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Studies in the field of rare earth elements

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Abstract

The article describes developed and implemented technologies in the field of rare earth elements. Besides, new promising technologies for the realization of the work, carried out at the Department of Chemistry MEPhI in recent years, are represented.

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1. Introduction

Joint works of MCTI named after D.I. Mendeleev and Moscow polymetals plant (MPP) in the field of chemistry and technology of extraction separation of rare earth elements (REE) has been conducting since 1965. After the closure of REE production at MPP, the authors of the developments continued their studies in the field of REE technology in MEPhI. Changing of Russian raw material base required not only to be engaged in extraction technology but to develop hydrometallurgical technologies of REE extraction from other sources.

In the early studies of the authors, main attention was paid to the study of the extraction of REE micro and macro amounts by the mixtures of tri-n-butyl phosphate (TBP) and some other neutral organophosphorus compounds with reagents of other classes: nitrate anion exchange of trialkylmethylammonium (TAMA), cation exchange di-2-ethyl-hexyl phosphoric acid (D2EHPA) and some others. It has been determined that the use of mixtures of extractants can improve the selectivity of separation or decrease the tendency of the system to sedimentation[1].

For the separation of REE when using the mixtures of extractants, the character of extraction isotherm and increase or decrease of the distribution coefficients (D) in the REE series with increasing of their atomic number (Z)

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play an important role. In assessing the possibility of using a mixture of extractants for the REE separation it is function D = f (Z) which is decisive.

The application of mixtures leads to a change in the nature of dependencies D = f (Z), that allows to:

- increase the selectivity of the group separation,
- increase the selectivity of separation of neighboring REE,
- separate one element from the others if this element changes its position in the REE series.

On the basis of the conducted studies, the following technologies given below, were developed and implemented.

2. Implemented Technologies

2.1. Technology of REE Separation of the Middle Group by the Extraction of TBP and TAMA mixtures

In the extraction of nitrate weak acid solutions (less than 0.5 mol /l of nitric acid), TBP mainly extracts the elements of the middle group with a maximum on neodymium-europium. Due to the peculiarities of filling of 4f shell in gadolinium ($4f^7$), failure of the distribution coefficient of this element is observed and there are prerequisites, which in case of favorable conditions, allow to separate samarium and partly europium from gadolinium. But even in this case, separation coefficients samarium – gadolinium, and especially, europium – gadolinium do not exceed values of 1.2-1.4, which is insufficient for effective separation. When TAMA is added to TBP due to synergetic effect, separation coefficients increases to 1.5-1.6. It helped to provide a countercurrent process for the separation of cerium REE, samarium and europium from gadolinium.

The process was carried out at MPP on two countercurrent cascades with obtaining samarium concentrate and gadolinium concentrate. It became possible thanks to the industrial implementation of TAMA synthesis by the method developed with the participation of V.V. Sergievskiy in MCTI named after D.I. Mendeleev.

2.2. Gadolinium Extraction Technology

To extract an individual rare earth element form the sum of REE, at least two cascades are required: one cascade to separate more extractable elements and the other one to separate less extractable elements.

To extract gadolinium, a two-stage technology was developed and implemented into production at MPP. This technology involves a cascade of separation of terbium and more extractable REE by mixture of D2EHPA and TBP and cascade of final purification from cerium REE by the mixture of TBP and TAMA. The technology provided obtaining of gadolinium oxide with the content of the basic substance more than 99.9%.

2.3. Technology of Purification from the Impurities of Europium and Gadolinium

An extractant, containing TAMA with the addition of TBP, was used for the purification of samarium concentrate from europium impurities. The process was carried out on the 70-stage cascade construction of centrifugal extractors of Research and Design Institute of Installation Technology (RDIIT). The concentration of europium in samarium decreased to 0.03-0.05 wt. %, which allowed to obtain metallic samarium, suitable for the production of samarium-cobalt magnets.

2.4. Technology of Terbium Extraction from the sum of REE

Two-cascade technology of terbium extraction with the concentration of the basic substance of 99.9% by the extraction of TBP and D2EHPA mixture was developed and implemented at MPP. In the first cascade, samarium, gadolinium and less extractable elements were separated from terbium and in the second cascade, dysprosium, holmium and more extractable elements were separated. Application of a mixture of extractants allowed to prevent the formation of sediments and increase the productivity of the process.