PHYSICAL–MATHEMATICAL MODEL OF URANIUM CONCENTRATE EXTRACTIVE RECYCLING IN THE CASCADE OF COUNTERCURRENT COLUMNS

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Mathematical model of extraction recycling uranium concentrate in cascade of countercurrent column cascade has been presented. The model describes nonequilibrium interconnected physical-chemical processes subject to a large number of components (uranium, nitric acid, iron, silicon, molybdenum, calcium etc.). On the basis of numerical implementation of mathematical model the software was developed and program-technical complex for increasing the efficiency and optimization of operating the extractive columns cascade and achieving the required technological parameters of the output solutions under changing characteristics of the initial solution was developed.

At present mathematical model approaches find wide application for optimization of chemical-engineering processes [1–4]. The aim of the given paper is the development of mathematical model and software for calculation of recycling uranium concentrated solutions in the cascade of countercurrent extractive columns, increase of efficiency of cascade functioning and achieve of the required technological parameters of the output solutions at changing characteristics of uranium concentrate.

In the given diagram uranium is extracted from feeding solution into organic phase (30 % tributyl phosphate is the diluent) in extractive column and impurities are partially introduced with water-tail solution (Fig. 1). Flow from the scrub column outlet is added into feeding solution. Organic phase enriched with uranium is supplied into scrub column where the subacid washing of extract is carried out for increasing uranium clarification. In re-extraction column uranium is extracted with water solution of nitric acid. In the latter column the extractant is reclaimed with sodium solution for its properties reduction. The extractant escaping the cascade is accumulated in idle capacity and then enters again to extraction column.

Wide use of column devices (pulse columns, Fig. 2) is stipulated by a number of their advantages: simplicity of arrangement; performance reliability; high capacity; absence of requirements for the presence of suspensions in solutions; absence of inner devices demanding check-up and repair; pulsing generation with outer pulser that allows securing hermetization of the device active volume; minor phase contact time.
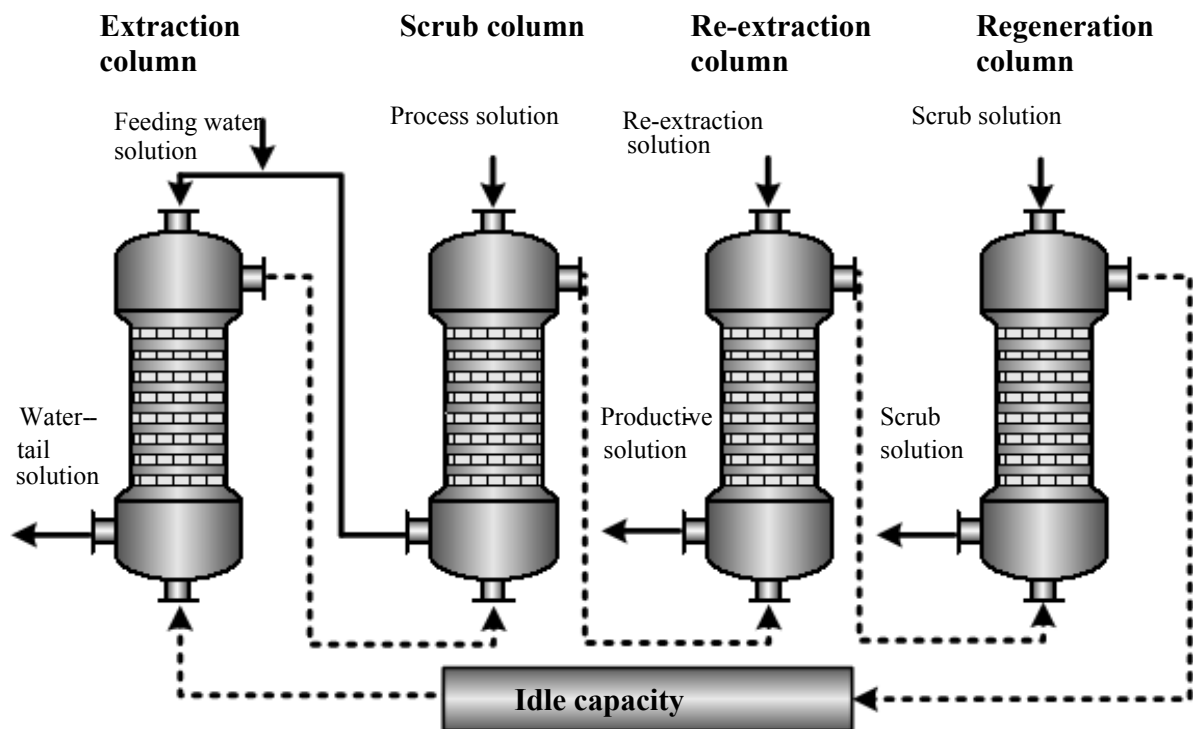

Fig. 1. *Flowsheet of extraction column cascade. Phase flux:* ••••➤ *– organic;* ➡ *– liquid*
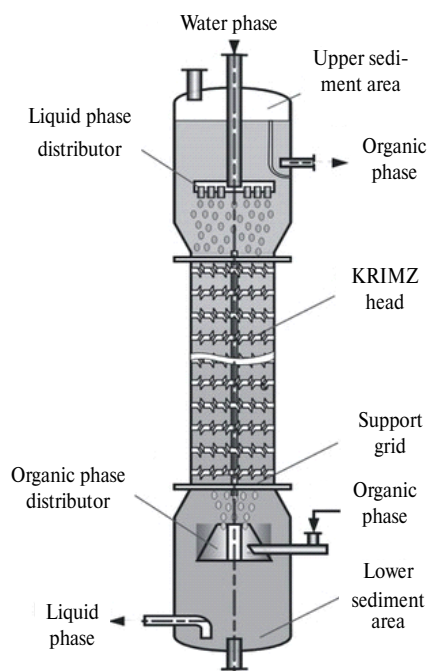
Fig. 2. *Pulse column*

Low contact time of phases results in the fact that extraction system «solution – extractant» turns out to be nonequilibrium along the whole column height. It causes great difficulties both in experimental laboratory modeling of the processes and in their description by mathematical models. Besides, the solutions supplied to the input of extraction block may differ considerably in their composition. Adequate mathematical model of extraction process allows solving many tasks in controlling technological process, forecasting optimal regimes of cascade operation depending on consumptions and compositions of input flows, supporting nuclear safety.

At the present time two main approaches are used for developing mathematical models of extraction process [1, 2]. The first approach is based on formal propagation of mixer-settler model to extraction column. The advantage of such approach is its simplicity. The column is divided into a set of stages and it is supposed that at each stage the equilibrium between liquid and organic phases is achieved. Such assumptions are rather oversimplified especially for multicomponent systems as the extractable components may have different stage height.

The approach based on construction of continual mathematical model in which component concentration changes in both phases continuously as column height function seems to be more perspective. Continual model is formed in the form of differential equations system in partial derivatives. Mass transfer through the interphase boundary is considered as the process consisting of three stages: delivery of allocated component and other components entering into the complex compound to the interphase boundary; cross of interphase boundary; removal of complex compound from the interphase boundary to the depth of solution. Simultaneously other products generated as a result of chemical interactions are diffused to the depth of solution. All stages may be complicated by different chemical reactions both in solution vo-

lume and at interphase boundary. Any stage or chemical reaction observed at mass transfer may turn out to be determinative for the rate of the whole process. In the given model describing noneqilibrium extraction process in the column the mathematical model based on diffusive kinetics when mass transfer rate is determined only by diffusion velocity to the interphase boundary and from it is used [5]. In contrast to the mixture-settler model in which the equilibrium at all components between the phases is achieved at each stage, in the given model in each minor element of the column the system «water solution – extractant» remains nonequilibrium.

The model includes the description of functioning pulse columns cascade subject to stray volume. It is supposed that in stray volumes solution component concentration does not change. Mass transfer between liquid and organic phases occurs in extraction column therefore, the highest value in developing mathematical model of cascade functioning has the model of nonequilibrium extraction process in the column

Mathematical model of pulse column includes the description of the following processes of mass transfer: convection mass transfer with a flow of liquid (organic) phase along the column, longitudinal phase mixture, mass exchange between liquid and organic phases. The behavior of three main components (nitric acid, uranyl and uranium) and impurities (iron, silicon, calcium, thorium, sulfur, sodium, carbonate and other), altogether N components is described in the model. The dependence of elasticity and density of solid phase on component concentration and temperature is taken into consideration. Liquid and organic phases are considered to be incompressible. The parameters of the system may change along the column height and in the course of time but remain constant in column arbitrary cross-section.

Differential equation system subject to nonlinear algebraic equations of extraction isotherms simultaneously with initial and boundary conditions describing the operation of the cascade of countercurrent extraction columns in unsteady state has the form:

$$\frac{\partial(x^i \Omega)}{\partial t} = \frac{\partial(v_B x^i \Omega)}{\partial Z} + \frac{\partial}{\partial Z} D_{np,B} \frac{\partial(x^i \Omega)}{\partial Z} - j^i;$$

$$\frac{\partial(y^i(1-\Omega))}{\partial t} =$$

$$= \frac{\partial(v_O y^i(1-\Omega))}{\partial Z} + \frac{\partial}{\partial Z} D_{np,O} \frac{\partial(y^i(1-\Omega))}{\partial Z} + j^i,$$

where x^i (y^i) is the concentration of i component in liquid (organic) phase; v_B (v_O) is the rate of liquid (organic) phase motion; WW is the liquid phase delay; $D_{np,B}$ ($D_{np,O}$) is the coefficient of longitudinal mixture of liquid (organic) phase; Z is the column height coordinate; j^i is the density of the flow of i component from liquid into organic phase. Density of i component flow between liquid and organic phases is determined by the expression:

$$j^i = k_x(x^i - x_p^i) = k_y(y_p^j - y^j),$$

$$k_x = \frac{D_{x,B}}{l_B} \cdot s_{y\partial}, \quad k_y = \frac{D_{y,O}}{l_O} \cdot s_{y\partial},$$

where k_x (k_y) is the coefficient of mass transfer rate in liquid (organic) phase; $D_{x,B}$ $(D_{y,O})$ is the diffusion coefficient for liquid (organic) phase; l_B (l_O) is the thickness of diffuse layer in liquid (organic) phase; s_{y0} is the specific area of interphase boundary surface. Extraction isotherms in general view are written in the form of equations:

$$f^{i'}(x_p^i, y_p^i, T) = 0; \quad (i', i = 1...N),$$

where x_p^i (y_p^i) is the equilibrium value of i component concentration in liquid (organic) phase; T is the temperature. i component concentration at the output of stray volume:

$$x_{out}^i(t) = x_{in}^i(t - \tau); \quad \tau = V/Q,$$

$$y_{out}^i(t) = y_{in}^i(t - \tau),$$

where x_{in}^i (y_{in}^i) and x_{out}^i (y_{out}^i) are the input and output concentrations of i component in liquid (organic) phase; τ and V are the delay time and volume; Q is the flow of phase passing through the idle capacity per unit time.

On the bases of numerical implementation of mathematical model the software was developed and program-technical complex was created for computing extraction cascade functioning to determine uranium and impurities propagation in cascade devices, their concentrations in output flows and these values dependence on parameters of cascade operation, consumptions and compositions of output flows. The software was developed in Borland C++ Builder 5 and represents a multithreaded, 32-bite, MDI application of Windows'98-XP. The mode of the main operating window of the program is presented in Fig. 3.

The software was applied for determining the influence of various factors on fulfillment of requirements made to concentrations of components in water-tail and productive solutions. Calculations were carried out for real geometrical sizes of a pieces of equipment, flows of liquid and organic phases, initial concentrations of various components. Adequacy of mathematical model was checked by comparing calculation results with experimental data characterizing column cascade operation.

The most important moment in cascade operation is uranium (VI) concentration in water-tail and productive solutions. It is seen from Fig. 4 that the time of the transient for re-extraction column amounts to 19 h from the beginning of cascade operation and after that the value of uranium concentration has not practically changed and amounts to 84 g/l. Decrease of re-extraction solution consumption by 20 % results in the fact that a part of uranium is not re-extracted and removed with organic phase flow. As a result, uranium is accumulated in regeneration column and idle capacity. The organic phase containing uranium enters from idle capacity to the extraction column where it partially transfers into liquid phase. As a result uranium (VI) concentration in water-tail solution (Fig. 5) increases beyond the values accepted by standards. The increase of feeding solution consumption results in the fact that organic phase is saturated with uranium with the result that a part of it is not extracted from liquid phase and a part of it is removed from the column in water-tail solution (Fig. 6). Increase of nitric acid concentration in feeding solution up to 130 g/l results in the
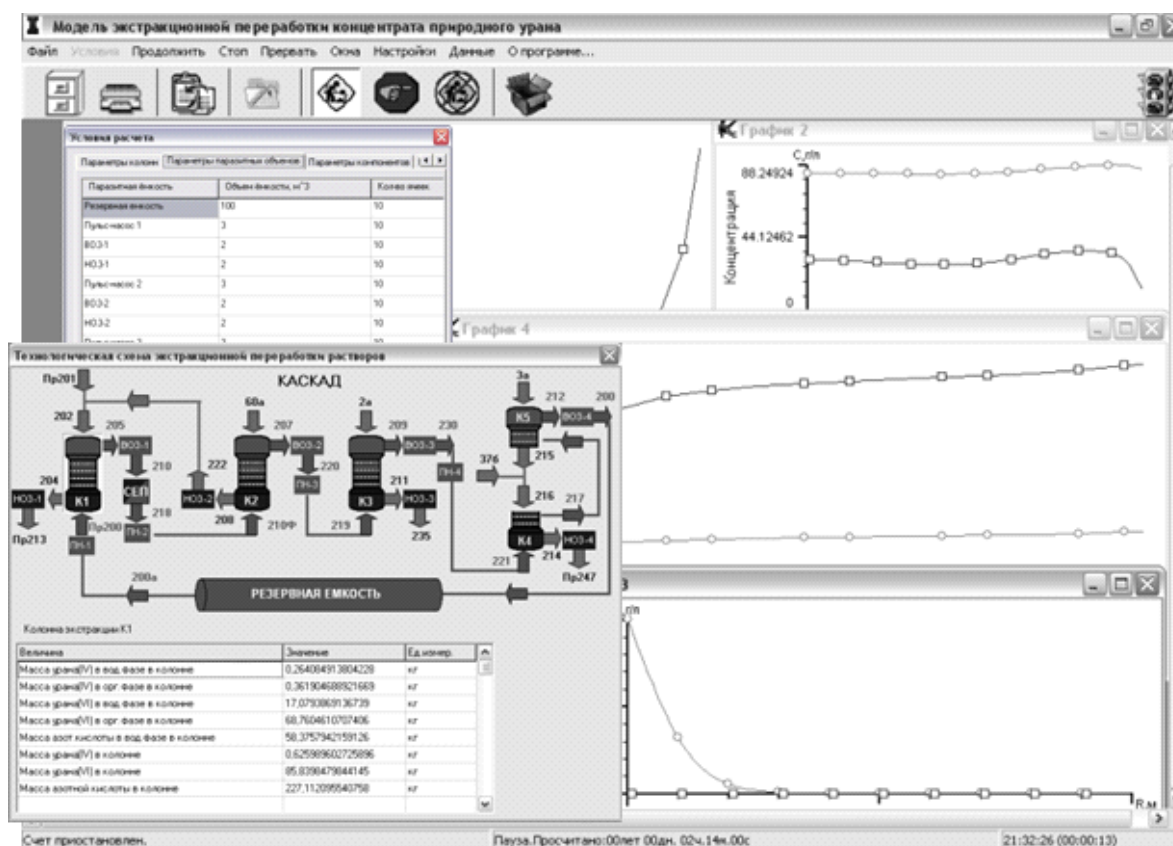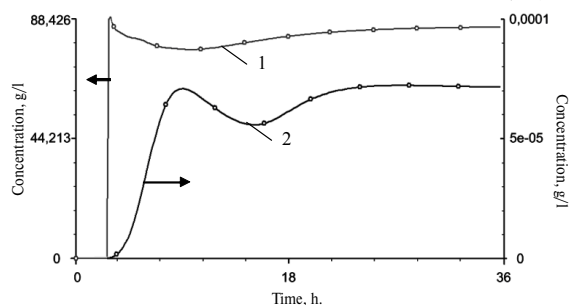

Fig. 3. *Main operating window of the software*

fact that uranium (VI) and uranium (IV) are not extracted rather well from liquid phase into organic one that results in their accumulation in extraction column and increase of concentrations in water-tail solution (Fig. 7).

Fig. 4. *Time dependence of uranium (VI) concentration in the base case in solutions: 1) productive and 2) water-tail one*
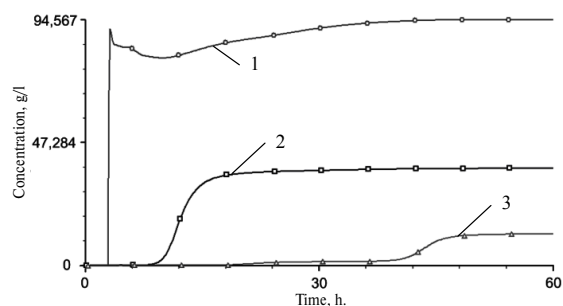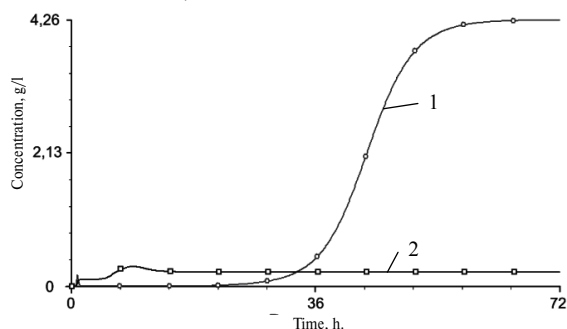

Fig. 5. *Time dependence of uranium (VI) concentration in: 1) productive, 2) scrub and 3) water-tail solutions at decreasi006Eg re-extraction solution consumption by 20 % in comparison with the base case*
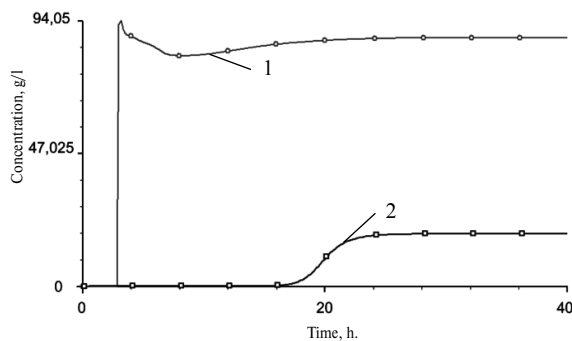
Fig. 6. *Time dependence of uranium (VI) concentration in 1) productive and 2) water-tail solutions at increasing feeding solution consumption of the base case by 15 %*

On the basis of the carried out experiments the conclusion was made that the most optimal parameters of extraction operation are the following values of the

initial concentrations of component: uranium (VI) is 300 g/l, HNO_3 is 120 g/l, solution consumption: feeding one is 2,8 m^3/h, the scrub solution is 1 m^3/h, re-extraction one is 0,5 m^3/h.

Fig. 7. *Time dependence of: 1) uranium (VI) and 2) uranium (IV) concentrations in water-tail solution at increasing nitric acid concentration in feeding solution by 10 % in comparison with the base case*

Conclusion

1. Physical-chemical processes occurring in the extraction device were analyzed. On the basis of this analysis the physical-mathematical model of extraction recycling uranium concentrate in countercurrent column cascade was developed.

2. With the help of separation method into physical processes the numerical implementation of physical-mathematical model was developed. On the basis of model numerical implementation the problem-oriented software for modeling extraction recycling uranium concentrate in countercurrent column cascade was created.

3. On the basis of test computation the verification and identification of mathematical model and software was carried out. The comparison of modeling results with experimental data shows the adequacy of the developed mathematical model.

4. With the help of the developed software the operation of extraction column cascade at different modes were calculated. The influence of liquid and organic phase consumption, nitric acid concentration on cascade operation efficiency was determined.

5. The created software may be used for increasing efficiency and optimization of operation of extraction column cascade, achieving the required technological parameters of the input solutions at changing characteristics of the initial solution.

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