PROGRESS IN SCIENCE AND TECHNOLOGY OF THE RARE EARTHS

稀土科学与技术进展

中国稀土学会 编

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内 容 简 介

本书内容主要为第八届国际稀土开发与应用研讨会的部分论文和摘要。国际稀土会议在中国、美国和欧洲国家轮流召开。迄今，中国稀土学会已成功举办八届国际稀土开发与应用研讨会（ICRE）。本书内容丰富，包括资源和环境领域的稀土地质矿山、采矿选矿、分离冶炼、循环利用和环境保护，以及稀土物理化学和稀土应用领域的永磁、发光、催化、储氢、超导、玻璃陶瓷、纳米材料等，反映了相关领域的最新科研动态。

本书可为科研机构、大专院校、政府部门、稀土企业等从事稀土采选冶、应用、环保工作的人员以及科研人员提供参考，也可供对稀土科研和产业感兴趣的有关人士阅读。

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Contents

Section A: Full Paper

Section B: Abstract

Section A: Full Paper

A High-Efficient System of the Ionic-Liquid Containing CHON-Type Extractant for Extraction and Recovery of Rare-earth Resources

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Abstract Our group focuses on the advanced field about developing novel "green" extractants (only C, H, O and N atoms), and the ionic liquid-mediated green extraction systems, which are applied in eco-friendly extraction and recovery of rare-earth resources. The diglycol amic acid derivative extractants were recently developed, which showed a high affinity for rare earth ions in ionic-liquid mediated extraction although a conventional and commercial phosphonic extractant did not. It is promising for effective recovery of the rare earth resources, such as Y, Eu, Tb, Nd, Pr, Dy and Lu, from waste phosphor powders, NdFeB magnets, and LYSO scraps. And it can be widely applied to supported liquid membrane system and silica gel/resin systems.

Keywords CHON-type extractant · Diglycol amic acid · Eco-friendly recycling · Ionic-liquid mediated extraction system · Rare-earth resources · Urban mine

1 Introduction

Currently, as new scarce strategic resources and from an economic growth point, the value of rare earths has been recognized with the rapid development of new industries such as the LED (light emitting diode) lighting industry, the electronic information industry, the automotive industry, etc. Furthermore, the price of rare earths has been increasing steadily. However, the output of rare earth resources has a strong regional dependence, in which China is dominant in the export of rare earth raw materials (about 90% market supply share), yet China rare earth output has been transforming from extensive availability to restricted availability since 2010, which is restricting the development of the above-mentioned new industries[1].

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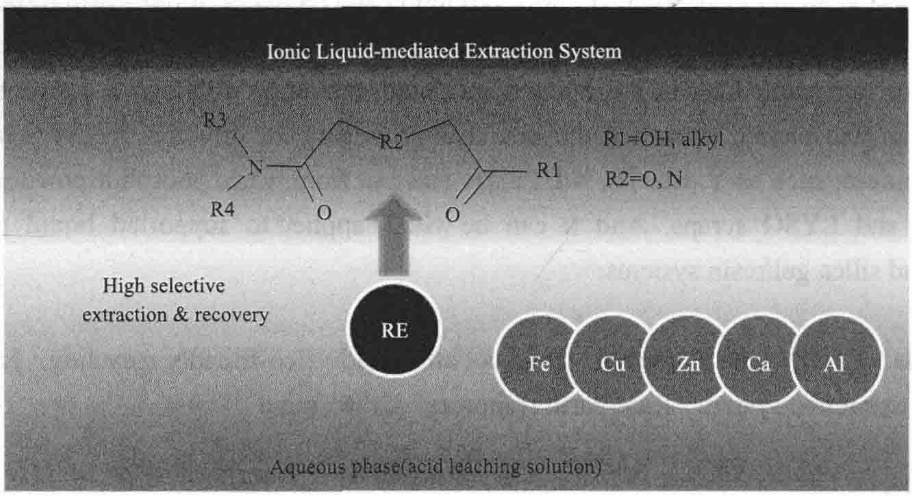
As an important nonrenewable natural resource, a stable supply of RE raw materials is crucial. In addition to mineral resource, secondary resource also has tremendous potential. An assessment of recycling potential global REs for the year 2020 is outlined, which includes magnetic storage media (Nd, Sm, Gd and Dy), lamp phosphors (Y, Ce, Eu and Tb) and so on[2]. The recycling of "urban mines" has become an important source for sufficient supplies of RE materials. Thus, what is urgently needed in RE recycling is a highly selective and efficient extractant which can obtain individual REs and useful concomitant elements at the same time.

In recent years, ionic liquids have been highlighted as an eco-friendly alternative to organic solvents due to their unique properties such as negligible vapor pressure, non-flammability and high thermal stability. Their physicochemical properties are readily selectable, which make hydrophobic ionic liquids suitable for solvent extraction.

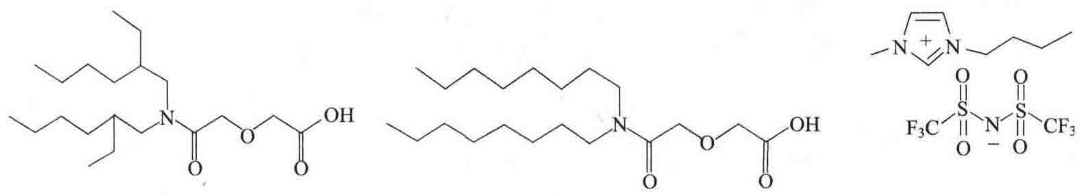
Recently, we reported efficient advanced extraction systems employing a novel extractant, DODGAA or DEHDGA, for the separation of rare earth metals from some transition metals such as Zn, Al and Fe in recycling processes[3].



The diglycol amic acid derivative extractants DODGAA and DEHDGA, which are composed of only C, H, O, and N atoms and have lower solubility in the aqueous phase than conventional commercial extractants such as PC-88A and D2EHPA, were developed. Additionally, they showed some advantages not shared by the commercial extractants. For example, they were readily soluble in ionic liquids such as [C4mim][Tf2N] and the metal ions could be completely stripped from the IL extracting phase using a dilute acid such as H_2SO_4, HCl or HNO_3. In this article, we examined the extraction of a series of rare earth metal ions from the acid leaching solution using IL systems in the separation and recovery of the different types of rare earth secondary resources[4].

2 Experimental

The recovery of rare earth metals from phosphor powders was examined. Leaching from a phosphor powder was carried out in two stages using the acid solution (5 M) as mentioned above. The first and second stage leaching solutions were prepared as feed solutions by diluting with sterile distilled water and adjusting the pH with 1 M NaOH solution. Extraction of metal ions from the feed aqueous solution to the IL [C4mim][Tf2N] phase containing desired concentration of DODGAA was performed. And performance evaluation of the diglycol amic acid DEHDGA functional XAD-type resin was carried out for the recycling and separation of the Lu (III) rare earth secondary resource from simulated leaching and real leaching solutions. These are discussed in terms of optimizing components of the recycling and separation process of Lu (III), such as the pH conditions of the mother liquor, solid-to-liquid ratio, extraction time, and operating temperature. Moreover, we also evaluated the recycle ability of the diglycol amic acid functional XAD-type resin. The molecular structures of extractants and the ILs used are shown in Fig. 1.



(A) DEHDGA (B) DODGAA (C) [C4mim][Tf2N]

Fig. 1 Structures of diglycol amic acid derivative extractants [(A) and (B)] and the ionic liquid (C)

3 Results and Discussion

3.1 Recovery of rare earth metals from leaching solutions of waste phosphor powder

The practical application for recovery of rare earth metals are investigated using leaching solutions of waste phosphor powder by IL-based DODGAA system. As shown in Fig. 2, IL [C4mim][Tf2N] containing extractant DODGAA, which exhibited a high affinity for rare earth metal ions, was applied as an extracting solvent. The rare earth metals such as Y, Eu, La and Ce were extracted selectively against some metal impurities such as Fe, Al, Zn, whereas in the conventional PC-88a system, separation of rare earth metals from same metal impurities was difficult[2]. Fig. 3 demonstrates the conceptual diagram based on the experimental results for the recovery of rare earth metals from waste phosphor powder of fluorescent lamps. The selective recovery of rare earth metals was possible from the leaching solutions by solvent extraction employing the IL-based DODGAA systems.

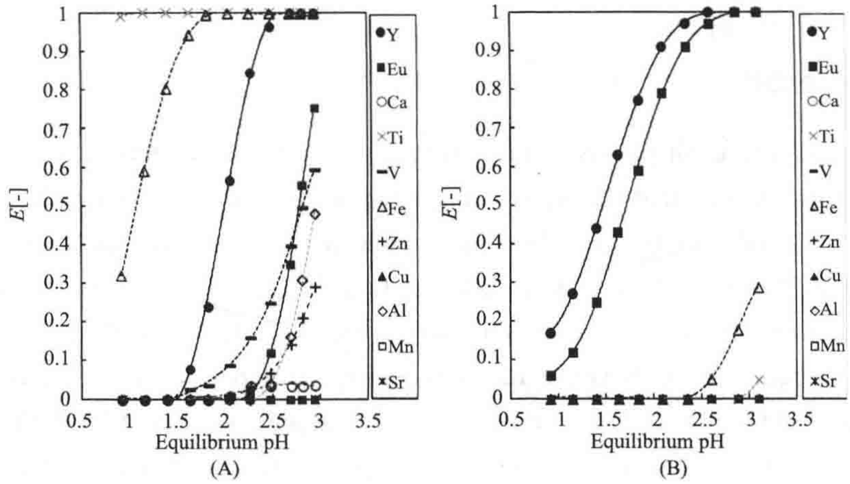


Fig. 2 Extraction behavior of metal ions dissolved in the simulated first-stage leaching solution: (A) PC-88A in *n*-dodecane system, (B) DODGAA in [C4mim][Tf2N] system. Feed phase: $[M_i]$ = 10 ppm, $[SO_4^{2-}]$ = 0.05 M; Extracting phase: [Extractant] = 10 mM, 30℃

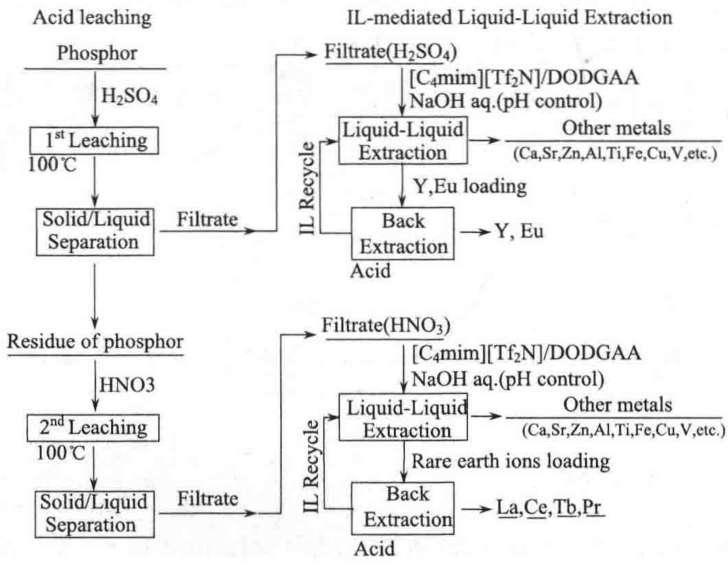


Fig. 3 Conceptual flowsheet for recovery of rare earth metals from waste phosphor powder of fluorescent lamps by wet process

3.2 Recovery of rare earth metals from leaching solutions of waste LYSO

Furthermore, recovery of high-value rare earth metals lutetium(Lu) are carried out from leaching solutions of waste LYSO using XAD-4 Resin-based DEHDGA-IL system. As shown in the following figures, XAD-4 Resin containing a diglycol amic acid derivative extractants DEHDGA and IL [C4mim][Tf2], which exhibited a high affinity for rare earth ions was used. Compared with that of the traditional CHON-type extractants, such as HTTA or CA-12, recovery rate of Lu(III) ions was significantly improved by using the DEHDGA-mediated resin system(Fig. 4). The conceptual flowchart for the process is shown in Fig. 5 which includes microwave-assisted hot acid leaching and resin adsorption technology. The $D_2EHDGAA$ functional XAD-type resin systems were prepared using the IL-immersion method, and $[C_4mim][Tf_2N]$-based $D_2EHDGAA$ impregnated XAD-4 resin demonstrated not only a promising recycling performance for the Lu rare earth secondary resource, but also a satisfactory thermal separation stability performance.

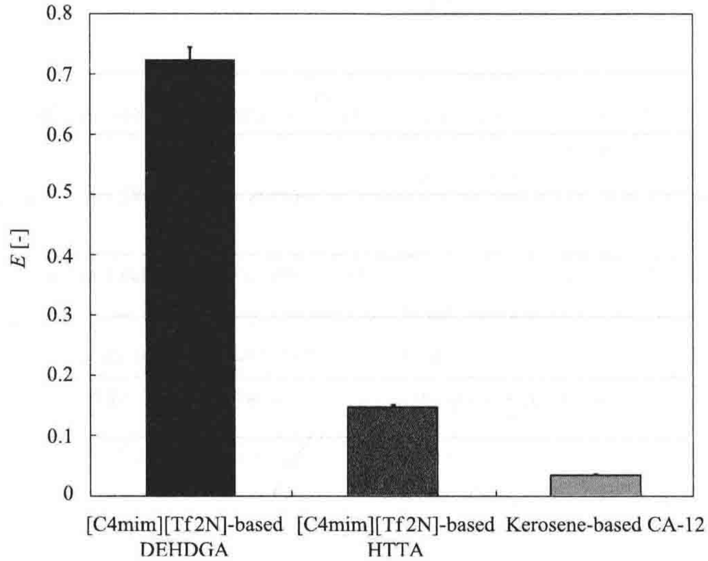


Fig. 4 The result of different CHON-type extractants for recycling of Lu rare earth secondary resources. The real leaching solution was used (Lu: 100 ppm and Y: 4.64 ppm): containing 50 mM of extractant, a solid-to-liquid ratio of 50 mg/ml, pH 1.4, and extraction time of 12 hrs at room temperature

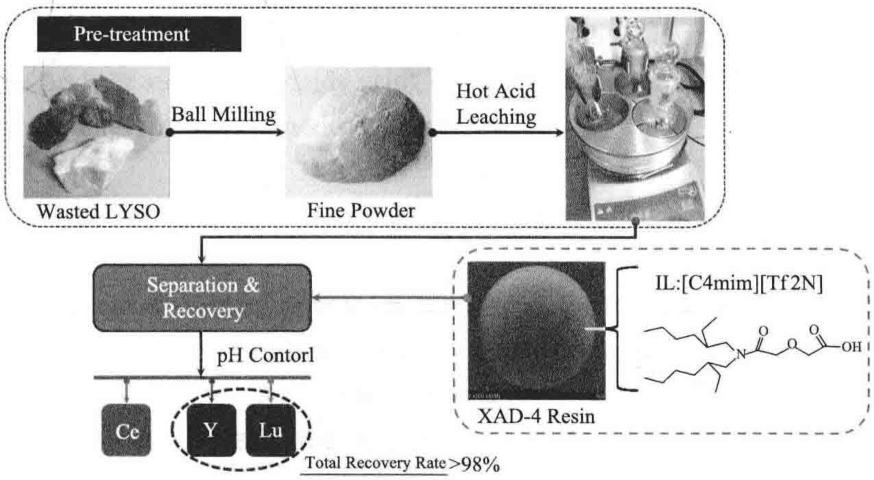


Fig. 5 Conceptual flowchart for recovery of Lu rare earth secondary resource from waste LYSO using a wet process and diglycol amic acid functional XAD-type resin

4 Conclusions

In future, the promising IL-based derivative extractant system will be applied to the practical recovery of rare earth secondary resources, especially for the recovery of Lu, in the waste and resources recovery industry.

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