot x_1 - 2{,}342 \cdot x_3 - 6{,}652 \cdot x_1^2 - 3{,}376 \cdot x_3^2 + 2{,}835 \cdot x_1 \cdot x_3 \quad (4)$$

For x_3=0

$$Y = 101{,}146 + 7{,}643 \cdot x_1 - 1{,}512 \cdot x_2 - 6{,}652 \cdot x_1^2 + 2{,}212 \cdot x_1 \cdot x_2 \quad (5)$$

The recommended optimal parameters necessary to obtain extraction efficiencies over 96 % are as follows:

1) uranium content in aqueous phase 313.6 g U/L;
2) free aacidity of aqueous phase 1:3; steps number 8.

The graphic representations of the mathematical models are presented in figure 1-3.

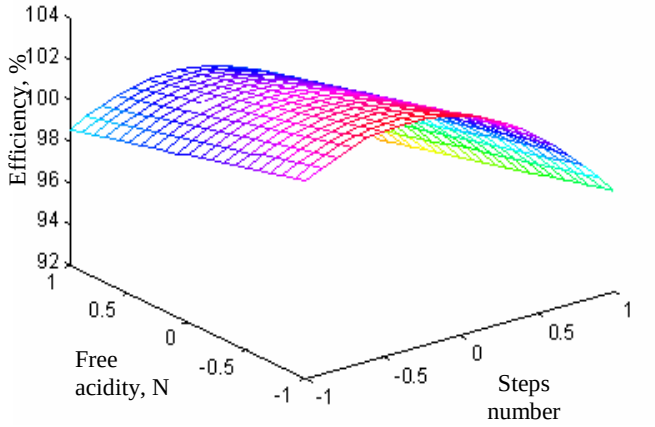

Figure 1. Effect of free acidity of aqueous phase and steps number of on the efficiency of extraction, when the content of uranium in aqueous phase is kept in focus

$$Y = 101{,}146 - 1{,}512 \cdot x_2 - 2{,}342 \cdot x_3 - 3{,}376 \cdot x_3^2$$

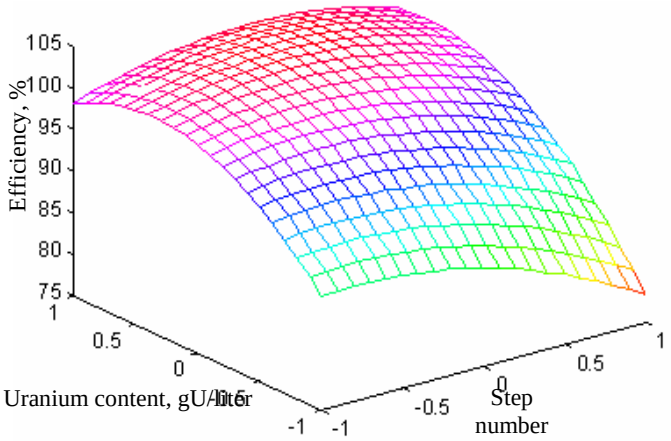

Figure 2. Effect of uranium content in aqueous phase and steps number on the efficiency of extraction when the free acidity is kept in focus

$$Y = 101{,}146 + 7{,}643 \cdot x_1 - 2{,}342 \cdot x_3 - 6{,}652 \cdot x_1^2 - 3{,}376 \cdot x_3^2 + 2{,}835 \cdot x_1 \cdot x_3$$

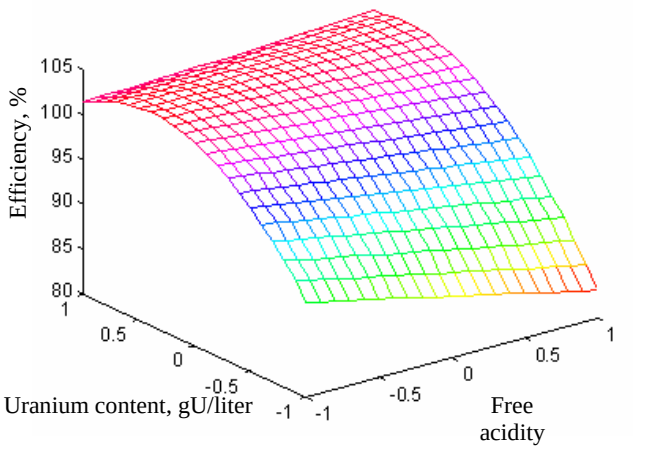

Figure 3. Effect of uranium content in aqueous phase and free acidity on the efficiency of extraction when the number of steps is kept in focus

$$Y = 101{,}146 + 7{,}643 \cdot x_1 - 1{,}512 \cdot x_2 - 6{,}652 \cdot x_1^2 + 2{,}212 \cdot x_1 \cdot x_2$$

4. Conclusions

The mathematical model obtained by the processing of experimental data describes the dependence of yield on technically and economically significant operational parameters.

The recommended optimal parameters necessary to obtain extraction efficiencies over 96 % are as follows:

1) uranium content in aqueous phase 313.6 g U/L;
2) free aacidity of aqueous phase 1:3,14;
3) steps number 8.

The proposed mathematical model is able to calculate the extraction efficiencies for uranium for any value of considered parameters (uranium content, aqueous - organic ratio, steps number, free acidity) only in the range of studied experimental values with a precision of 95%.

This paper emphasizes the major factors that influence the uranium extraction efficiency, namely uranium content, aqueous - organic ratio, steps number, free acidity in the studied experimental values range.

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