



Removal of Al, Fe and Si from complex rare-earth leach solution: A three-liquid-phase partitioning approach



Na Sui^{a,b}, Kun Huang^{a,*}, Jieyuan Lin^{a,b}, Xiaopei Li^{a,b}, Xiaoqin Wang^{a,b}, Chuanxu Xiao^{a,b}, Huizhou Liu^{a,*}

^a State Key Laboratory of Biochemical Engineering, Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China

^b University of Chinese Academy of Sciences, Beijing 100049, PR China

ARTICLE INFO

Article history:

Received 18 November 2013
Received in revised form 17 February 2014
Accepted 22 February 2014
Available online 12 March 2014

Keywords:

Three-liquid-phase partitioning
Fe, Al and Si
Rare earths
Group separation

ABSTRACT

A new strategy was suggested to remove Fe, Al and Si impurities from rare-earth leach solution by controlling partitioning and selective enrichment of those impurities and rare earths in three-liquid-phase systems. Experimental results indicated that aqueous pH value and addition of water-soluble complexing agents or their mixtures into initial aqueous solution have significant influence on three-liquid-phase partitioning of Fe, Al, Si and rare earths. When only 1,10-phenanthroline was added, Fe and Si can be “filtered” into PEG-rich middle phase of three-liquid-phase system (Cyanex 272/PEG 2000/(NH₄)₂SO₄-H₂O) without affecting separation of heavy and light rare-earth ions in top organic and bottom salt-rich phase, respectively. Al remained in bottom phase. However, addition of EDTA and 1,10-phenanthroline promoted enrichment of Fe, Al and Si into PEG-rich middle phase, and almost all of rare earths were concentrated in salt-rich bottom phase. Those rare earths in salt-rich phase after removal of impurities can be further separated by another three-liquid-phase system of Cyanex 272/PEG 600/(NH₄)₂SO₄-H₂O. Heavy, middle and light rare earths, Yb, Eu and La, can be selectively enriched into different liquid phases. Therefore, separation of non-rare-earth impurities from rare earths, and then between light, middle and heavy rare earths can be achieved by two stages of three-liquid-phase partitioning. The present work highlights three-liquid-phase system can be a potential separation media for removal of Fe, Al, Si from complex rare-earth leach solution and group separation of different target metals into different liquid phases.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Rare earths (REs) are very important strategic metals for modern high technology application [1]. In practical processes for extraction and separation of rare earths, the interference from non-rare-earth impurities, such as Fe, Al and Si, is always unavoidable [2]. For example, the existence of those impurity ions always results in serious emulsification in traditional solvent extraction, making separation efficiency between rare-earth ions dropping [3]. In order to achieve group separation and purification of rare earths effectively, it is required to remove those impurity ions from rare-earth leach solutions before separation. However, removal of Fe, Al, Si and purification of rare earths by traditional precipitation with chemical reagents, alkali neutralization, ion exchange resin or solvent extraction are always inefficient due to low content of target rare-earth ions in initial feed-in solutions and the partition

behaviors of those non-rare-earth ions are similar with those of rare-earth ions [4]. Those methods reported in literatures have some unconquerable limitations. The precipitation may bring about lower recovery of target products. The severe loss of rare earths is unavoidable in the process of alkali neutralization. The co-precipitation of Fe, Al and Si with rare earths may easily occur [5], which is bound to cause high consumption of chemical reagents and high processing cost. In addition, possible environmental pollution from raffinates might happen with the application of oxalate if the reactions were controlled improperly. The extraction-elution resin method is not economically feasible when the concentrations of Fe, Al and Si are comparatively high. And traditional solvent extraction has no selectivity for impurity ions and rare-earth ions. For instance, in the extraction process of rare-earth ions from rare-earth chloride aqueous solution by 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A), part of Al can be co-extracted with rare-earth ions [6]. On the other hand, the extraction order of metal ions from hydrochloric acid medium follows as Sc³⁺ > Fe³⁺ > Lu³⁺ > Yb³⁺ > Er³⁺ > Y³⁺ > Ho³⁺ [7]. Therefore, Fe is readily to be co-extracted into organic phase by

* Corresponding authors. Tel.: +86 (10) 82544910; fax: +86 (10) 62554264 (K. Huang). Tel./fax: +86 (10) 62554264 (H. Liu).

E-mail addresses: khuang@ipe.ac.cn (K. Huang), hzliu@ipe.ac.cn (H. Liu).

di(2-ethylhexyl)phosphoric acid. Consequently, pretreatment of the feed-in solutions and multiple steps of two-phase equilibria are indispensable in rare-earth extraction and purification processes.

Three-Liquid-Phase Extraction (TLPE) is a new technique by using a three-liquid-phase co-existing system to simultaneously separate multiple target components. Owing to increase of equilibrating phase number [8], TLPE exhibits obvious separation advantages over traditional solvent extraction. The three liquid phases co-existing in Three-Liquid-Phase System (TLPS) have different physicochemical properties and phase structures, so as to create different separation selectivity for different target components. Different components can be separated and enriched into different liquid phases in TLPS. The TLPS, composed of an organic phase and polymer-based aqueous two phases, have been confirmed that it is especially suitable for simultaneous separation of three or more target metals by only one-step extraction. As for the complicated solutions containing multiple target metals, simultaneous extraction and group separation of different metals can be realized in TLPS by extracting or leaving them in different phases. The PEG-based TLPS has an application in separation of Ti(IV), Fe(III) and Mg(II) [9]. Ti(IV) and Fe(III) could be extracted into trialkylphosphine oxide (TRPO)-rich organic top phase and poly(ethylene glycol) (PEG)-rich middle phase, respectively, with adjustment of pH and addition of ethylenediaminetetraacetic acid (EDTA), while Mg(II) remained in salt-rich bottom phase. Enhancing separation of Fe(III), Ti(IV) and Mg(II) has been achieved by reduction of Fe(III) to Fe(II) followed by the coordination with 1,10-phenanthroline (phen). The results confirmed that Fe was extracted into PEG-rich phase with a mass fraction nearly 100% [10]. The TLPS consisting of diisooamyl sulfide (S201)/polyethylene oxide–polypropylene oxide random block copolymer (EOPO)/Na₂SO₄–H₂O has been employed to separate platinum group metals such as Pt(IV), Pd(II) and Rh(III) [11]. The mass fraction of Pd(II) extracted into S201 organic top phase reached 99 wt%. The distribution percentage of Pt(IV) enriched into EOPO-rich middle phase was about 90 wt%, and 95 wt% of Rh(III) was left in Na₂SO₄–H₂O bottom phase, respectively. Our previous work demonstrates that it is possible for group separation of light, middle and heavy rare earths by TLPS of Cyanex 272/PEG/(NH₄)₂SO₄–H₂O [12]. Three rare earths, La, Eu and Yb, were selected as typical elements to represent light, middle and heavy rare-earth group. It was found that La was concentrated in salt-rich bottom phase, Eu into the PEG-rich middle phase and most of Yb extracted into Cyanex 272 organic top phase. In fact, group separation of six rare earths, La, Ce, Eu, Gd, Yb and Lu, was also conducted by proposed TLPS. Similar results were obtained. Most of La and Ce remained in salt-rich bottom phase. Yb and Lu were extracted into organic top phase. Eu and Gd were transferred into polymer-rich middle phase. However, the practical leach solution of rare-earth minerals usually contains non-rare-earth impurity ions, such as Fe, Al and Si. The previous works did not consider the influence from those impurity ions on three-liquid-phase partition behaviors of rare earths. The partitioning of rare earths may be difficult to control in the presence of impurities, such as Fe, Al and Si. In fact, the existence of Fe, Al and Si may disturb selective partitioning of light, middle and heavy rare-earth ions in three-liquid-phase systems. Therefore, it is necessary to investigate partitioning and enrichment behaviors of Fe, Al and Si impurities in three-liquid-phase extraction processes [13–15].

The aim of present work is focused on developing a new approach of TLPE to control different partition behaviors of impurities, Fe, Al and Si, and rare-earth ions into different liquid phases, respectively. In addition, it is expected to achieve enrichment of those non-rare-earth ions into one of the liquid phases without affecting extraction and separation of rare earths. The influence of initial aqueous pH value and complexing agents on partitioning

of Fe, Al and Si in TLPS of Cyanex 272/PEG 2000/(NH₄)₂SO₄–H₂O, and the influence from three-phase partitioning of Fe, Al and Si on separation of rare earths were investigated. The present work is a promising exploration to employ the new technique to remove Fe, Al and Si impurities from leach solution containing multiple rare earths, so as to achieve group separation of different target metals.

2. Materials and methods

2.1. Chemicals and reagents

Bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272, purity of 85 wt%) was kindly supplied by Cytec Canada and used as received. Polyethylene glycol (PEG) with average molecular weight of 600 and 2000 (denoted as PEG 600 and PEG 2000, respectively) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. The salt stock solution (40% w/v (NH₄)₂SO₄) was prepared by dissolving an appropriate mass of solid (NH₄)₂SO₄ in deionized water. Stock solution of La(III), Eu(III) and Yb(III) were prepared following procedures of previous report [12]. Three rare earths, La, Eu and Yb, were selected as typical elements to represent light, middle and heavy rare-earth group. Stock solutions of Fe(III) and Al(III) were prepared by dissolving their analytical chlorides in dilute hydrochloric acid. Stock solution of Si(IV) was prepared by dissolving sodium silicate in dilute sodium hydroxide. The initial concentrations of Fe(III), Al(III) and Si(IV) in aqueous solutions were 15 mmol/L, 30 mmol/L and 25 mmol/L, respectively, according to the analytic results of Fe, Al and Si in rare-earth leaching solution obtained from China minmetals rare earth Co. Ltd. Hydroxylamine hydrochloride was selected as reducing agent of Fe(III) and its solution (11.5 mmol/L) was prepared by dissolving hydroxylamine hydrochloride in deionized water. Ethylenediamine tetraacetic acid (EDTA) was used as a complexing agent, which was dissolved in deionized water. The concentration of EDTA was 0.17 mol/L. 1,10-Phenanthroline (phen) was chosen as another complexing agent, and the solution (35 mmol/L) was prepared by dissolving certain amount of 1,10-phenanthroline hydrochloride in deionized water. All other chemicals were of analytical grade.

2.2. Three-liquid-phase extraction and separation

The Fe, Al, Si and La, Eu, Yb stock solutions, respectively of 1 mL, were mixed together in graduated centrifugation tubes. 1 mL of hydroxylamine hydrochloride solution was added. Then the stock solutions of phen or EDTA were also added when necessary. Detailed experimental procedure and formation of three-liquid-phase system can be referred in our previous work [12].

2.3. Determination of Fe, Al, Si, La, Eu and Yb and their partitioning

After phase separation, the concentration of Fe, Al, Si, La, Eu and Yb in polymer-rich phase and salt-rich phase were analyzed by an OPTIMA 5300 DV inductively coupled plasma optical emission spectrometer (ICP-OES, PekinElmer, USA) at the wavelength of 238.2 nm, 396.2 nm, 251.6 nm, 398.9 nm, 382.0 nm and 328.9 nm, respectively. The concentrations of metal ions in organic top phase were calculated from mass balance. The metal extraction experiments followed by analysis of samples were conducted several times to check repeatability and accuracy of measurements. The error in analysis was within ±3%.

The mass fractions of metal ions in each phase of TLPS can be calculated according to following equations. Mass fractions of metal ions in organic top phase, polymer-rich middle phase and salt-rich bottom phase were expressed as follows:

Download English Version:

<https://daneshyari.com/en/article/641357>

Download Persian Version:

<https://daneshyari.com/article/641357>

[Daneshyari.com](https://daneshyari.com)