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Extraction Chromatographic Separation of Rare-Earth Metals in a Cascade of Centrifugal Extractors

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Abstract—Liquid–liquid chromatographic processes, in particular, separation of rare-earth metals, were proposed to be performed in a cascade of centrifugal mixer–settler extractors. Various modes of extraction chromatographic processes of rare-earth metal separation were theoretically analyzed.

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An important problem of today is to develop new, highly efficient technologies for producing rare-earth metals and improve the existing ones, which are already used in industry. Liquid extraction is widely used both in separation of rare-earth metals (as well as radioactive elements and nonferrous and noble metals) from leaching solutions of mineral and secondary raw materials, and in subsequent processes of separation of components and their fine cleaning [1–7]. Note that new selective extractants are now intensely searched for [8–11], whereas the process (equipment and operations) design of extraction separation of rare-earth metals receives much less attention.

Extraction in hydrometallurgy is typically carried out in cascades of series-connected mixer–settlers or in single-stage centrifugal extractors [12, 13]. In a cascade of extractors, the following stages are usually performed: extraction of metal salts from an aqueous solution with an extractant dissolved in an organic phase, washing of an extract with an aqueous solution of metal salts, and stripping of a desired component (or group of components) with water.

Recently, application of chromatographic methods to separation of rare-earth metals has also been studied [1, 14–17]. The most promising of them in this field seem to be liquid–liquid chromatographic processes [18–21]. In liquid–liquid chromatography, a liquid phase called the mobile phase is pumped through an apparatus (chromatograph) and repeatedly contacts a second liquid phase called the stationary phase, which is retained in the apparatus in the free state. Unlike countercurrent extraction, which within a single stage can separate only binary mixtures, liquid–liquid chromatography within a single stage can separate multicomponent mixtures. Another advantage of chromatographic methods of separation is low reagent consumption, which allows one to use new,

highly efficient, albeit expensive, extractants for producing pure and ultrapure substances.

A disadvantage of chromatographic methods is low performance caused by low capacity of centrifugal chromatographs used for performing liquid–liquid chromatographic processes.

In this work, liquid–liquid chromatographic processes, in particular, separation of rare-earth metals, are proposed to be carried out in a cascade of centrifugal extractors. Extraction chromatographic processes of rare-earth metal separation in such a cascade are theoretically analyzed.

CASCADE OF CENTRIFUGAL EXTRACTORS AS A SYSTEM FOR LIQUID–LIQUID CHROMATOGRAPHY

Liquid–liquid chromatographic processes are conducted in apparatuses of two types: hydrostatic (series-connected chambers in which phases contact are mounted on the surface of the cylinder of an ordinary centrifuge) and hydrodynamic (where the phases contact in a coil wound on the bowl of a planet centrifuge) [18–20]. As noted above, a disadvantage of these apparatuses is their low performance caused by their low capacity. The performance of extractors is several orders of magnitude higher than that of chromatographs. In principle, liquid–liquid chromatographic processes can be carried out in cascades of mixer–settlers [22]. However, because of the large volume of settlers, the chromatographic separation is of low efficiency since the fractions of components spread as they move along the cascade. A cascade of single-stage centrifugal extractors is free of this disadvantage. Here, single-stage centrifugal extractors with mixing of phases under gravity, e.g., those of the TsENTREK type, are considered [13]. The volume of the settling

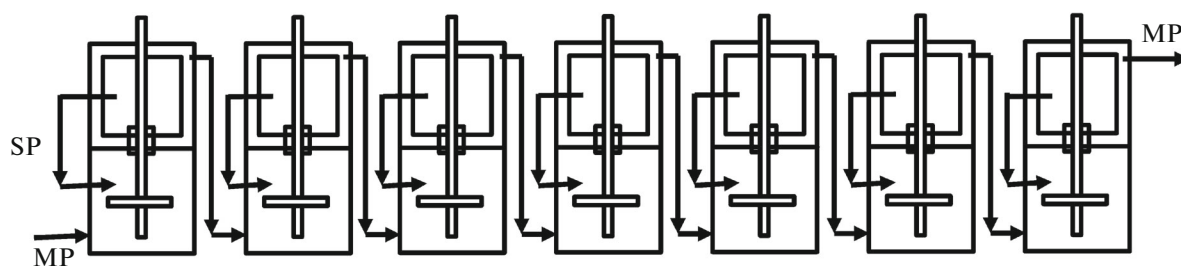


Fig. 1. Schematic of a cascade of single-stage centrifugal extractors for liquid–liquid chromatographic separation. SP stands for stationary (organic) phase; MP, for mobile (aqueous) phase.

chamber at a mixer–settler stage is typically many times the volume of the mixing chamber, whereas the volumes of the mixing chamber and the decantation chamber at a centrifugal extractor stage are approximately equal [13].

Figure 1 shows a schematic of a cascade of single-stage centrifugal extractors for liquid–liquid chromatographic separation. Unlike countercurrent extraction, stages of the cascade of centrifugal extractors are coupled only by the flow of the aqueous phase. The organic phase is retained in the cascade by its recirculation between the mixing and decantation chambers at each stage of the cascade.

The cascade of extractors includes vessels for a metal salt solution in the aqueous phase and for the pure, metal-free aqueous phase and works as follows. Initially, all the stages of the cascade are filled with an extractant-containing organic phase, and the pure aqueous phase is pumped through the cascade at a certain rate while recirculating the organic phase until hydrodynamic equilibrium (the constancy of the ratio between the phases at the stages) is reached. Then, instead of the pure aqueous phase, the metal salt solution in the aqueous phase is fed to the cascade for a certain time at the same rate. After the loading of the mixture of metals to be separated is completed, the feeding of the pure aqueous phase to the cascade is resumed. Further, the process is repeated. At the outlet of the cascade, fractions of separated metals are periodically removed.

THEORETICAL ANALYSIS

In the mixing chamber of a centrifugal extractor, the agitator finely divides one of the phases and brings the phases into intimate contact, and in the decantation chamber, which is a centrifugal separator, the phases are rapidly separated. Therefore, the extraction chromatographic process in the cascade of extractors can be described using a model of equilibrium steps. For further analysis, the following notation is introduced: $K_D = y/x$ is the equilibrium partition coefficient of a component between the organic and aqueous phases; x is the concentration of the component in

the aqueous phase; y is the concentration of the component in the organic phase; N is the number of equilibrium steps (number of extractors in the cascade); $X = x/\bar{x}$ is the dimensionless concentration; $\bar{x} = Q/V_c = x_s F \tau_s / V_c$ is the average concentration in the cascade after the completion of the loading; F is the volumetric flow rate of feeding of the aqueous phase to the cascade; $Q = x_s F \tau_s$ is the amount of the component fed to the cascade for loading time τ_s ; $V_c = V_o + V_a$ is the volume of the cascade of extractors; V_o and V_a are the volumes of the organic and aqueous phases in the cascade, respectively; $S_f = \frac{V_o}{V_o + V_a} = \frac{V_o}{V_c}$ is the fraction of the volume of the organic phase at the steps of the cascade of extractors; $t = \tau \frac{F}{V_c} = \frac{\tau}{\tau_c}$ is the

dimensionless time; $\tau_c = \frac{V_c}{F}$ is the average residence time of the aqueous phase in the cascade; and $t_s = \tau_s F / V_c$ is the dimensionless loading time.

Using this notation and the previously obtained results [23, 24], the theoretical dependences necessary for analyzing separation processes can be represented in the form

$$0 \leq t \leq t_s, \quad (1)$$

$$X(t) = \frac{1}{t_s} \left[1 - e^{-aNt_s} \sum_1^N \frac{(aNt_s)^{i-1}}{(i-1)!} \right],$$

$$t > t_s,$$

$$X(t) = \frac{1}{t_s} e^{-aN(t-t_s)}$$

$$\times \sum_1^N \left\{ \frac{[aN(t-t_s)]^{N-i+1}}{(N-i+1)!} \left[1 - e^{-aNt_s} \sum_1^i \frac{(aNt_s)^{i-1}}{(i-1)!} \right] \right\}, \quad (2)$$

$$a = \frac{1}{1 - S_f + S_f K_D}. \quad (3)$$

Equations (1) and (2) describe the changes in the concentration in the aqueous phase flow leaving the

cascade during and after the loading of the mixture, respectively.

Let us consider several variants (modes) of extraction chromatographic separation of rare-earth metals in the cascade of centrifugal extractors. Extractants for separation of rare-earth metals are characterized by wide ranges of both partition coefficients and separation factors. Analysis below is made at a separation factor of neighboring rare-earth metals of 2 and within two ranges of partition coefficients: low (on the order of 1) and high (on the order of 10).

Low Partition Coefficient Range

Performed within this range are, e.g., extraction of rare-earth metal nitrates and chlorides with solutions of binary extractants in toluene from aqueous salt-free solutions [1] and extraction of rare-earth metals in the nitric acid–di(2-ethylhexyl)phosphoric acid system [14].

It was shown [25, 26] that, at low partition coefficients, the chromatographic separation efficiency can be significantly increased by replacing the steady-state (continuous) mode of feeding of the mobile phase to a column by a discrete (cyclic) mode. The separation efficiencies in the two modes as estimated in terms of number of theoretical steps (plates) are interrelated by the expression

$$N_c = N \frac{1+k'}{k'} \quad (4)$$

Figure 2 presents the outlet concentration profiles calculated by Eqs. (2)–(4) for a ternary mixture with the partition coefficients $K_{D1} = 0.4$, $K_{D2} = 0.8$, and $K_{D3} = 1.6$ at various loading times in the modes of continuous and cyclic feeding of the aqueous phase flow to a 50-step cascade. As is seen from Fig. 2, an increase in the loading time from $t_s = 0.004$ (when the fed amount of the solution of components is equal to the volume of the aqueous phase at one step of the cascade) to $t_s = 0.1$ (when the fed amount of the solution of components is equal to the volume of the aqueous phase at 25 steps, i.e., in a half of the cascade) hardly influences the separation quality. A further increase in the loading time to $t_s = 0.2$ noticeably decreases the component separation quality. Moreover, Fig. 2 suggests that the cyclic mode of feeding of the aqueous phase flow markedly improves the component separation.

High Partition Coefficient Range

As follows from formulas (4), at high partition coefficients, the chromatographic separation efficiencies in the continuous and discrete modes of feeding of the mobile phase become virtually equal. Therefore, the separation process is influenced only by the mode

of feeding of the aqueous solution of the mixture being separated to the cascade.

Figure 3 shows the outlet concentration profiles calculated by Eqs. (2) and (3) for a ternary mixture with the partition coefficients $K_{D1} = 4$, $K_{D2} = 8$, and $K_{D3} = 16$ at various times of loading of the mixture to a 50-step cascade. One can see from Fig. 3 that an increase in the loading time to $t_s = 0.8$ (when the fed amount of the solution of components is equal to the volume of the aqueous phase at 200 steps, i.e., is four times the volume of the aqueous phase in the cascade) has almost no effect on the separation quality. Only at a loading time of $t_s = 1.6$, the component separation quality deteriorates.

Thus, the performance of extraction systems with high partition coefficients is many times that of systems with low partition coefficients. However, the retention times of fractions of components in the latter case are also higher.

Above, separation processes with batch feeding of a mixture to be separated to an extraction chromatographic separation system were considered. In practice, it is preferable to carry out such processes in a continuous semibatch mode with regular feeding of the mixture at specified time intervals. The time interval between two consecutive loads of the mixture should be sufficient to separate the fractions of the slowest (in motion along the cascade) component of the first load (the component with the highest partition coefficient) and the fastest component of the second load (the component with the lowest partition coefficient). If the first load of the mixture is done at the time $\tau_1 = 0$ and the second and subsequent loads are done in time intervals τ_2 , then the process can be modeled and the outlet concentration profiles can be calculated using the formulas

$$t > t_s, \\ X_1 = \frac{1}{t_s} e^{-Na(t-t_s)} \\ \times \sum_1^N \left\{ \frac{[Na(t-t_s)]^{N-i+1}}{(N-i+1)!} \left[1 - e^{-Nat_s} \sum_1^i \frac{(Nat_s)^{i-1}}{(i-1)!} \right] \right\}, \quad (5)$$

$$t > t_2, \\ X_2 = \frac{1}{t_s} e^{-Na(t-t_2)} \\ \times \sum_1^N \left\{ \frac{[Na(t-t_2)]^{N-i+1}}{(N-i+1)!} \left[1 - e^{-Nat_s} \sum_1^i \frac{(Nat_s)^{i-1}}{(i-1)!} \right] \right\}, \quad (6)$$

$$t > (n-1)t_2,$$

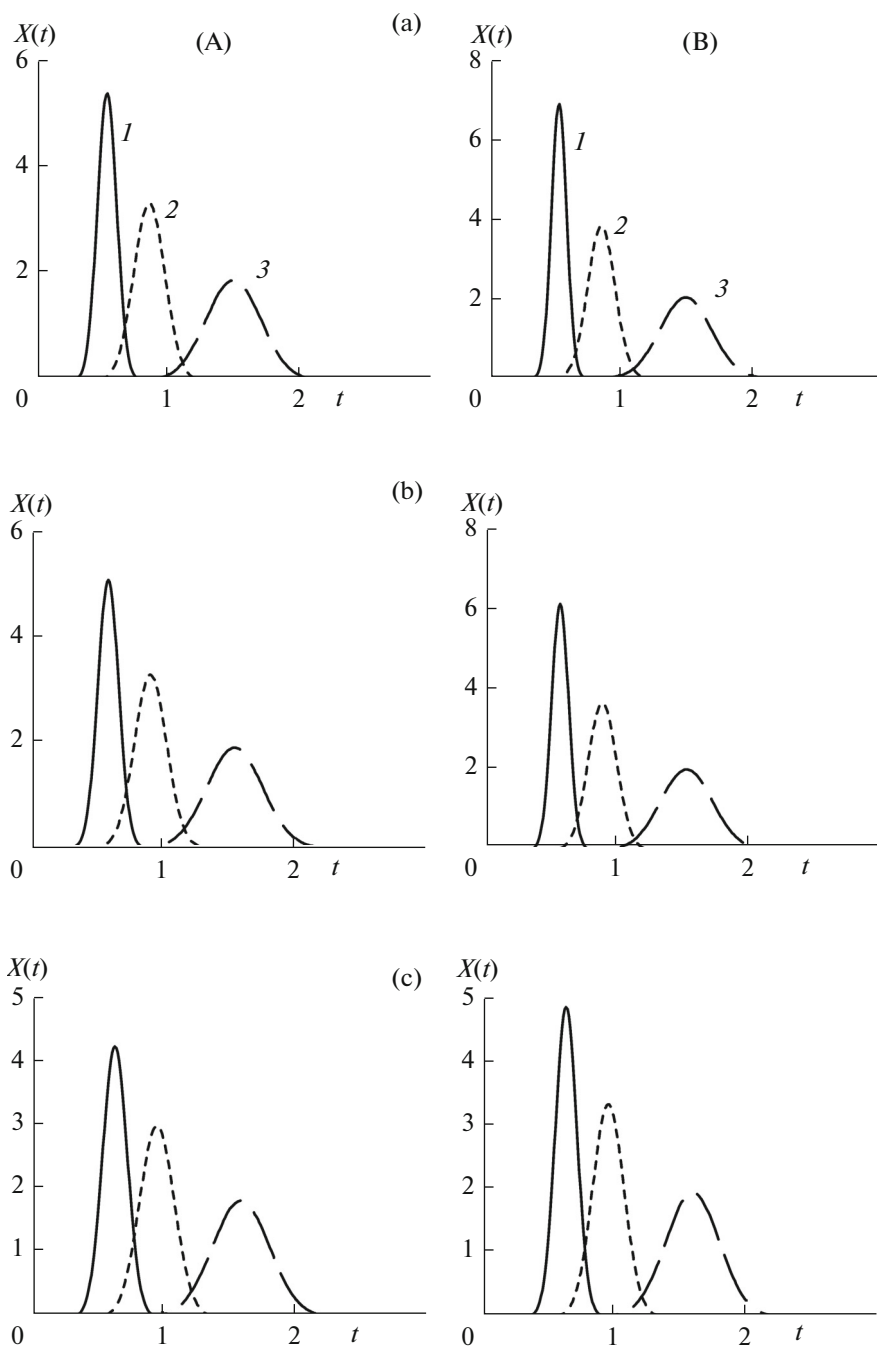


Fig. 2. Calculated outlet concentration profiles for a ternary mixture ((1) $K_{D1} = 0.4$, (2) $K_{D2} = 0.8$, and (3) $K_{D3} = 1.6$) with (A) continuous and (B) cyclic feeding of the aqueous phase flow to a cascade ($N = 50$, $S = 0.8$) at various loading times t_s = (a) 0.004, (b) 0.1, and (c) 0.2.

$$X_n = \frac{1}{t_s} e^{-Na[t-(n-1)t_2]} \times \sum_1^N \left\{ \frac{\{Na[t-(n-1)t_2]\}^{N-i+1}}{(N-i+1)!} \left[1 - e^{-Nat_s} \sum_1^i \frac{(Nat_s)^{i-1}}{(i-1)!} \right] \right\}, \quad (7)$$

where $t_2 = \tau_2 F / V_c$ is the dimensionless time interval between loads of the mixture to the cascade.

Equations (5), (6), and (7) describe the outlet concentration profiles of components of the first, second, and n th loads, respectively.

In Fig. 4, for a ternary mixture with $K_{D1} = 4$, $K_{D2} = 8$, $K_{D3} = 16$, the outlet concentration profiles are presented for the components with the maximal ($K_{D\max} = K_{D3} = 16$) and minimal ($K_{D\min} = K_{D1} = 4$) partition coefficients after the second load at various loading

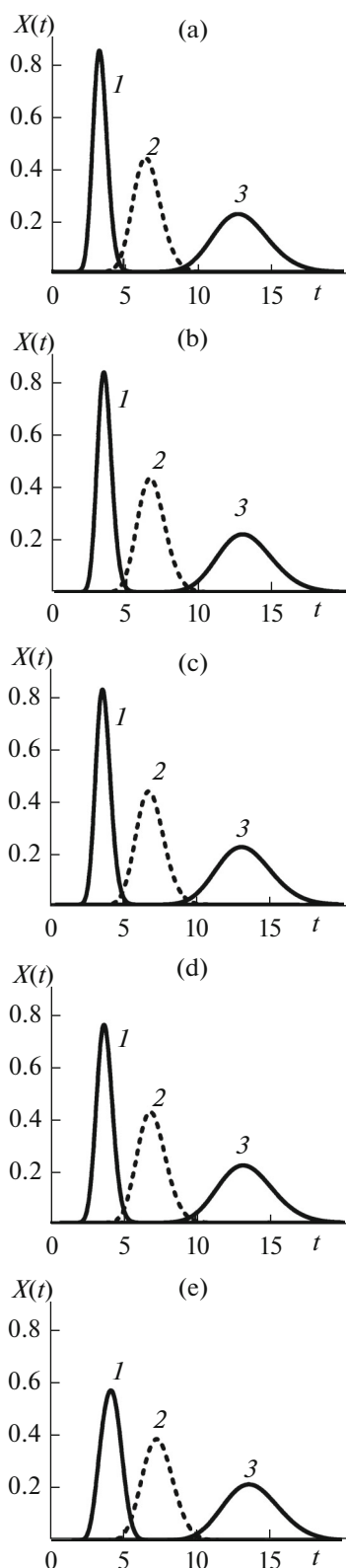


Fig. 3. Calculated outlet concentration profiles for a ternary mixture ((1) $K_{D1} = 4$, (2) $K_{D2} = 8$, and (3) $K_{D3} = 16$) loaded to a cascade ($N = 50$, $S = 0.8$) at various loading times t_s = (a) 0.004, (b) 0.2, (c) 0.4, (d) 0.8, and (e) 1.6.

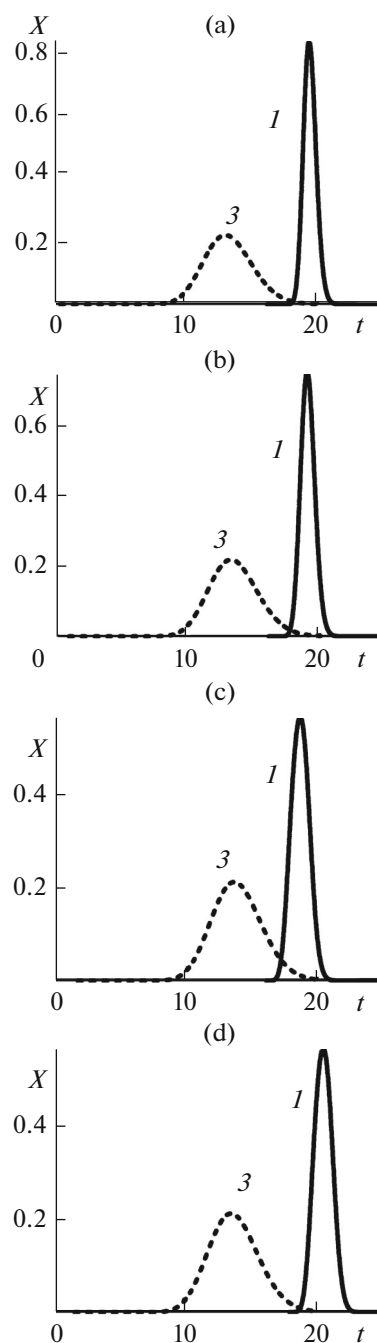


Fig. 4. Calculated outlet concentration profiles of the components with the maximal ((3) $K_{Dmax} = K_{D3} = 16$) and minimal ((1) $K_{Dmin} = K_{D1} = 4$) partition coefficients after the second load to a cascade ($N = 50$, $S = 0.8$) at (a) $t_s = 0.2$ and $t_2 = 16$, (b) $t_s = 0.8$ and $t_2 = 16$, (c) $t_s = 1.6$ and $t_2 = 16$, and (d) $t_s = 1.6$ and $t_2 = 18$.

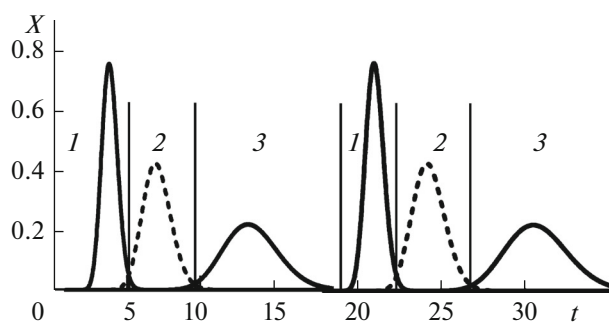


Fig. 5. Calculated outlet concentration profiles and fraction withdrawal boundaries for components of a mixture ((1) $K_{D1} = 4$, (2) $K_{D2} = 8$, and (3) $K_{D3} = 16$) after two loads ($N = 50$, $S = 0.8$, $t_s = 0.8$, $t_2 = 18$).

durations as calculated by Eqs. (5) and (6). Figure 5 shows the calculated outlet concentration profiles and fraction withdrawal boundaries after two loads. As is seen from Fig. 4, an increase in the duration of loading of the mixture to the cascade to $t_s = 0.8$ does not require one to increase the time interval between loads. Only at a loading duration of $t_s = 1.6$, the time interval between loads should be increased from $t_2 = 16$ to $t_2 = 18$ (Figs. 4c, 4d).

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