Modeling of Extract Uranium, Plutonium and Neptunium Purification Process from Fission Products in Liquid Chromatography Columns

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Chromatography is one of the highly effective methods for mixture separation. It has been and is widely used in different industrial fields, from food to the nuclear sector. Relevant performance of this method is in any case associated to high costs and, often, the chromatographic separation of complex mixtures is one of the most expensive steps in the entire production process. The development of an adequate mathematical model of the chromatographic column will allow designing a control system to optimize the plant operation modes, and will help to avoid errors during design, installation and commissioning. Using a computer simulation of this technology will allow passing from the time-consuming, expensive and dangerous natural experiments to numerical experiments. The application of the equilibrium-dispersive chromatography model for the design of the extract uranium, plutonium and neptunium purification process from fission products in coupled liquid chromatography columns were investigated in this paper. The model was included in the complex's composition of closed nuclear fuel cycle.

1. Introduction

The efficiency of the radiochemical industrial apparatus depends on a lot of parameters, such as: geometry of the apparatus, temperature, pressure, concentration of substances. An adequate mathematical model of the process or apparatus allows to determine the most significant factors of the process and develop an accurate control system for this process. The application of an adequate model makes it possible to select the most effective control algorithm for the developed installation, to predict emergency situations etc. This approach can significantly reduce or avoid natural modeling cost.

Therefore, mathematical modeling is one of the important stages in the synthesis of control systems and optimization of industrial systems. The development of a extract uranium, plutonium and neptunium purification process from fission products model will significantly improve the efficiency of the paired columns.

Extractive chromatography is a known method for the separation of complex mixtures in the nuclear industry. To implement this approach, the chromatographic column is filled with a carrier (silica, alumina) - substance which is indifferent to the target mixture and to the applied solvent. The carrier retains liquid on its surface, forming a stationary phase (Figure 1).

Chromatography solution consisting of several components, supplied to the column until the concentration of output target component does not exceed a predetermined threshold value. After that moment, the washing process begins.

Redistribution of mixture substances between two immiscible liquid phases is performed in the chromatographic column. To obtain a clear separation is necessary that the components do not interact with the carrier, and that their distribution ratios differed from each other. Only observance of these conditions allows obtaining separate zones of pure substances.
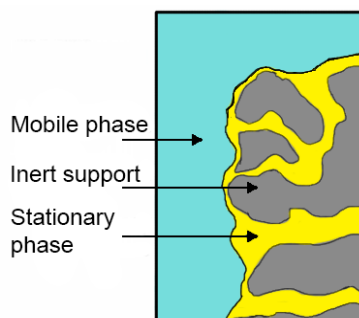
Figure 1: The surface of porous silica granule.

2. Mathematical model of the separation process

The equilibrium-dispersive chromatography model by Schmidt-Traub (2015) has been selected to simulate the liquid chromatography columns. This model is based on the material balance and mass transfer rate.

For an adequate simulation of the mixture separation process, mathematical model must take into account the basic processes occurring in the column, such as the mobile phase motion dynamics, mass transfer kinetics and adsorption processes. For optimization of separation process by using a mathematical model, the model should take into account not only the conditions for the physical and chemical processes, but also the design of the column (column height, cross-sectional area), the composition of the feed solution, the composition of the organic phase and equipment operation modes.

Equilibrium-dispersive model (Schmidt-Traub, 2015) was used for a description of these processes:

$$\frac{\partial c_i}{\partial t} + F\frac{\partial q_i}{\partial t} + u\frac{\partial c_i}{\partial z} = D\frac{\partial^2 c_i}{\partial t^2} \tag{1}$$

where q and c are the stationary and the mobile phase concentrations of the compound, respectively, t is the time, z the distance along the column, u the linear velocity, and $F = (1−ε)/ε$ is the phase ratio, with $ε$ the total column porosity of the column. q is related to c through the isotherm equation. The BET isotherm, described by Horvátha (2010), was used in this work. This isotherm may be represented by Eq(2).

$$q = \frac{qs \cdot bs \cdot c}{(1 - bl \cdot c)(1 - bl \cdot c + bs \cdot c)} \tag{2}$$

where qs is the saturation capacity of the stationary phase, q and c are the concentrations of the solute in the stationary phases, bs and bl are equilibrium constants of adsorption on the surface of the stationary phase and on the absorbed layer of solutes.

Pressure sensors will produce evaluation of the substances concentration in the column. It is planned to use sensors produced by «Manotom», Russian Federation, company for pressure measurement application. In the simulation of separation process mathematical modeling of pressure sensors was carried out. For calculation of pressure in the column, it was decided to apply the Eq(3), which should give a sufficient calculation accuracy for use in creating chromatography column ACS.

$$P = \overline{\rho_c} \cdot g \cdot h \tag{3}$$

where g – acceleration of gravity; h – column height; $\overline{\rho_c}$ – the average density of substance in the column.

The average density of the substance in the column can be calculated by the Eq(4) where $\overline{\rho_c}$ the average density in the simulated material layer, N_l number of layers.

$$\overline{\rho_c} = \sum_{i=1}^{N_l} \frac{\overline{\rho_l}}{N_l} \tag{4}$$

The average density of substances in the one column layer is defined by the Eq(5):

$$\overline{\rho_l} = \sum_{i=1}^{k} \frac{V_i}{V} \cdot \rho_i \tag{5}$$

where V_i – volume of element i in layer; V – volume of layer; ρ_i – density of element i; k – number of element.

3. Results and discussion

Model adjustment was performed experimentally. Searching of the model parameters was carried out by minimizing standard deviation of the simulation results from the experimental data. To adjust the model butylbenzene separation experiment data described in Gritti et al. (2002) was used. Comparison of experimental and simulated data is shown in Figure 2. The correlation coefficient of the experimental data with the results of the simulation is 0.99 %, which allows expressing the adequacy of the proposed model.

Figure 3 shows the dependence of the pressure on the outlet of the column against time. Pressure is calculated according to Eq(3). To simplify the calculation and visualization, pressure values in initial time are considered as zero.

The adjusted model was used to conduct numerical experiments of butylbenzene separation. These experiments are described in Gritti et al. (2002). Graphs of the butylbenzene concentration at the column outlet are shown in Figure 4a and Figure 4b.

Comparison of simulation data presented in Figures 4a and 4b, with the experimental data shows that the developed model has sufficient accuracy, despite the assumptions made. The correlation between an experimental data and simulated data is 0.989 and 0.991. Relative error peak is 1.07 % for the experiment shown in the Figure 4a and 2.213 % for experiment shown in the Figure 4b.

This model is used to develop an optimal control algorithm for automatic control system of coupled chromatographic columns, presented in Figure 5.
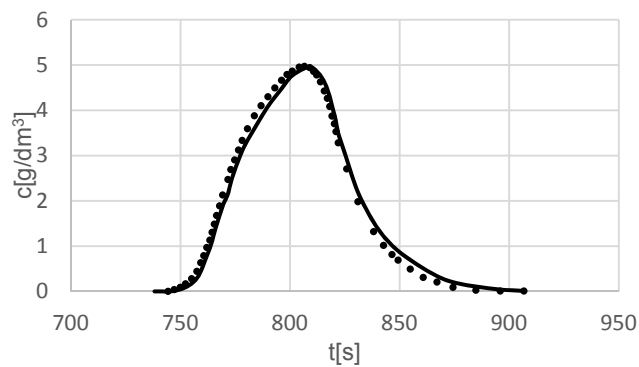

Figure 2: Comparison between an experimental band profile (dots) and the calculated profile (solid line). $C_0 = 6.89$ g/cm^3; $t_p = 42$ s; $L_f = 2.88$ %
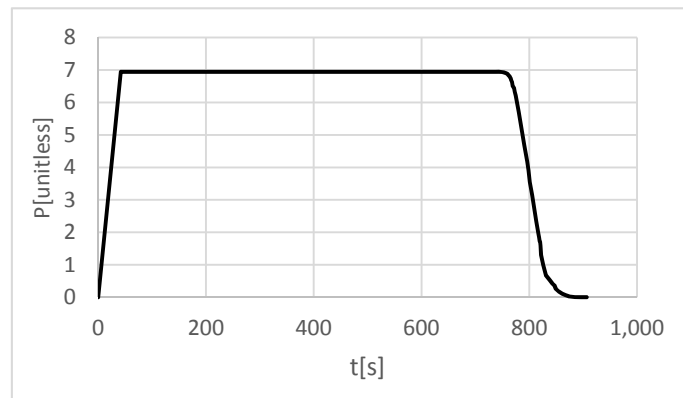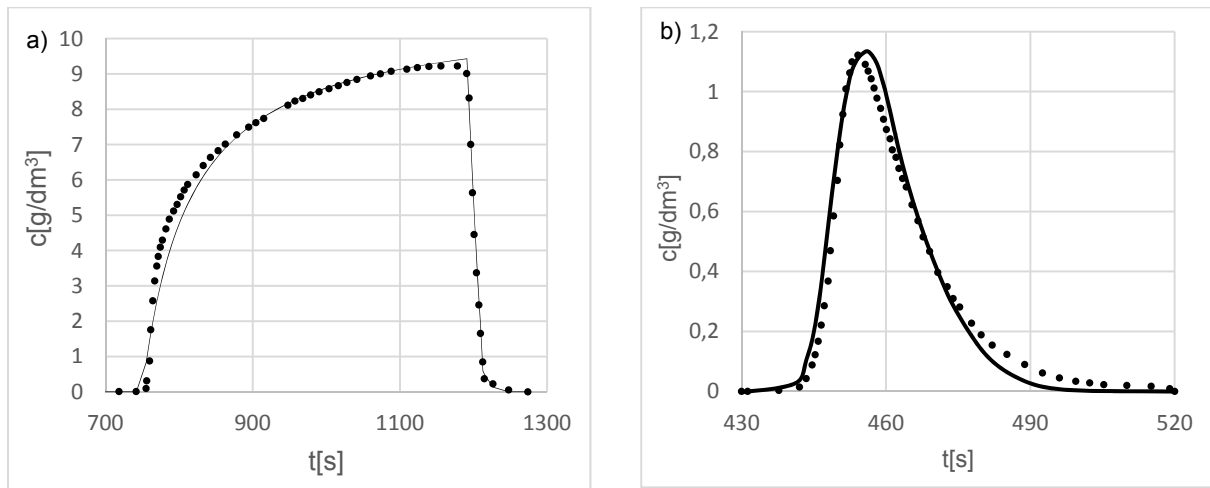

Figure 3: Calculated pressure profile

Figure 4: Comparison between an experimental band profile (dots) and the calculated profile (solid line). (a) $C_0 = 9.56$ g/cm^3; $t_p = 360$ s; $L_f = 34.3$ %; $N = 1,600$; (b) $C_0 = 4.70$ g/cm^3; $t_p = 4.8$ s; $L_f = 0.12$ %; $N = 1,600$.
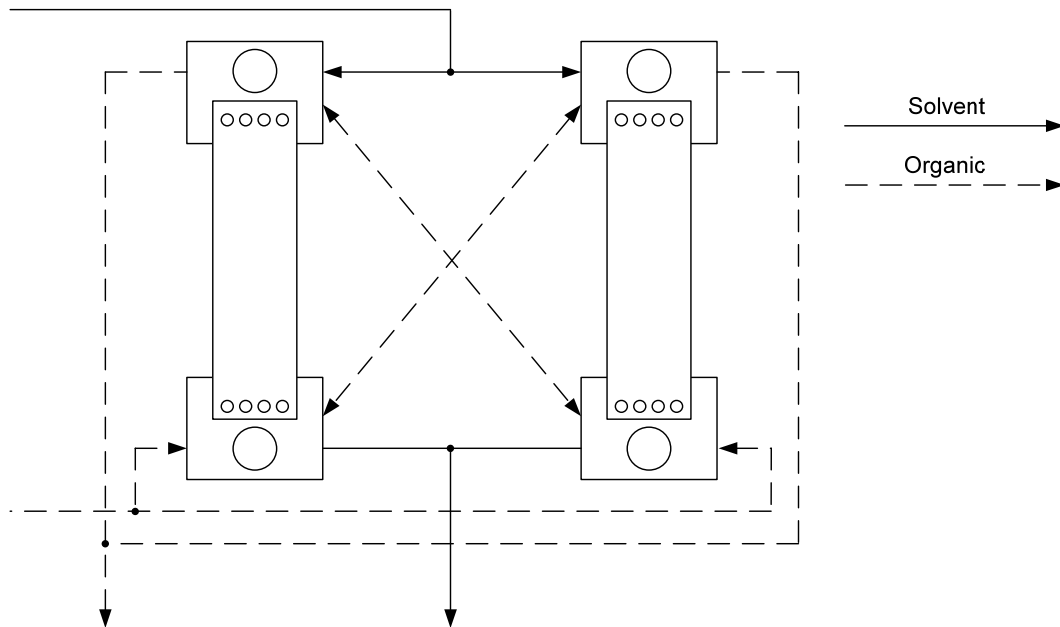

Figure 5: Scheme of extract uranium, plutonium and neptunium purification unit

These chromatographic columns are connected to each other by the system of valves. Control over the current state of the process is performed by using pressure sensors, which determine the phase boundary. These sensors are installed in separation chamber of each column, and are connected to sensor control block.

Extract and purification solution supply occurs by pumps. One of the pumps is placed in organic line, another in solvent line. In this unit, we can provide cyclical extract purification process. The main steps of this process are shown in Figure 6.

A resulting model is implemented in SimSAR software, taking into account the results obtained in the Goryunov et al. (2011). Another example of model implementation in SimSAR showed in Ochoa Bique et al. (2016). Figure 7 shows a model general form.

Results of simulation are showed in Figure 8. This Figure presents the trends of components mass fractions in the columns outlet depending on time.
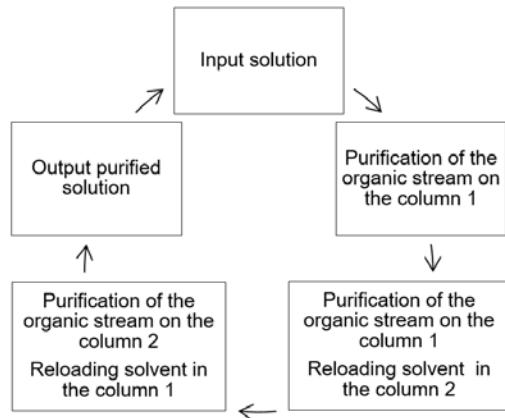
Figure 6: Scheme of extract uranium, plutonium and neptunium purification unit
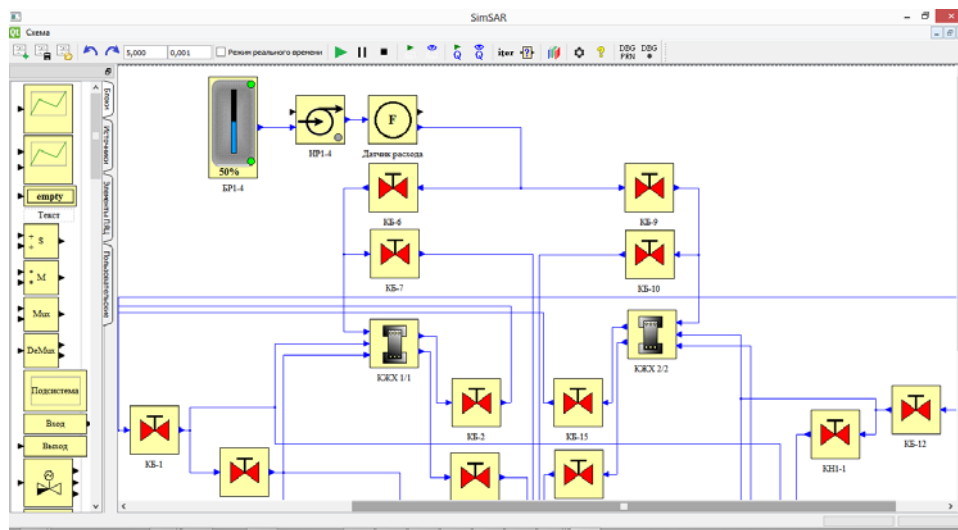

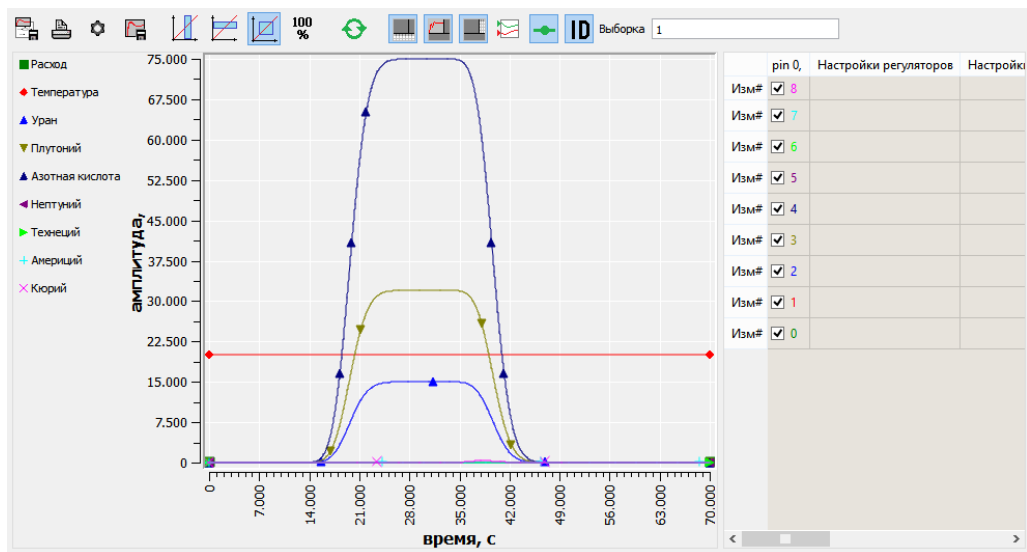Figure 7: A general form of liquid chromatography column in SimSAR software

Figure 8: Components mass fraction over the time

Implementation of the various operating modes using the developed mathematical model would allow finding the optimal control algorithm. Application of this optimal control algorithm in the plants would increase the production efficiency of purification process.

4. Conclusions

According to the obtained results, an equilibrium-dispersive model can be used for mathematical description of extract uranium, plutonium and neptunium purification process from fission products in coupled liquid chromatography columns. The application of this model will allow to perform an initial analysis of the purification unit, shown in the Figure 5, and describe it as a technological control object. A mathematical description of the control object will be used for optimization of extract uranium, plutonium and neptunium purification process from fission products control algorithm and for the synthesis of the automatic control system.
Further, it is planned to test model against real data.

Acknowledgments

References

Chursin, Y.A., Gozhimov, A.I., Liventsov, S.N., Shmidt, O.V., 2016, Mathematical model of separation of transplutonium and rare earth elements by ion-exchange chromatography method with complexation during elution, Chemical Engineering Transactions, 52, 199-204.

Gritti F., Piatkowski W., Guiochon G., 2002, Comparison of the adsorption equilibrium of a few low-molecular mass compounds on a monolithic and a packed column in reversed-phase liquid chromatography, Journal of Chromatography A, 978 (2002) 81–107.

Goryunov, A.G., Liventsov, S.N., Rogoznyi, D.G., Chursin, Yu. A., 2011, A dynamic model of a multicomponent nonequilibrium extraction process in a pulsating column, Radiochemistry, 53, 278-283.

Horváth K. Jacob N. Fairchild, Kaczmarski K., Guiochon G., 2010, Martin-Synge algorithm for the solution of equilibrium-dispersive model of liquid chromatography, Journal of Chromatography A, 1217 (2010), 8127–8135.

Ochoa Bique, A., Gozhimov, A., Chursin, Y., Manenti, F., Schmidt, O., 2016, Modeling of uranyl nitrate hexahydrate crystal growth in linear crystallizer for nano cleaning using simsar software, Key Engineering Materials, 683, 563-568.

Schmidt-Traub H., Schulte M., Seidel-Morgenstern A., 2012, 2005 Preparative Chromatography, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 485-566. ISBN: 978-3-527-32898-7978-3-527-32898-7.