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New Methodological Approach to Investigation of Kinetics of REE Extraction in Nonstationary Conditions

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Abstract: The influence of periodical oscillations of the temperature on extraction and stripping processes in the extraction systems was studied. Two extraction systems were investigated: (1) 6 mol · L^{-1} $NaNO_3$-$Nd(NO_3)_3$-$Pr(NO_3)_3$-TBP-kerosene and (2) [$Nd(NO_3)_3$ · 3TBP]-[$Pr(NO_3)_3$ · 3TBP]-kerosene - 0.1 mol · L^{-1} HNO_3. Mathematical modeling of the nonstationary membrane extraction has been enhanced by including the dependence of the extraction rate constants on temperature. The values of activation energy for direct and reverse extraction and stripping reactions of Pr and Nd were calculated from experimental temporal dependencies of metal concentration and temperature by solving the reverse kinetics problem using the proposed mathematical model. A series of experiments with periodical oscillations of the temperature on the extraction system for the separation of rare earth elements (REE) using bulk liquid membrane between two extractors were performed. The mathematical model adequately describes the experimental data. The optimization of the extraction process for separation of REE by liquid membrane, under the influence of periodical oscillation of the temperature, was made based on the extraction rate constants and activation energies. The optimal conditions of separation by liquid membrane were found: frequency and amplitude of thermal oscillations, liquid membrane flow rate, and optimal ratio between organic and aqueous phase in extractors.

Key words: kinetics; extraction; non-stationary; rare earths

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Rare earth elements (REE) and their compounds are widely used in modern areas of science and technology. The largest application is in the liquid extraction method found to separate metals in groups and to isolate individual compounds. A great deal of scientific work has been completed in this field over the last several decades. Technologies were also developed to isolate, separate and recover elements in pure form. An overwhelming majority of the investigations are based on achieving equilibrium conditions during the separation process. However, separation factors achieved under such an approach for chemically similar elements are small.

Separation and isolation of REE, and other chemically similar elements, demands investigation of new separation methods. Separation of chemically similarly elements in nonequilibrium conditions is a perspective method to increase separation factors.

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Almost all modern processes of elemental and isotope separation are based on the achievement of stationary conditions in the system. In these conditions, the separation of elements with similar properties is difficult. Separation and isolation of lanthanides and other elements with similar properties requires searching for new methods of elemental separation. New methods of element separation using nonstationary processes, based on differences in kinetics of chemical reactions are under development. Realization of the process in nonstationary conditions using the phenomena of oscillating extraction allows the use of differences in kinetics of ion complexation and extraction rates[1,2]. One of the possible ways to deflect the system from the equilibrium state is periodical thermal influence on extractors. This method is similar to multiple repetitions of processes, described in literature as "parametric pumping"[3]. This can change and essentially enrich existing methods of isolation and separation of elements and isotopes. However, periodical influence of the temperature on extractors is not described in the literature.

1 Experimental

Different modifications of the same experimental setup were used to investigate nonstationary extraction systems, determine extraction rate constants and activation energy of REE. The flow sheet of the general experimental setup for investigation of nonstationary extraction systems (Fig. 1) is as follows: the emulsion is pumped from thermostatic extractors 16, 17 to centrifugal separators 5, 6 through the turbidimeters 11, 12 by peristaltic pump 10. After separation from the separator 5, the organic phase flows to extractor 17 and from separator 6, the organic phase flows to spectrophotometer 8 for analysis and then flows to extractor 16. Passing through both aqueous phases, the organic phase forms a bulk liquid membrane. After spectrophotometers 7, 9 the aqueous phases come back to their corresponding extractors. Data acquisition of pH, red/ox potential of aqueous phase, temperature and emulsion turbidity is performed with a frequency above 1 Hz using DAQ board in computer 18 and specially designed software. Diode-array spectrophotometers acquire spectra every 6 ~ 15 s. By deconvolution of each spectrum, using specially designed software, we can determine the concentration of several elements.

2 Kinetics Extraction Investigation Using Lewis Cell

One-extractor (Lewis cell) modification of the experimental setup is used to get concentration profiles (Fig. 2) and to calculate the mass transfer coefficients of Nd(NO)$_3$ and Pr(NO)$_3$ extraction by 0.5 mol · L^{-1} TBP in kerosene. The initial part of the kinetics curve is used to calculate direct extraction rate constants and the final part is used to calculate the reverse rate constants.

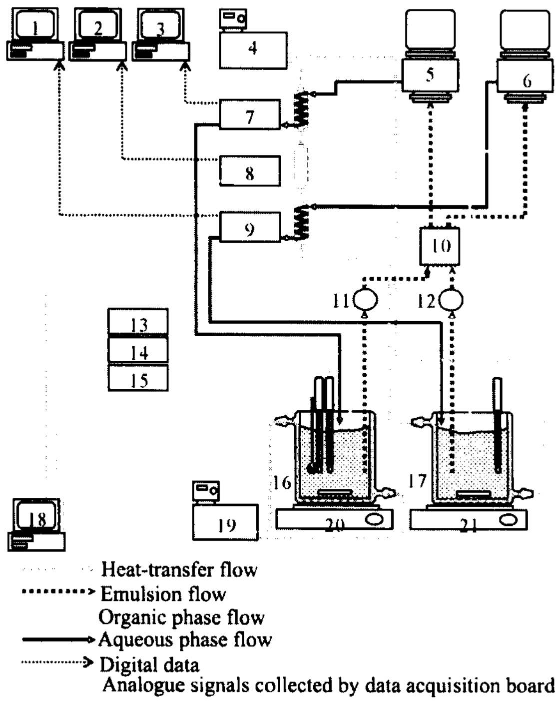

Fig. 1 Experimental setup

1 ~ 3, 18 - Computers; 4, 19 - Thermostats; 5, 6 - Centrifugal separators EC-33 NIKIMT; 7 ~ 9 - Spectrophotometers SF2000 OKB Spectrum; 10 - Peristaltic pump; 11, 12 - Turbidimeters; 13 - pH-meter; 14, 15 - Potentiometers; 16, 17 - Extractors; 20, 21 - Magnetic stirrers

Nd and Pr extraction rate constants could be calculated according to reaction from equation with the assumption that the first-order reaction for Nd and Pr extraction by TBP occurs within the experimental conditions[4].

$$Me^{3+} + 3(NO_3^-) + 3\overline{TBP} \rightleftharpoons \overline{Me(NO_3)_3 3TBP} \quad (1)$$

$$\frac{\partial(\overline{[Me(NO_3)_3 3TBP]})}{\partial t} = \overline{k} \cdot [Me^{3+}] \cdot [\overline{TBP}] \quad (2)$$

As the concentrations of Nd and Pr in the organic phase are very small (Fig. 3), the concentration of free TBP could be considered constant and equal to 0.5 mol · L^{-1}. Concentrations of Nd and Pr in the organic phase (M · dm^{-3}) depend on time (min) at the beginning of the extraction (Fig. 3) as follows:

$$C_{Nd} = 5.35 \cdot 10^{-5} \cdot t - 0.000251$$

$$C_{Pr} = 1.19 \cdot 10^{-4} \cdot t - 0.000576 \quad (3)$$

Value $\overline{k}$ is calculated according to Eq.(4):

$$\overline{k} = \frac{\partial(\overline{[Me(NO_3)_3 3TBP]})}{\partial t} \cdot \frac{1}{[Me^{3+}] \cdot [\overline{TBP}]} \quad (4)$$