# Improvement and bench-testing of computer simulation of transient behavior in the PUREX process units of various function and structure

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## Introduction

Solvent extraction of actinides by diluted tributylphospahte (TBP) from nitrate media is the basis of modern reprocessing of nuclear power plant spent nuclear fuel (NPP SNF), as well as that of auxiliary nuclear material production (zirconium, hafnium, rare earths). The optimization of these processes aimed at decrease in the SNF reprocessing cost and ecological acceptability requires an adequate computer simulation model for calculation of steady state component distribution through the stages of each extraction unit as well as the model for calculating the transient regime for predicting the consequences of various alternatives of situation development, Results of these simulations make possible reducing the number of costly rig trials and pilot operations.

## Experimental and calculation methods

The analysis of published and newly obtained data on the influence of component concentration and temperature made possible to describe the equilibrium extraction of $HNO_3$ and hexa- and tetravalent actinides as well as Zr and $HTcO_4$ from nitric acid solutions into 30% TBP in the Purex process conditions in different extraction units except the kinetics of ox-red reactions because of uncertainty of induction period. Distribution coefficients are calculated using the improved Rozen's model which is based on the semi-empirical extraction equations for equilibrium constants (***K***) of component extraction

$\ln K = a_0 - a_1 I^{1/2} + a_2 I - a_3 I^{3/2} + a_4 I^2$ , where ***I*** is the ionic strength.

A computer code (**Fig. 1**) based on this model has been developed for simulation of the head and backwashing units of various PUREX process options for high burn-up spent fuel from NPP with WWER (PWR) water-cooled reactors. Calculations are based on equation of non-stationary material balance:

$$W_{x,i}\frac{dX_{i,j}}{dt} + W_{y,i}\frac{dY_{i,j}}{dt} = L_{i-1}X_{i-1}(t - t^{x}_{i-1}) + V_{i+1}Y_{i+1,j}(t - t^{y}_{i+1}) - L_i X_{i,j}(t) - V_i Y_{i,j}(t)$$

Using these models, we performed comparative calculations of the beyond design-basis regime in similar flowsheets of the head contactors of RT-1, "Breakthrough" Project (Experimental Complex constructed on the site of the Siberian Chemical Combine) and Pilot Demonstration complex (PDC) at Zheleznogorsk MCC (**Fig. 2a, b, c**). In the "Breakthrough" and PDC flowsheet the process is performed in centrifugal contactors with the delay of <1 min per step, while in the rig corresponding to the RT-1 flowsheet it is performed in mixer–settlers with the total delay of ~5 min per step. Trials for all flow-sheets were performed in the continuous mode of the Purex process, involving extraction of actinides, two-zone scrubbing of the solvent product in the same unit, reductive or complexing stripping of Pu, back extraction of U, and carbonate regeneration of the solvent. The extraction-scrubbing unit **b** differs from **a** in Pu(IV) and $HNO_3$ concentration in the feed, while unit **c** is divided into separate extraction and scrubbing blocks and is characterized by lower acidity in the feed and raffinate as well as by Zr co-extraction with Cr(VI) providing precipitation-free evaporation of the raffinate.

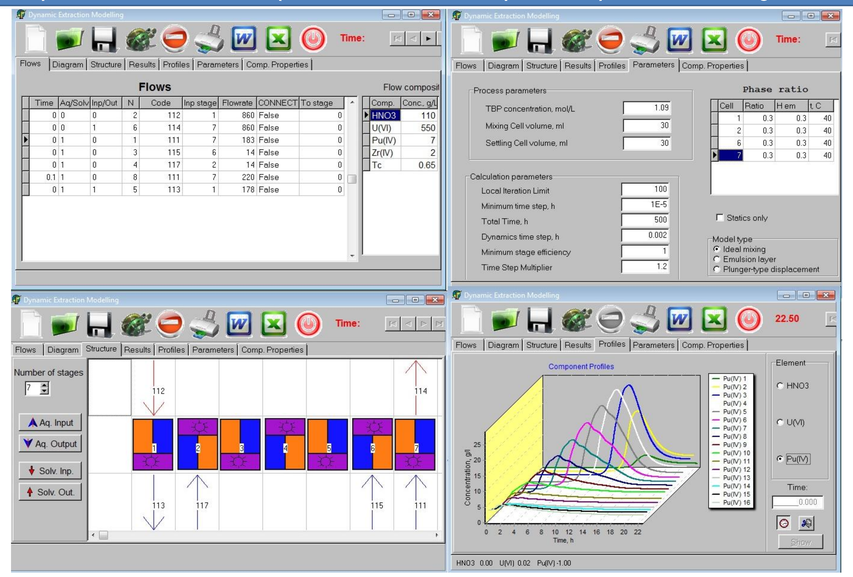


Figure 1. Interface of the dynamic model.

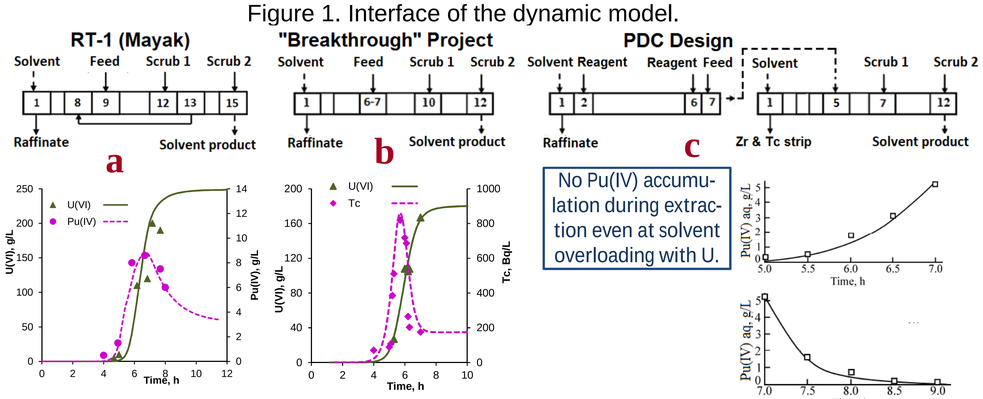


Figure 2. Experimental (points) and calculated (lines) concentrations of fuel components in the 3rd stage of the head extraction unit (a, b) and complementary to scrubbing unit (c) in the progress of the beyond-design-basis regime.

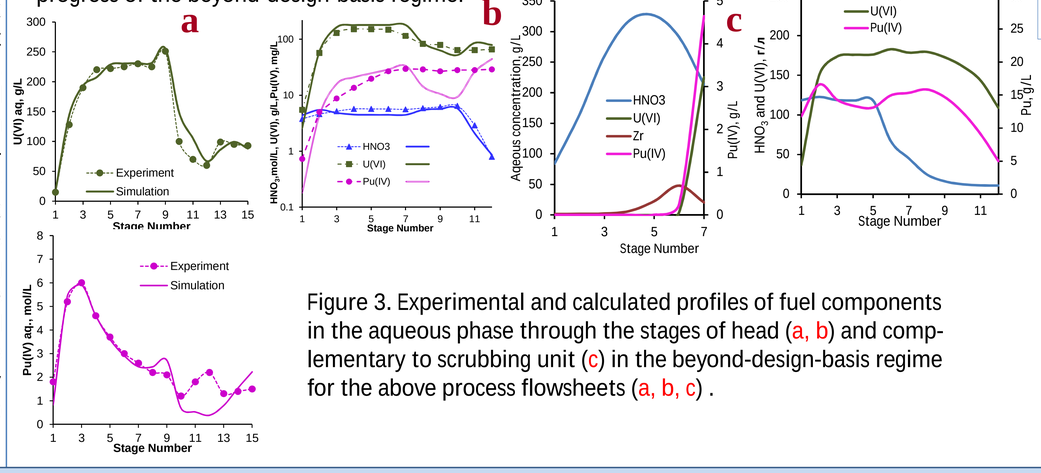


Figure 3. Experimental and calculated profiles of fuel components in the aqueous phase through the stages of head (a, b) and complementary to scrubbing unit (c) in the beyond-design-basis regime for the above process flowsheets (a, b, c) .

## Results and discussion

**Fig. 2a** and **3a** show that the maximum Pu(IV) accumulation has been observed in the 3rd stage of the head extraction-scrubbing unit after 30 one stage volume exchanges and is triple to the feed Pu concentration at the 3% of theoretical U&Pu solvent overloading and typical ~3 mol/L $HNO_3$ in the raffinate. Zr and Tc accumulation has occurred in the same way (**Fig. 2b**). If extraction and scrubbing units are separated (**Fig. 2c**) no Pu accumulation has taken place in the extraction unit, while the maximum Pu accumulation has been observed in the third stage of the extraction zone complementary to the scrubbing zone which also serves for Zr stripping (**Fig. 3c**). It is convenient for Pu neutron detection in the absence of Am and Cm dropped to the HL raffinate.

A separate rig trial has shown that the Pu accumulation in the uranium-free zone does not occur at higher acidity of the aqueous phase (> 4.2 mol/L $HNO_3$) and higher process temperature (so called IMPUREX process) because of Pu(IV) co-extraction with U(VI) (**Fig. 3b**).

The simulated distribution of the extractable fuel components is in good agreement with results of the rig trials both for mixer-settlers and centrifugal contactors, considering the ideal mixing in a settling chamber for entering the beyond-design-basis regime while the return from this regime to the normal one is better described by plug-flow model.

The effect of Zr co-extraction with the Cr(VI) anion fed as a separate small stream resulting in complete recovery of Zr in the extraction zone is demonstrated in **Fig. 4**. It can be seen that stopping this stream leads to a reversible decrease in the Zr recovery and to a sharp increase in the entrainment of aqueous microemulsion containing $^{137}Cs$. This fact confirms the assumption that the Zr extraction in the cascade in the presence of U and at increased $HNO_3$ concentration has micellar character without Cr(VI). However, this effect couldn't be simulated yet.

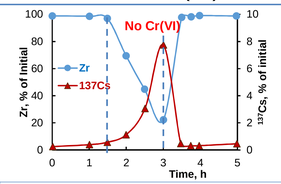


Figure 4. Relative content of $^{137}Cs$ and Zr in the solvent product of the head contactor of EDC as a function of the time from the start of the rig trial.

The rig trials on beyond-design-basis regime in uranium backwashing unit have indicated on the applicability of the above model (**Fig. 5a, b**).

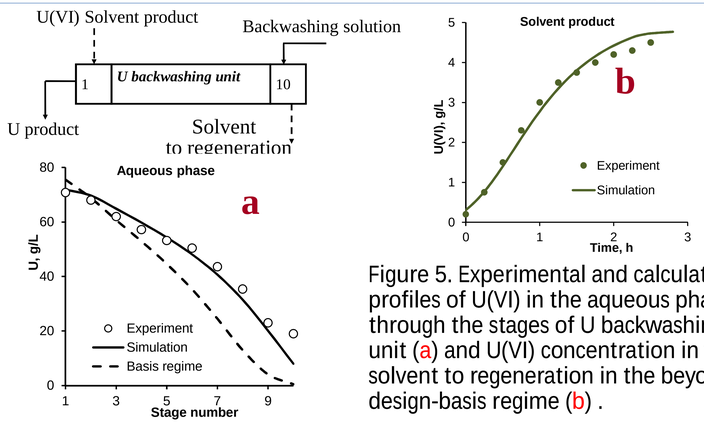


Figure 5. Experimental and calculated profiles of U(VI) in the aqueous phase through the stages of U backwashing unit (a) and U(VI) concentration in the solvent to regeneration in the beyond-design-basis regime (b) .

## References

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Software package "Dynamics" is registered under certificate RU No 2014614164, Russian Soft. Bul. N 5, 2014