Solvent Extraction of Rare Earth Elements by Synergic Mixtures based on Quaternary Ammonium Salts

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Relevance of the research. Rare earth elements (REEs) have found wide application in electronics, chemical, metallurgical, nuclear chemical, glass, automotive and other important industries. Previously, in the USSR there was a well-developed industrial production of all types of REEs compounds. According to the scale of REEs production, the USSR shared 1-2 places with the USA. In post-perestroika Russia, REEs production fell to a low level. The main needs for REEs consumption in the Russian Federation were met by more than 80% due to imports from China, which led to a significant dependence in REEs consumption on China's position. In recent years, the global demand for REE has grown rapidly due to its widespread use, both in the latest high-tech sectors of the civilian industry and in the military-industrial complex. In 2011, at the peak of the maximum increase in prices for REEs products from China, in the Decree of the Government of the Russian Federation No. 42 dated January 21, 2014, the task was set to restore REEs production in the Russian Federation on the basis of new, efficient and competitive technologies.

One of the directions of development of new extraction technologies is associated with the use of synergistic mixtures of extractants of different classes to increase the extraction of REEs from technological solutions for processing mineral raw materials and to increase the separation coefficients of the nearest pairs of elements. One of the features of synergistic mixtures based on quaternary ammonium salts (QAS) is their ability to extract REEs from solutions with a low concentration of nitric acid, which is most used in REEs technology. This makes it possible to use such mixtures for the development of resource-saving, economically cost-effective REE production, which fully complies with the objectives of the Decree of the Government of the Russian Federation No. 42 of January 21, 2014.

The purpose of the work - development of the chemistry of synergetic extraction of REEs of the light group with mixtures of methyltri-n-octylammonium nitrate (TOMAN) with TBP, as well as determination of the compositions of synergetic mixtures and conditions for the extraction separation of group concentrates into individual elements from nitrate solutions with a low concentration of nitric acid.

Tasks:

To achieve the set goals, the following main tasks were formulated and solved:

– to study the chemistry of extraction of La, Ce(III), Pr and Nd with TOMAN-TBP mixtures from individual nitrate solutions with a low concentration of nitric acid by isomolar series methods and mathematical modeling of extraction isotherms;

– to determine the areas of manifestation of synergetic extraction with TOMAN-TBP mixtures, the compositions of synergetic mixtures and extracted synergetic complexes for LREE;

– to determine the conditions for the separation of the nearest pairs of LREE with high separation coefficients from mixed low-acid nitrate solutions without a salting agent with synergistic mixtures of TOMAN-TBP;

– calculate the parameters of countercurrent extraction cascades with flushing to separate the REEs of the light group along the lines La/Ce(III), Ce(III)/Pr, La/Pr from mixed low-acid nitrate solutions with synergistic mixtures of TOMAN-TBP;

– based on the results of the theoretical calculation of countercurrent cascades, to separate the model concentrate of La, Pr and Nd oxides along the La/Pr line from mixed low-acid nitrate solutions with TOMAN-TBP mixtures on a laboratory 60-stage cascade based on dividing funnels.

Scientific novelty.

– It has been established that the chemistry of synergetic extraction of nitrates La, Ce(III), Pr and Nd by TOMAN-TBP mixtures from nitrate solutions with a low concentration of nitric acid is determined by the formation of mixed synergetic complexes of the composition $(R_4N)n[Ln(NO_3)_{3+n}*m(R'O)_3PO]$, where n=1-4, m=1-6, depending on the molar ratio Ln:TOMAN:TBP.

– It has been established that the main motive for changing the composition of mixed complexes is the substitution of phosphoryl groups of TBP with nitrate with an increase in the proportion of TOMAN in the mixture and, conversely, the substitution of nitrate groups of TOMAN with phosphoryl with an increase in the proportion of TBP in the mixture.

– The areas of manifestation of synergetic extraction of La, Ce(III), Pr and Nd with 1.0 M isomolar mixtures of TOMAN-TBP in toluene from nitrate solutions with a low concentration of nitric acid have been determined.

– The compositions of extracted synergistic complexes of nitrates La, Ce(III), Pr and Nd in a wide range of changes in the concentration of lanthanides have been determined.

– For each extracted synergetic complex, thermodynamic extraction constants and hydrate parameters Hi were calculated and tabulated, describing the isotherms of extraction of nitrates La, Pr and Nd by 1.0 M isomolar mixtures of TOMAN-TBP in toluene.

– New calculated data confirming the concept of non-stoichiometric complexation have been obtained for the extraction isotherms of nitrates La, Pr and Nd obtained in the work with 1.0 M isomolar mixtures of TOMAN-TBP in toluene.

– Based on the calculations carried out, mathematical equations are determined and presented for the extraction isotherms of La, Pr and Nd nitrates studied in the work with 1.0 M isomolar mixtures of TOMAN-TBP in toluene.

Theoretical and practical significance of the work.

– The theoretical significance of the work lies in the thermodynamic substantiation of the chemistry of synergetic extraction of nitrates La, Ce(III), Pr and Nd with TOMAN-TBP mixtures from low-acid nitrate solutions, the development of mathematical models of lanthanide extraction isotherms by synergetic extractants based on solving the equation of the Law of Acting Masses written in terms of the activity of all components of the extraction equilibrium.

– The conditions for the extraction separation of La, Ce(III), Pr and Nd concentrates into individual elements by synergistic mixtures of TOMAN-TBP from low-acid nitrate solutions have been established.

– A theoretical calculation of the parameters of countercurrent extraction cascades with flushing for the separation of REEs of the light group along the lines La/Ce(III), Ce(III)/Pr, La/Pr from low-acid nitrate solutions with synergistic mixtures of TOMAN-TBP has been carried out.

– Laboratory tests of the extraction separation of a model concentrate of La, Pr and Nd oxides along the La/Pr line from low-acid nitrate solutions with a synergetic mixture of 0.6 M TOMAN-2.4 M TBP in dodecane on a 60-stage laboratory countercurrent cascade were carried out, confirming the high efficiency of the use of synergetic mixtures TOMAN-TBP for the separation of REEs of the light group.

The main provisions for the defense.

– chemistry of synergetic extraction of La, Ce(III), Pr and Nd nitrates by TOMAN-TBP mixtures from low-acid nitrate solutions according to the isomolar series method;

– results of mathematical modeling of isotherms of extraction of La, Pr and Nd nitrates by synergistic mixtures of TOMAN-TBP from low-acid nitrate solutions;

– compositions of synergistic mixtures of TOMAN-TBP and conditions for the separation of REEs of the light group into individual elements from low-acid nitrate solutions;

– calculations of parameters of extraction countercurrent cascades with flushing for separation of REEs of the light group along the lines La/Ce(III), Ce(III)/Pr, La/Pr;

– results of laboratory tests of separation of a model concentrate of La, Pr and Nd oxides along the La/Pr line from low-acid nitrate solutions with a synergetic mixture of 0.6 M TOMAN-2.4 M TBP in dodecane on a 60-stage laboratory countercurrent cascade.