Rare Earth Separation in China[*]

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Abstract: During the last decade, China rare earth (RE) industry has made significant progress and become one of the most important producers in the world. In this paper, the recent developments in both fundamental research and industrial application are briefly reviewed: (1) the development and application of Theory of Countercurrent Extraction, (2) the novel solvent extraction process and its application in industry for separating heavy rare earth elements (Tm, Yb, Lu), yttrium (Y), and scandium (Sc), (3) the on-line analysis and automatic control of countercurrent extraction, (4) the eco-friendly process for RE/Th separation of bastnasite in Sichuan Province and electrochemical process for Eu/RE separation, and (5) the optimized flowcharts for typical rare earth minerals in China.

Key words: countercurrent extraction; rare earth separation; solvent extraction; on-line analysis; automation; eco-friendly process

Introduction

With the governmental support, the academic efforts, and the collaborations between the institutions and enterprises, China has made great progress in both fundamental research and industrial applications in the rare earth separation during the past decade, even though there are still some techniques to be improved. In this paper, rare earth (RE) separation in China are briefly reviewed with the following aspects: (1) the development and application of Theory of Countercurrent Extraction, (2) the novel solvent extraction process and its application in industry for separating heavy rare earth elements (Tm, Yb, Lu), yttrium (Y), and

scandium (Sc), (3) the on-line analysis and automatic control of countercurrent extraction, (4) the eco-friendly process for RE/Th separation of bastnasite in Sichuan Province and electrochemical Process for Eu/RE separation, and (5) the optimized flowcharts for typical rare earth minerals in China including the hyperlink process which has been developed recently[2].

1　Progress of Theory of Countercurrent Extraction

In 1970s, Xu established the Theory of Countercurrent Extraction, a milestone in rare earth separation, especially in the solvent extraction[3,4]. The computer simulation of the dynamic process, reflux model, third outlet, and one-step scale-up was studied previously[5].

1.1　Phase transfer catalysis stripping in D2EHPA-N235 system

Phase transfer catalysis (PTC) concept was first introduced to the rare earth solvent extraction by Yan et al.[6] and Zhang[7], and PTC stripping (PTCS) in

D2EHPA-N235 system has been studied in detail. In the process, D2EHPA acts as an extractant and N235 as a PTC reagent. The protons are carried by N235 from the aqueous phase to the organic phase when the concentration of N235 is 0.1 mol/L with PTCS mechanism; hence the stripping turns to be a homogeneous-like reaction. Extracting, scrubbing, and stripping behaviors of the rare earth ions and protons for separating ionic-adsorptive rare earth deposit and bastnasite are investigated in the medium of hydrochloric or sulfuric acid. PTCS can enhance largely the efficiency of the stripping, especially for the separation of the heavy rare earths[6,7].

1.2 Theory of Countercurrent Extraction with an inconstant mixed extraction ratio

In the previous work[3,4], a model with a constant mixed extraction ratio was assumed to calculate the mass balance and extraction equilibrium in the solvent extraction process. However, this assumption is not valid in the heavy rare earth system due to the high equilibrium acidity. Therefore, a new model with an inconstant mixed extraction ratio was developed. Using this more general model, we construct a set of simulation programs to describe the running status and design the parameters, which are in agreement with that in the industrial practice. The new simulation is also available to design the parameters for the stripping section[8,9].

1.3 Hyperlink process and its design

Normally, rare earth ions are extracted by the saponificated extractant and transferred into the organic phase in the solvent extraction process, where the acidic extractant is first saponified by the base. Then, the loaded rare earth ions are stripped from the organic phase into the aqueous phase by the acid. Therefore, the acid and the base are the main consumptions in the solvent extraction process, and the equilibrium acidity of the stripped rare earth solution is one of the main pollution resources. In order to reduce the consumption of the chemicals, as well as the waste solution pollution, a "hyperlink process"[10] was designed and developed. The organic and aqueous phases loaded rare earth ions are used as the new kinds of extractant and scrubbing or stripping solution, respectively, to replace the original saponified extractant and acid solution without rare earth loaded. Compared with the traditional process, chemical consumption can be reduced nearly 30%.

1.4 Optimization of the dynamic simulation and static design

The basic step for the dynamic simulation of countercurrent extraction is the calculation of extraction equilibrium in a single stage. In order to speed up the dynamic simulation of countercurrent extraction, we optimize the calculation of extraction equilibrium in a single stage with a modified Newton algorithm. The convergence of calculation is accelerated greatly and the simulation is improved[11]. Meanwhile, an integrative feedback method was also applied in the simulation to adjust automatically the flow rates of inputs and shorten the calculation time for dynamic simulation. Since the mass transfer in a real cascade is more complicated than that in the "funnel method" experiment, a novel model including the structure of the real mixer-settler extractor is proposed. Compared with the calculation based on the "funnel method" model, the results of dynamic simulation for the real cascade are more exact[12].

For the static design of multi-component and multi-outlet countercurrent extraction process, the major problem is that the composition of each outlet cannot be directly deduced from the separation indices. Presuming the initial composition of each outlet based on the separation requirement, a new algorithm is proposed to calculate the extraction equilibrium and the mass balance throughout the whole extraction cascade to modulate the composition of each outlet. Through the definite time of iterations, the exact balanced composition of each outlet can be achieved. Thus, the stage numbers of the extraction cascade can be controlled right by comparing the composition of each outlet according to the separation requirement, and the feeding position can be controlled and determined in the mean time with the optimized results.

Both programs of the dynamic simulation and static calculation are developed under object-oriented Borland C++ 5.0, running at 32-bit Windows system such as Windows 95. The kernel algorithm is optimized for high efficiency and reliability and the programs are good at the computation speed and friendly flexible user-interface[13].