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 flow-charts 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].

1.5 Novel algorithm in mixer-settler extractor

Static design of multi-component and multi-outlet of the rare earth extraction system is carried out with a novel algorithm. First, the relative flow rate of each outlet is calculated according to extraction requirements. Secondly, the mass balance and extraction equilibrium of countercurrent extraction are studied in this system. Furthermore, the recursion in the separation system is operated through these relationships. The key point of the algorithm is to introduce a specific variable for continuously manipulating recursion results. Once all corresponding parameters are optimized properly, the system will approach the balance step by step through iterations. Finally, a series of the parameters such as the stage numbers and the flow rate of different solutions are optimized. The accurate algorithm of static design for the multi-component and multi-outlet rare earth countercurrent extraction investigated here is valuable to the countercurrent extraction theory and its applications[14].

Based on our previous work about the algorithm of static design for the multi-component and multi-outlet rare earth countercurrent extraction, the computational program under 32-bit Windows operation system is composed and verified by the dynamic simulation for different rare earth separation processes with satisfactory results. This static design program can be used to design the optimum parameters to control the rare earth countercurrent extraction process with high speed and accuracy. In order to introduce the application of the program, the optimized parameters of a ten-component and three-outlet process is presented and verified by the dynamic simulation[15].

2 Novel Separation Process of Heavy Rare Earth

2.1 Separation of Tm, Yb, and Lu

Without an adequate market, heavy rare earth such as Tm, Yb, and Lu were almost deposited as concentrate before 1990s, and only a few amount of the heavy RE were separated by ion exchange process with P507 (PC-88A) resin. Based on the increasing demands of heavy RE products, now a number of plants establish separation lines to purify these elements. The most popular solvent extraction method is using P507 or Cyanex272 as extractant with lower equilibrium acidity. The additives of modified P507 were also adopted

to separate Lu in practice. Naphthenic acid or related carboxylic acid derivative were also used to separate the heavy rare earth in a very long cascade. Although the efficiency was not satisfactory, the chemical consumption was economical enough. Electrochemical method is also piloted to obtain Yb. This makes the separation of Tm, Yb, and Lu more effective by solvent extraction[16-18].

2.2 Purification of Y

As a host material, yttrium is the main component of phosphors. The largest market of yttrium is composed of CRT, PDP, Lamp, LED, and other phosphors, and the high purity of the yttrium compounds is needed for the composite oxides of Y+Eu, Y+Tb, and Y+Zr. Y-rich concentrate produced from Longnan mineral or from the separation of ionic-adsorptive minerals by P507-HCl process is the unique raw materials. Its chloride salt is separated from other heavy rare earth in saponified naphthenic acid. The contaminant of light rare earth elements and bivalent ions such as calcium were removed in P507-HCl cascade, and then yttrium ($\geqslant 99.999\%$) is co-precipitated with other elements, i.e., Eu, Tb, and Zr, by purified oxalic acid. Decomposing the oxalate in furnace leads to the formation of the Y-contained oxide or composite[16].

In order to meet the requirement for different grades of the same rare earth element in the market, a multi-outlet process for two-component system is proposed. Within this new process, the quantity and quality of products can be controlled conveniently according to the market demands, and the manufacturing cost can be also reduced significantly[19,20].

2.3 Purification of Sc

Since it contains trace-amount scandium (the content of Sc_2O_3 in REO is 0.04 wt.%), the ionic-adsorptive rare earth deposit is a new valuable resource for scandium. Wei et al.[19] investigated the concentration and purification of scandium from ionic-adsorptive rare earth deposit with an acidic extractant HA. In order to concentrate and purify scandium from the rare earth, the extraction behavior of both lanthanide and scandium has been studied systematically. The results indicate that the separation factor ($\beta_{Sc/Ln}$) between lanthanide and scandium decreased with increasing pH of the aqueous phase and with the increasing purity of

scandium. The optimum process is designed as two steps. Scandium was concentrated from 0.04 wt.% to 25 wt.% by a crosscurrent extraction in the first step and afterwards the scandium concentration was purified to 99.99% or 99.999% by a countercurrent extraction process[21].

3 On-line Analysis and Automation of RE Separations

3.1 On-line analysis

An [241]Am-excited energy dispersive X-ray fluorescence spectrometry is introduced in an on-line analysis method. The γ-ray with 59.6 keV energy acts as an excitation for rare earth samples in both aqueous and organic phases collected from the solvent extraction process. As a result, characteristic *K* series X-ray fluorescence of the rare earths is emitted and detected by a high purity planar Ge detector after transmitting Be window. The signals are amplified by pre-amplifier and main amplifier, and the analogy signals are converted to digital ones. The whole energy spectrum is recorded by a multi-channel board and saved into the personal computer. The rare earth composition of the samples is analyzed on-line with the intensity of the spectra. The spectra are stripped off the background including Compton scattering and [241]Am excitation peaks, and smoothed once. Individual rare earth element is selected as a self-inner standard to compose a self-absorption function by the least-square method. The functions of individual element are combined to derive simultaneous equations for the mixture of the rare earth samples. The concentration of each component in the rare earth sample is determined by iterations. Element from La to Tm including Y can be analyzed with this model. In order to verify the detecting range of the method, samples of light, medium, and heavy rare earth are prepared in both aqueous and organic phases for the measurement. Compared with the standard composition and the measured results of inductivity coupled with plasma spectrometry (ICP), this method is satisfactory in on-line analysis of rare earth separation with its advantages such as rapid, accurate, and non-destructive[22-25].

3.2 Automation of the RE separation process

Newton-Raphson algorithm is applied to investigate the extraction equilibrium of multi-component system. The distribution of each component in both phases is calculated by the mass balance and extraction equilibrium with certain extracting flow rate, scrubbing flow rate, and extraction ratio. The dynamic simulation is greatly accelerated by Newton-Raphson algorithm. Furthermore, the optimized point with the maximum purity gradient for on-line detection is explored in the sensitivity of purity gradient and measurability of on-line analysis, and thus the diagnostic strategies are deduced. The responses of fluctuation in extracting flow rate, scrubbing flow rate, feeding flow rate, and feed composition are simulated with the open-loop calculation. In order to manipulate the process in the steady status with the lowest chemical consumption and the highest speed, the optimized adjustment strategy is investigated and verified by the dynamic simulation[26-28]. The knowledge base for the expert system on rare earth countercurrent extraction (version 3.0, ESRECE3.0) is built up. The software is developed under Windows desktop and programmed by Visual Basic 3.0 for Windows environment. Auxiliary data including the product indexes and prices, design of the mixer-settler extractor, and analytical standards are supplied in the database[29-32].

Based on the Theory of Countercurrent Extraction, the optimum parameters can be obtained by the static calculation for two- and three-outlet processes in two-, three-, and multi-component processes. In order to verify the feasibility of the designs, the dynamic simulation by computer is developed, which can be used to design any countercurrent extraction process for separating the rare earths. As a result, the expert system for rare earth countercurrent extraction, ESRECE3.0, is set up. The interface is friendly in popular Windows style. ESRECE3.0 can select process parameters automatically from a set of optimized parameters in different extraction conditions, and simulate the dynamic process from starting to steady status for various real cascades. It can also be used to investigate open-loop responses and determine the control indexes, which is beneficial to the automation of the real cascades. Furthermore, ESRECE3.0 visualizes the results in both static design and dynamic status. Additionally, ESRECE3.0 is comprised of

knowledge base in which the data from the individual experiment and production line are recorded. The information is saved and related to static and dynamic simulation, and used to adjust and control the production lines[33].

A distributed control system (DCS) is applied in Baotou Rare Earth High Technology Co., Ltd. by Chai and his co-workers in Northeast University, China. Another DCS simulation system is established and is applied in Jiangxi Golden Century Rare Earth New Materials Inc. Many other parts of control are also studied in Shanghai Yuelong and other rare earth separation plants[34].

4　RE/Th and Eu/Re Separation Processes

4.1　Eco-friendly RE/Th separation

Bastnasite in Sichuan was discovered in 1980s. Besides the rare earth, there are approximately 0.2 wt.% thorium and 9 wt.% fluoride. The former is radioactive and the later harmful. Li and his co-workers developed an eco-friendly process with a new extractant to separate cerium from thorium and RE, and then, N1923 is used to separate thorium from RE. In this process, F⁻ is recovered[35]. This process is also valuable to solve the similar problem in Baotou RE metallurgy. Purity, recovery, and thorium residue are listed in Table 1.

Table 1　Purity and recovery of the products

Element	Purity (%)	Recovery (%)	Th mass fraction (10^{-6})
Ce	99.99	85	100
RE(La-rich)	-	90	5
Th	95	90	-
F	-	50	-

4.2　Electrochemical Eu/RE separation

Ce, Pr, Sm, Eu, Tb, Tm, and Yb in lanthanide family are characterized with floating valence. Normally, the separation factors vary little for different RE ions with the same valence. However, it changes obviously for those with different valences. Usually, Eu(III) is reduced to Eu(II) by reductant such as zinc that will introduce the impurity. Long et al.[36] use electrochemical method instead of zinc reduction to make the system clean, and the purity of europium

(Eu_2O_3/REO) can be improved to 99.9995% with the recovery higher than 90%. Compared with the traditional zinc reduction method, this process is simpler, lower cost, and environmental friendly[36]. A production line with 15 t europium annual capacity is working in Gansu RE Group Co., Ltd.

5　Typical Optimized Flowcharts of RE Separation

5.1　Separation of bastnasite or/and monazite

There are more than 60 000 t to 80 000 t bastnasite or/and monazite separated every year in China with 25 000 t coming from Sichuan Province. Some of them are used directly to produce Si-Fe-RE alloys; the rest is converted to rare earth chloride for separation. Normally, bastnasite in Baotou is decomposed with sulfuric acid to obtain rare earth sulphate first, and then, it is precipitated as carbonates. Finally, it is dissolved in hydrochloric acid to be converted to rare earth chloride, as the feed of the solvent extraction process.

Typical rare earth separation flow charts are depicted in Fig. 1.
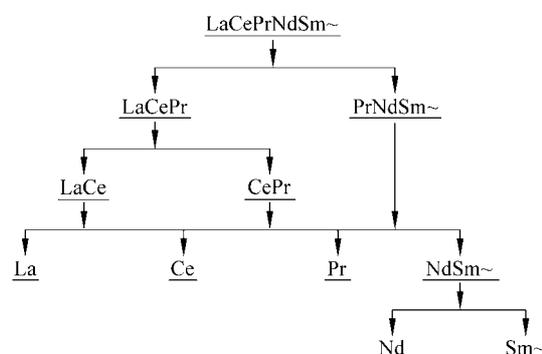
Fig. 1　Flowsheet for bastnasite and/or monazite.

5.2　Separation of ionic-adsorptive RE deposit

Ionic-adsorptive RE deposit is a specific mine which is rich in the medium and heavy rare earth elements, and can be classified as low-, middle- and high-yttrium mines according to their content of yttrium. The annual productions of the middle- and high-yttrium mines are around 25 000 t and 15 000 t, respectively. P507 and naphthenic acid are the two main extractants diluted with kerosene. Naphthenic acid is diluted with kerosene and added iso-octane alcohol as additive to separate yttrium from other lanthanides. Almost all the

aqueous phases are in the medium of hydrochloric acid, except that nitric acid is adopted to replace Cl⁻ for the separation of the other elements. The typical optimized flowchart is shown in Fig. 2.
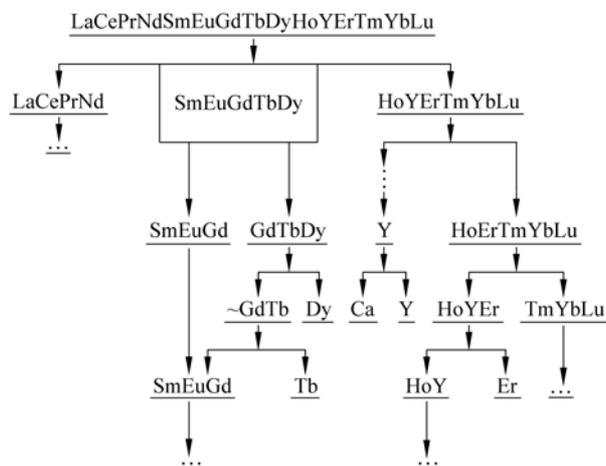
Fig. 2   Flowsheet for ionic adsorptive RE deposite.

5.3   Neural networks and hyperlink process in solvent extraction

Neural networks are introduced into the design of rare earth separation process. Analytical relationships between the feasible processes, flowsheets, and components are derived, respectively. It is explained in detail by an example of light rare earth separation. Furthermore, the fixed investment for the rare earth and solvent set in cascades, and the consumption of chemicals in different processes with various praseodymium concentrations are compared. The reasonable range for praseodymium concentrations is deduced in the separation of bastnasite. Additionally, the costs of several separation flowsheets for bastnasite in Sichuan are reviewed. The optimized process can be concluded by comparing the technical and economical indices[37-46].

Hyperlink process was introduced in solvent extraction in the past few years. It can improve the performance of the whole process in both technical and economical indices. For the sake of the commercial secrets, such process is not elucidated here in detail. The chemical consumption and waste solutions can be decreased in 30%-50% to optimize the current flowcharts. It could be also applied in other elements separation by chromatography. This is a breakthrough in the rare earth separation by solvent extraction.

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