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ACS Sustainable Chem. Eng., **Just Accepted Manuscript** • DOI:
10.1021/acssuschemeng.7b01682 • Publication Date (Web): 21 Jul 2017

Downloaded from <http://pubs.acs.org> on July 28, 2017

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Enrichment of low concentration rare earths from leach solutions of ion-adsorption ores by bubbling organic liquid membrane extraction using N1923

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ABSTRACT

A new bubbling organic liquid membrane extraction using primary amine N1923 at large aqueous-to-oil phase ratios was suggested to extract and enrich extremely low concentration rare earths from the acidic sulfate leach solutions of ion-absorbing type rare-earth ores. It was revealed that bubbling organic liquid membrane extraction was in fact an interfacial chemical reaction of organic extractant molecules absorbing at the surface of organic liquid membrane supported by gas bubbles with the target metal ions in the aqueous solutions. Rare earths with concentration about 100 mg/L can be extracted selectively and enriched efficiently into the organic extractant liquid membrane layer covered on the surface of dispersed gas bubbles. However, Al in leach solutions was not extractable and remained in the raffinate, due to a kinetic non-equilibrium separation behavior of rare earths and Al on the surface of organic liquid membrane. It was the differences in reaction rate of rare earths and Al with primary amine N1923 that intensified their separation. The separation coefficient of rare earths to Al could reach 44.89. The extraction raffinate, flowing-out from the extraction tower after large-phase-ratio extraction, contains aluminium sulfate and can be returned back to displace traditional ammonium sulfate for performing in-situ leaching of rare earths from the ion-adsorption ores. The leaching percentage of rare earths was high up to 84.4%. The present work highlights an environmentally friendly and green sustainable new approach to treat the ion-adsorbing type rare-earth ores by combining leaching and solvent extraction processes together to solve the problems from ammonia and nitrogen pollution during traditional processes using ammonium sulfate to leach rare-earth ores and ammonium bicarbonate to precipitate rare earths.

KEYWORDS: Bubbling organic liquid membrane extraction; Ion-absorbing type rare-earth ores;

44 N1923; Rare earths; Al

45

46 INTRODUCTION

47 Ion-absorbing type rare-earth ores are rich in South China.¹⁻³ Because of its containing
48 almost all of rare earth elements (REEs) and especially high content of middle and heavy rare earths,
49 extraction and separation of rare earths from ion-adsorption ores have attracted extensive attention in
50 the past decades.⁴⁻⁶ Up till now, in-situ leaching of rare earths from ion-adsorption ores by acidic
51 $(\text{NH}_4)_2\text{SO}_4$ solution has been a main technique popularized in China.⁷⁻⁹ However, the content of
52 aluminum oxide (Al_2O_3) in the ion-adsorption ores in South China are always above 15%.¹⁰
53 Therefore, the acidity of $(\text{NH}_4)_2\text{SO}_4$ aqueous solutions employed to leach ion-adsorption ores could
54 not be so high, in order to prevent the leaching of Al and other impurities.¹¹⁻¹³ Decreasing the acidity
55 of leaching aqueous solutions usually results in incomplete leaching of rare earths, and produces a
56 large amount of aqueous solutions containing low concentration rare earths. The weather in Southern
57 China is rainy, so that the concentrations of rare-earth ions in the leach solution are extremely low,
58 generally being less than 0.5 g/L, or even lower for leaching of tailings.¹⁴ As for an example, the
59 concentrations of rare earths in the leaching solutions of the tailings from Ganzhou, Jiangxi Province,
60 are even less than 100 mg/L. In order to improve the leaching of rare earths, increasing the added
61 dosage and the acidity of $(\text{NH}_4)_2\text{SO}_4$ leaching solution were required. However, that might result in
62 the increase of Al leaching in the solutions and a large number of ammonium sulfate remaining in the
63 tailing ores, and bring about serious ammonia- nitrogen pollution towards environments.¹⁵⁻¹⁷

64 Recently, chemical precipitation¹⁸⁻²⁰ and ion-adsorption²¹⁻²³ are widely adopted for enrichment

of low concentration rare earths from the leaching solutions of ion-adsorption ores. The ion-adsorption method is simple and easy to be operated. However, the saturated adsorption capacity is low, and the adsorption rate is slow. In addition, the regeneration of the adsorbent for reusing need to be further investigated. Chemical precipitation is a main method widely employed in industrials. The specific technical processes to enrich rare earths from the leaching solutions of ion-adsorption ores by chemical precipitation are described in Fig.1. Rare earths can be precipitated using oxalic acid or ammonium bicarbonate. The rare-earth mixtures precipitated are forwarded to refinery for separation of single rare-earth products. However, chemical precipitation is not economic for enrichment of rare earths with extremely low concentrations in the leaching solutions of ion-adsorption ores. Generally, the cost for rare-earth precipitation accounts for 30% of the total cost for production of per tons of rare-earth oxides. The consumed chemical agent increases when the concentrations of rare earths in leaching aqueous solutions are extremely low, and in most cases, precipitation of rare earths were incomplete when some soluble slats formed between rare-earth ions and K^+ and Na^+ ions. Furthermore, the precipitated particles might be hard to be separated and recovered due to its fine size. Therefore, the total percent recovery for rare earths by chemical precipitation is very low. The separation selectivity for rare earths is also poor during precipitation processes, especially when aluminum ions co-exists in solutions. Almost all of aluminum ions co-precipitate with rare-earth ions. The co-precipitation of aluminum and rare earth ions decrease the purity of final rare-earth products and increase the cost of subsequent purification significantly.

In order to solve the problem of Al co-precipitation with rare earths, pre-precipitation of Al is usually employed by adding ammonium bicarbonate and adjusting the aqueous pH values to remove

Al previously from the leaching solution, as shown in Fig.1.²⁴ Most of Al could be removed during the process of pre-precipitation. However, previous experiments indicated that the pre-precipitation process is difficult to be controlled, and about 5 to 15% of rare earths were lost with the pre-precipitation of Al.

Figure 1. The traditional precipitation method for extraction of rare earths from the in-situ leach solutions of ion-adsorption ores

Solvent extraction has ever been employed for separation and extraction of rare earths from the ion-adsorption ores.²⁴⁻²⁶ As depicted in Fig.2, rare earths can be extracted and enriched into the organic phase, either directly from the leaching solution of the ores, or from the solution after pre-precipitation of Al impurities. The rare earths loaded in the organic phase are stripped and further enriched into the stripping solution. Then, rare earths in the stripping solution can be precipitated by ammonium bicarbonate or oxalic acid for subsequent refinery. However, separation and extraction of rare earths directly from the leach solution of the ion-adsorption ores by traditional solvent extraction

is not economic, and it is difficult for enrichment of rare earths with extremely low concentrations in the feed-in aqueous solution, due to the aqueous-to-oil phase ratios in traditional equipment are extremely low. On the other hand, although solvent extraction has obvious advantage over traditional chemical precipitation for selective separation of other co-existed impurities, especially for removal of Al, the final rare-earth products still contain a small amount of Al, due to unavoidable co-extraction of Al with rare earths in traditional solvent extraction process. In order to ensure a higher percent extraction for rare earths, P507 and other acidic phosphoric extractant must be saponified previously. However, a large amount of wastewaters containing emulsified oil and high concentration of salts will be generated and might cause serious environmental pollution.

Figure 2. Solvent extraction of rare earths from the in-situ leach solutions of ion-adsorption ores

Previous literatures reported that primary amine N1923 can be employed to displace P507 for preventing the co-extraction of Al. Rare earths can be extracted efficiently from the acidic sulfate

aqueous solutions, while Al remains in the raffinates.²⁷⁻²⁹ Therefore, separation of rare earths from Al and other impurities can be achieved. In addition, saponification was not required by using N1923. The pollution from ammonia, nitrogen and phosphorus can be avoidable. However, previous works were all carried out in traditional extraction equipment, such as in mixer-settler, which is not suitable or at least not economic for treating the leaching solutions of ion-adsorption ores containing extremely low concentration rare earths. Repeated equilibrating operations aimed to remove co-existed impurity ions, and/or to decrease the final rare-earth concentrations in the raffinates make the processes costly. Operation at large aqueous-to-oil phase ratios might be difficult and easily to cause severe emulsion and loss of organic extractants. The raffinates contained emulsified oil or organic extractant might create new pollution to the environment. Therefore, development of new methods for extraction and enrichment of rare earths with extremely low concentrations in the leaching solutions of ion-adsorption ores, not only can remove impurity Al, but also prevent ammonia and nitrogen pollution, are needed.

Our previous works suggested a new bubbling organic liquid membrane extraction technique at large aqueous-to-oil phase ratios for extraction and enrichment of rare earths with extremely low concentrations in the leach solutions of ion-adsorption ores.³⁰⁻³⁵ The pilot experiments demonstrated that the aqueous-to-oil phase ratios of the new technique could reach more than 600:1, and the final residual total concentration of rare earths in the raffinates decreased to less than 0.01 mg/L, even the initial rare-earth concentrations in the feed-in aqueous solutions were below 100 mg/L. Rare earths could be extracted efficiently with large enrichment ratios into the organic liquid membrane of extractant, P507, covered on the surface of dispersed gas bubbles. That novel extraction technique

136 solves the difficulty to extract and enrich rare earths with extremely low concentrations in the acidic
137 sulfate leach solutions of ion-adsorption ores.

138 The aim of present work is to explore whether primary amine N1923 can be employed to
139 displace P507 for performing bubbling organic liquid membrane extraction at large aqueous-to-oil
140 phase ratios to extract and enrich rare earths with extremely low concentrations in the acidic sulfate
141 leach solution of ion-adsorption ores. The extraction and enrichment of rare earths, especially the
142 behavior of impurity Al, during the processes of bubbling organic liquid membrane extraction were
143 investigated. Another aim of the work is detect whether Al can be removed efficiently and remained
144 in the raffinates after bubbling organic liquid membrane extraction, and whether the raffinates
145 containing aluminum sulfate can be returned to displace ammonia sulfate for leaching of the
146 ion-adsorption ores. The leaching efficiency of rare earths using the raffinates from large-phase-ratio
147 extraction was compared with the traditional processes using ammonia sulfate. The present work
148 highlights a novel approach to treat the rare-earth ion-adsorption ores by combining leaching and
149 solvent extraction processes together to solve the problems from ammonia and nitrogen pollution
150 during traditional processes using ammonium sulfate to leach rare-earth ores and ammonium
151 bicarbonate to precipitate rare earths.

152

153 **EXPERIMENTAL SECTION**

154 **Chemicals and Reagents.**

155 The experimental feed-in aqueous solutions were the in-situ leaching solutions from the
156 ion-absorbing type rare-earth ores in Dongjiang, Longnan, Ganzhou, Jiangxi, PRC., kindly provided

by Ganzhou Rare Earth Group Co. Ltd.. Before using, the in-situ leaching solutions were filtered with an industrial microporous filter (0.45 micron) to remove the tiny mineral particles suspending in them.

The total RE₂O₃ content in the samples of rare-earth ores was 0.028 wt%, in which the ion phase of the RE₂O₃ in the rare-earth ores sample was 80.27 wt%. The chemical analysis of the leaching solutions are given in Table 1.

Table 1. Chemical analysis of the leach solutions of ion-adsorption ores

Elements	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
Concentration /(mg/L)	64.09	3.47	0.51	1.63	9.06	5.26	<0.1	10.13	1.53
Elements	Dy	Ho	Er	Tm	Yb	Lu	TRE*	Al	pH
Concentration /(mg/L)	8.36	1.75	5.12	0.76	4.62	0.40	116.68	27.70	4.45

Note: TRE-total concentration of rare earths in the leach solutions

Industrial-grade of primary amine N1923, purchased from Xiamen Pioneer Technology Co., Ltd., was used as the organic extractant. Sec-Caprylic alcohol, purchased from Sinopharm Chemical Reagent Co., Ltd., was used as the co-extractant. Kerosene, purchased from China Petrochemical Corporation (Sinopec Group), was used as the diluent. All of those organics were used as received, without further purification.

The stock organic solutions were prepared by mixing N1923 with sec-Caprylic alcohol and kerosene. The volume concentrations of N1923, and sec-Caprylic alcohol in the stock organic solutions were 20% and 10%, respectively.

Industrial-grade of sulphuric acid and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd.. The other chemicals were of analytical grade.

176

177 **Experimental Apparatus.**

178 All experiments were conducted at room temperature in a large-phase-ratio bubbling organic
179 liquid membrane extraction tower reported in previous works.³⁴

180

181 **Experimental Procedures.**

182 *Single-tower extraction.*

183 50 L of the stock organic solutions and 150 L of the rare-earth leaching solutions were
184 employed for single-tower extraction experiments. First, air was blown into the extraction tower
185 from the bottom inlet. The volume flow rate of air was 0.1 m³/h. And then, 150 L of the leaching
186 solution was pumped into the tower from the top inlet. When gas bubbles were blown out from the
187 top end of gas needles stably, the organic solution was pumped into the organic bubble film generator
188 from the inlet of organic phase at the bottom of the extraction tower, so that the so called organic
189 bubbles, on the surface of which were covered a thin layer of organic extractant liquid membrane,
190 could be blown out from the nozzles. The volume flow rate of the organic phase and the aqueous
191 phase were respectively 30 L/h and 100 L/h. After phase contacting, the organic bubbles were
192 destroyed when they passed through the organic phase demulsification section, and agglomerated
193 together to form a continuous organic bulk phase, and then the loaded organic phase overflowed
194 from the outlet at the top of the extraction tower. The loaded organic phase was re-pumped into the
195 organic bubble film generator from the inlet at the bottom of the extraction tower.

196 In those experiments, both the aqueous solution and organic phase passed through the extraction
197 tower circularly, but not been discharged out of the tower until final equilibrium. Aqueous samples in
198 the tower were taken at different times from the raffinate outlet.

199

200 ***Countercurrent double-tower extraction.***

201 100 L of the stock organic solutions and 300 L of the rare-earth leaching solutions were
202 employed for double tower extraction experiments. Two single towers were connected in cascade for
203 performing countercurrent double tower extraction, as shown in Fig.3. The 300L of the rare-earth
204 leaching solutions was pumped into the first tower, then flew into the second tower, and finally
205 discharged out of the towers. At the same time, 100L of the stock organic solution was pumped into
206 the second tower, then flew into the first one, and finally back to the second. The organic solution
207 pass through the two towers circularly, but the rare-earth leaching solution passed through the towers
208 only once and discharged out of the towers directly. Other procedures were the same as described
209 previously. The volume flow rate of the organic phase and the aqueous phase were respectively 30
210 L/h and 100 L/h. The volume flow rate of air was 0.1 m³/h. The aqueous samples flowing out from
211 the raffinate outlet of the second tower were taken at different times for analysis of rare earths and Al.
212 The experimental apparatuses are depicted in Fig.3.

Figure 3. Countercurrent double tower extraction

Re-using of the organic phase after stripping.

In experiments, when the concentrations of rare earths in the organic phase reached 3g/L, the loaded organic phase was discharged out of the extraction tower, and stripped using 1mol/L H_2SO_4 aqueous solutions for 2hrs. The regenerated organic phase after stripping was pumped back to the extraction towers for re-using. The operation and sampling methods were the same as described previously.

Re-using of the raffinates after bubbling organic liquid membrane extraction.

The aqueous solutions flowing out from the towers after bubbling organic liquid membrane extraction were employed for leaching of the rare-earth ores again. First, a required amount of dry rare-earth ore powder were added into a hollow glass column, under which was connected a sand

core funnel to avoid the ores flow out of the glass column but simultaneously to permit the aqueous solution pass through. The inner diameter of the glass column was 30mm, and the height was 320 mm. Then, a required volume of the raffinates discharged out of the extraction towers after bubbling organic liquid membrane extraction were sprayed into the top of the glass column to pass through the ores. In each experiments, the aqueous solution employed for leaching of the rare-earth ores were previously added into a certain amount of aluminum sulfate, and the mass concentration of aluminum sulfate in the aqueous solution was adjusted to 0.58 wt%. The pH value of the aqueous solution was 3.5. The aqueous samples flowing out from the bottom of the glass column were taken at different times for analysis of rare-earth concentrations. The experimental apparatus was depicted in the Fig.4.

Figure 4. Leaching ion-adsorption ores using the raffinates from bubbling organic liquid membrane extraction

Experimental Analysis.

The concentration of rare earths and Al in the aqueous samples was analyzed by an Agilent 7900 ICP-MS system (Agilent Technologies, USA). A pH meter (pH211, HANNA, Italy) was used to determine the pH values of the aqueous solutions.

RESULTS AND DISCUSSION

Single-tower Extraction.

Fig.5 depicts the final residual concentrations of various rare-earth ions and total rare earth concentration in the aqueous solution flowing out from a single tower, when the feed-in aqueous solution and organic phase passed through the extraction tower circularly and were not discharged out of the tower. As shown in Fig.5, the total concentration of rare earths could decrease to below 0.1 mg/L after extraction equilibrium. Extraction of rare earths with extremely low concentrations was feasible by organic extractant liquid membrane covered on the surface of dispersed gas bubbles, even the initial feed-in concentrations were less than 100 mg/L. However, Al in the feed-in leaching aqueous solution could not be extracted. After extraction for 13 hrs, the concentration of Al in the raffinate still remained at 28.3 mg/L, almost the same as its initial concentration in the feed-in aqueous solutions. Compared to traditional solvent extraction by mixer-settlers, the suggested new method by bubbling organic liquid membrane extraction could separate rare earths from impurity aluminum efficiently. The separation coefficient of rare earths to Al could reach 44.89, while in traditional mixer-settler, the separation coefficient is only 1.99. During the processes of enrichment of rare earths from the leaching aqueous solutions, aluminum remained in the final extraction raffinate.

Figure 5. The concentrations of rare earths and Al in the flowing-out aqueous solutions from a single tower
(The feed-in aqueous solution and organic phase passed through the extraction tower circularly. Both of them were not discharged out of the tower. The volume flow rate of the feed aqueous phase was 100 L/h. The volume flow rate of the organic phase was 30 L/h. The volume flow rate of air was 100 L/h. TRE means the total concentrations of rare earths.)

As we known, N1923 could separate rare earths and Al in sulfuric acid solutions.²⁷ However, in the traditional processes by mixer-settlers, such a separation was difficult. Part of Al still transferred into the organic phase, due to its poor separation coefficient. We supposed that the reasons why rare earths could be selectively extracted, but almost all of aluminum left, by using the suggested bubbling organic liquid membrane extraction, may be attributed to a kinetic non-equilibrium separation between rare earths and Al. It is the difference in extraction rate of rare earths and Al that intensified the separation of rare earths from the aqueous solutions containing aluminum. The researches into extraction mechanism of rare earths by phosphonate ester extractant indicate that, three typical steps might be involved in the extraction: target metal ions diffuse and mass transfer

from aqueous bulk phase onto the interface of water and oil two phases, extractant molecule react with the target metal ions on the interface to form the extracted complexes, and then the extracted complexes formed on the interface transfer into the organic bulk phase. Generally, the diffusional mass transferring rate of metal ions from aqueous bulk phase to the interface, and the extracted complexes formed on the interface transfer into the organic bulk phase is the kinetic rate-controlling steps. Although the extractability of rare earths and Al are different, the difference in apparent extraction rate of rare earths and Al are hard to be controlled during the traditional processes by mixer-settlers. Therefore, the separation between rare earths and Al was poor, even using N1923.

The large-phase-ratio bubbling organic membrane extraction is conducted in a non-equilibrium extraction state. The organic extractant with extremely small volume is dispersed and spread on the surface of the gas bubbles, due to the surface activity of organic extractant molecules. The extraction of target metal ions is in fact conducted on the thin layer of the organic liquid membrane covered on the surface of dispersed tiny gas bubbles. Therefore, the contact area between aqueous and organic two phase play an important role in determining the extraction rate. The extraction rate depends mainly on the chemical reaction rate of extractant molecules and target metal ions on the surface of those tiny gas bubbles. The influence from the diffusion mass transferring process of the target metal ions from aqueous bulk phase onto the interface and the extracted complexes formed on the interface transfer into the organic bulk phase could be ignored. The chemical reaction rate of extractant molecules with aluminum is essentially less than that with rare-earth ions.²⁸ Therefore, the differences in reaction rate of rare earths and Al would be intensified during the processes of bubbling organic membrane extraction. That difference in reaction rate drives the separation of rare earths and Al efficiently, and most of Al were remained in the extraction raffinates.

Countercurrent Extraction using Double Towers Connected in Cascade.

In order to confirm the conclusion above, the experiments of countercurrent extraction using

double towers connected in cascade were performed. The results are depicted in Fig.6.

Figure 6. The concentrations of rare earths and Al in the flowing-out aqueous solutions from the double towers connected in cascade for countercurrent extraction

(The organic phase passed through the double towers circularly, but the feed aqueous solution passed through the double towers only once and were discharged out of the towers directly. The volume flow rate of the feed aqueous phase was 100 L/h. The volume flow rate of the organic phase was 30 L/h. The volume flow rate of air was 100 L/h. TRE means the total concentrations of rare earths.)

As can be seen from Fig.6, during the first 10hrs, the residual concentrations of rare-earth ions in the aqueous solution remain below 3 mg/L, and Al could not be extracted, as observed previously. However, after extraction for 12 hrs, the residual concentrations of rare-earth ions in the aqueous solution increased gradually, and part of Al was extracted. We supposed that this phenomenon might be attributed to the extraction of rare earth reaching its saturation capacity in organic phase. In our experiments, the organic phase pass through the two extraction towers circularly, but the rare-earth leaching solution passed through the towers only once and discharged out of the tower directly, therefore, the extraction rate of rare earths might be subject to the saturation capacity of rare-earth sulfates in the organic phase. As we known, the solubility of aluminum sulfate in N1923 organic

phase is larger than that of rare earth sulfates. Therefore, there occurs a competition between rare-earth and Al ions for N1923 molecules. Aluminum sulfate would displace rare earth sulfates appearing in the loaded organic phases. Such a competition was not obvious before the extraction of rare earths reaches its saturation capacity, due to the extraction rate of rare earths were faster than that of Al. Therefore, the concentration of Al ions in the extraction raffinates decreased only slightly.

In order to demonstrate above viewpoints, the loaded organic phase after extraction for 31 hrs was treated by using a mixed aqueous solution of 60%v/v NH_4Cl and 40%v/v hydrochloric acid. The total volume of the leaching aqueous solutions passed through the extraction tower is 3m^3 during 31 hrs. The experimental results for stripping of rare earths in the loaded organic phase is shown in Table 2.

Table 2. Stripping of rare earths from the loaded organic phases of countercurrent double-tower extraction

Operation	The first-stage	The second-stage
	stripping	stripping
Stripping time (hrs)	6	6
Rare-earth concentration in stripping solutions (g/L)	7.22	0.11
Al concentration in stripping solutions (mg/L)	14.30	4.38

Note: The total volume of the loaded organic phase for stripping is 100L. The stripping operation were performed twice. As for each time of stripping operation, the loaded organic phase was contacted with 50L of mixed aqueous solution of 60%v/v NH_4Cl and 40%v/v hydrochloric acid. The organic to aqueous phase ratios was 2:1.

From Table 2 we can see that there occurs a little amount of aluminum in the stripping solution, but the separation efficient of Al and rare earths is still larger than 31.47. In order to prevent the co-extraction of aluminum, the loaded concentration of rare earths in the organic phase should be

controlled below 3g/L. The aim is to ensure enough driving force for extraction of rare earths and separation of aluminum efficiently.

Table 2 also shows that the total rare-earth concentration in the stripping solution after first-stage stripping is 7.22 g/L, which means that the suggested large-phase-ratio bubbling organic membrane extraction can enrich rare earths more than 70 times, compared to its initial concentration in the leaching solution of ores. In addition, the content of aluminum in the final rare-earth products is only 0.25%, which is far lower than that obtained by traditional precipitation or solvent extraction in mixer-settler.

Recycling Utilization of the Regenerated Organic Phases.

Experiments on recycling for reusing the organic phase after stripping of rare earths were performed. Before each time of recycling, the regenerated organic phases were firstly acidified by 1 mol/L H₂SO₄ aqueous solutions. The experimental results are shown in Fig.7.

Figure 7. Recycling for reusing the regenerated organic phases for countercurrent extraction in the double towers connected in cascade

(The regenerated organic phases were passed through the double towers circularly, but the feed-in aqueous solution passed through the double towers only once and were discharged out directly. The percent stripping of rare earths in each time of recycling were kept about 95%. The volume flow rate of the feed aqueous phase was 100 L/hr. The volume flow rate of the organic phase was 30 L/hr. The volume flow rate of air was 100 L/hr. TRE means the total concentrations of rare earths.)

As can be seen in Fig.7, the regenerated organic phase still can enrich rare earths and separate Al efficiently. The rare-earth concentrations in the flowing-out aqueous solutions decreased to below 3 mg/L, when percent stripping of rare earths in each time of recycling were kept about 95%. After extraction for 21hrs, the rare-earth concentrations in the rafffinates increased a little to 5.30 mg/L. However, the concentration of aluminum in the flowing-out aqueous phase was still 20.4 mg/L, which is same as that in the initial leaching aqueous solutions of ores. Therefore, the regenerated organic phase can be reused for performing large-phase-ratio bubbling organic membrane extraction.

For each time of recycling, the loaded organic phase after extraction for 21 hrs was treated by using the mixed aqueous solution of 60%v/v NH_4Cl and 40%v/v hydrochloric acid. The total volume of the leaching aqueous solutions passed through the extraction tower is 2.1m^3 during 21 hrs. The experimental results of rare earth stripping is shown in Table 3.

Table 3. Stripping of rare earths from the regenerated organic phases for recycling

Operation	The first-stage stripping	The second-stage stripping
Stripping time (hrs)	6	6
Rare-earth concentration in stripping solutions (g/L)	4.46	0.06
Al concentration in stripping solutions (mg/L)	5.74	0.58

Note: The total volume of the loaded organic phase for stripping is 100L. The stripping operation were performed twice. As for each time of stripping operation, the loaded organic phase was contacted with 50L of

378 mixed aqueous solution of 60%v/v NH_4Cl and 40%v/v hydrochloric acid. The organic to aqueous phase ratios was
379 2:1.

381 From Table 3, we know that the total concentrations of rare earths in the first-stage stripping
382 solution is 4.46g/L, also were enriched more than 70 times. Similarly, the content of aluminum in the
383 final rare-earth products is only 0.14%, which is also far lower than that obtained by traditional
384 precipitation or solvent extraction in mixer-settler.

386 **Leaching of Rare-Earth Ores using the Raffinates from the Large-Phase-Ratio**
387 **Bubbling Organic Liquid Membrane Extraction.**

388 The extraction raffinates flowing-out from the extraction tower after large-phase-ratio bubbling
389 organic membrane extraction were reused for leaching rare-earth ores. During the processes of
390 leaching using above raffinates, aluminum sulfate would be consumed gradually. Therefore, before
391 using for leaching, a certain amount of $\text{Al}_2(\text{SO}_4)_3$ was added into the raffinates, and the mass
392 concentration of $\text{Al}_2(\text{SO}_4)_3$ in the aqueous solution was adjusted to 0.58 wt%. The experimental
393 results are depicted in Fig.8.

Figure 8. Leaching of rare-earth ores using the raffinates from the large-phase-ratio bubbling organic liquid membrane extraction

As can be seen in Fig.8, the bubbling extraction raffinates flowing-out from the extraction tower exhibit an excellent leaching behavior for ion-adsorption ores. After leaching for 9 days, the total concentration of rare earths in all the solution collected could reach 57.29 mg/L, and the leaching percentages of rare earth is high to 84.4%. Previous literatures indicate that it is feasible by using the aqueous solutions of aluminum sulfate to replace ammonium sulfate for leaching rare earths to reduce the consume of ammonium sulfate and avoid the pollution from ammonia and nitrogen.³⁷ Therefore, here in we suggest a new processing procedure to treat the ion-adsorption type rare-earth ores, as shown in Fig.9.

Figure 9. A suggested processing procedure for enrichment and separation of rare earths from the acidic sulfate leach solutions of ion-absorbing type rare-earth ores

Large-phase-ratio bubbling organic membrane extraction is suggested to extract and enrich rare earths with extremely low concentrations in the sulfate leach aqueous solutions of ion-adsorption ores. When the concentration of rare earths in the loaded organic phases reaches a certain value, such as 3 g/L, rare earths are stripped from the loaded organic phase, and the regenerated organic phase can be returned back for reusing. The extraction raffinates containing Al can be returned back for leaching of ion-adsorption ores.

During the processes of large-phase-ratio bubbling organic membrane extraction, the saponification of organic phase, N1923, is not required. The regenerated N1923 requires only to be acidified by 1 mol/L H₂SO₄ aqueous solutions before reusing, and therefore no ammonia and nitrogen pollution during the processes. In addition, the organic oil contents in the raffinates flowing

out from the towers after large-phase-ratio extraction were below 5 mg/L, COD were less than 50 mg/L, and the organophosphorus contents in the raffinates were below 0.3 mg/L. Therefore, such a kind of extraction raffinates containing $\text{Al}_2(\text{SO}_4)_3$ can be returned back to the leaching process to replace ammonium sulfate for leaching rare earths from ion-adsorption ores. No any wastewaters were generated in whole processes due to the recycling of extraction raffinates. Therefore, the new processes are environmentally friendly and are suitable to extract and enrich rare earths from the acidic sulfate leaching aqueous solution of ion-adsorption ores, even the leaching aqueous solution contains a large amount of Al impurities. Large-phase-ratio bubbling organic liquid membrane extraction can also be employed to treat the leaching aqueous solution of the tailing ores to avoid other heavy metal pollution in waste waters from the mining regions. It can be expected the new technique might has potential industrial application in the future.

CONCLUSIONS

In summary, the present work suggested an environmentally friendly and green sustainable new technique by combining leaching and solvent extraction processes together to treat the ion-absorbing type rare-earth ores. Extraction and enrichment of extremely low concentration rare earths from the acidic sulfate leach solutions of ion-adsorption ores could be achieved by performing a new bubbling organic liquid membrane extraction at large aqueous-to-oil phase ratios using primary amine N1923. Experimental results revealed that rare earths with extremely low concentrations about 100 mg/L can be enriched efficiently into the organic extractant liquid membrane layer covered on the surface of dispersed gas bubbles. The aqueous-to-oil phase ratios during the bubbling extraction processes

could reach more than 600:1, and the residual concentrations of rare earths in the flowing-out raffinates from the extraction towers were below 0.1 mg/L. The co-existing impurity ions, especially Al, in the acidic sulfate leach solutions cannot be extracted, and remained in the raffinates, due to a kinetic non-equilibrium separation behavior of rare earths and Al during the processes of bubbling organic liquid membrane extraction. It was the differences in reaction rate of rare earths and Al with primary amine N1923 that intensified their separation. The separation coefficient of rare earths to Al could reach 44.89. The extraction raffinate, flowing-out from the extraction tower after large-phase-ratio extraction, contains aluminium sulfate and can be returned back to displace traditional ammonium sulfate for performing in-situ leaching of rare earths from the ion-adsorption ores. The leaching percentage of rare earths was high up to 84.4%.

Large-phase-ratio bubbling organic membrane extraction can be employed to treat various aqueous solutions containing low concentration rare earths, including the leaching wastewaters of tailing ores of ion-absorbing type rare-earth ores, and it is a promising approach to solve the problems from ammonia and nitrogen pollution during traditional processes using ammonium sulfate to leach rare-earth ores and ammonium bicarbonate to precipitate rare earths. It can be expected the suggested new technique might has potential industrial application in the future.

ACKNOWLEDGMENTS

This work was financially supported by National Natural Science Foundation of China (Nos. 21606248, 51574213, 51074150) and Key Project of Chinese National Programs for Fundamental Research and Development (973 Programs Nos. 2012CBA01203, 2013CB632602).

REFERENCES

- (1) Xu, G. X., Eds. Rare earths, 2nd ed. (Chinese Edition); Beijing Metallurgical Industry Press: Beijing, 1995.
- (2) Chi, R. A.; Tian, J. *Weathered crust elution-deposited rare earth ores*; Nova Science Publishers: New York, 2008.
- (3) Chi, R. A.; Tian, J. *Chemical metallurgy of weathered crust elution-deposited rare earth ores*; China Science Publishing & Media Ltd.: Beijing, 2006.
- (4) Xiao, Y. F.; Feng, Z. Y.; Huang, X. W.; Huang, L.; Chen, Y. Y.; Liu, X. S.; Wang, L. S.; Long, Z. Q. Recovery of rare earth from the ion-adsorption type rare earths ore: II. Compound leaching. *Hydrometallurgy* **2016**, *163*, 83-90.
- (5) Huang, X. W.; Long, Z. Q.; Wang, L. S.; Feng, Z. Y. Technology development for rare earth cleaner hydrometallurgy in China. *Rare Metals* **2015**, *34*, 215-222.
- (6) Kanazawa, Y.; Kamitani, M. Rare earth minerals and resources in the world. *J. Alloy. Compd.* **2006**, *408*, 1339-1343.
- (7) He, Z. Y.; Zhang, Z. Y.; Yu, J. X.; Xu, Z. G.; Chi, R. A. Process optimization of rare earth and aluminum leaching from weathered crust elution-deposited rare earth ore with compound ammonium salts. *J. Rare Earth* **2016**, *34*, 413-419.
- (8) Tian, J.; Chi, R. A.; Yin, J. Q. Leaching process of rare earths from weathered crust elution-deposited rare earth ore. *T. Nonferr. Metal. Soc.* **2010**, *20*, 892-896.
- (9) Tian, J.; Tang, X. K.; Yin, J. Q.; Luo, X. P.; Rao, G. H.; Jiang, M. T. Process optimization on

-
- leaching of a lean weathered crust elution-deposited rare earth ores. *Int. J. Miner. Process.* **2013**, *119*, 83-88.
- (10) Zhang, C. G.; Mao, Y. H.; Rao, G. H.; Ouyang, K. X. Leaching relationship of rare earth and non-rare earth elements in ion adsorption type rare earth ore. *Chin. J. Rare Metals* **1991**, *6*, 175-179.
- (11) Li, Y. X.; He, X. B.; Gu, Z. Y.; Hu, P. G. Precipitation reaction of RECl_3 with NH_4HCO_3 and co-precipitation behavior of accompanying impurity ions. *Chin. Rare Earths* **1999**, *20*, 19-22.
- (12) Chung, D. Y.; Kim, E. H.; Lee, E. H.; Yoo, J. H. Solubility of rare earth oxalate in oxalic and nitric acid media. *J. Ind. Eng. Chem.* **1998**, *4*, 277-284.
- (13) Zhang, T.; Zhang, Z.; Xu, Z.; Li, Q.; Chi, R. Study of leaching of rare earth from weathered crust elution-deposited rare earth ores with mixed ammonium salts. *Nonferrous Metals (Extr. Metall.)* **2014**, *8*, 30-33.
- (14) Li, Y. X.; Zhou, X. M.; Liu, Y. Z.; Li, D. P.; Li, J.; Tang, Q. Development of high efficiency extraction and separation technologies of rare earths from ion-adsorbed type deposit. *J. Chin. Rare Earth Soc.* **2012**, *30*, 257-264.
- (15) Yang, X. J.; Lin, A. J.; Li, X. L.; Wu, Y. D.; Zhou, W. B.; Chen, Z. H. China's ion-adsorption rare earth resources, mining consequences and preservation. *Environ. Dev.* **2013**, *8*, 131-136.
- (16) Tian, J.; Yin, J. Q.; Tang, X. K.; Chen, J.; Luo, X. P.; Rao, G. H. Enhanced leaching process of a low-grade weathered crust elution-deposited rare earth ore with carboxymethyl sesbania gum. *Hydrometallurgy* **2013**, *139*, 124-131.
- (17) Xiao, Y. F.; Huang, X. W.; Feng, Z. Y.; Dong, J. S.; Huang, L.; Long, Z. Q. Progress in the green extraction technology for rare earth from ion-adsorption type rare earths ore. *Chin. Rare Earths* **2015**,

- 504 36, 109-115.
- 505 (18) Li, Y. X.; Huang, T.; Li, M.; Zhou, X. Z. Crystallization and morphological evolution of yttrium
506 carbonate. *J. Rare Earth* **2006**, *24*, 64-68.
- 507 (19) Li, Y. X.; Li, M.; He, X. B.; Gu, X. Y.; Hu, P. G.; Zhou, X. Z. The composition and crystalline
508 phase type of products obtained by precipitating yttrium ion with ammonium bicarbonate. *Chin. J.*
509 *Inorg. Chem.* **2002**, *18*, 1138-1142.
- 510 (20) Wang, J. F.; Zhu, D. M.; Fang, X. H.; Qiu, T. S.; Liu, Y. B.; Zhu, H. L. Enhanced characteristics
511 and mechanism of static magnetic field on ion-absorbed rare earth precipitation. *Int. J. Miner.*
512 *Process.* **2017**, *158*, 13-17.
- 513 (21) Ogata, T.; Narita, H.; Tanaka, M. Adsorption behavior of rare earth elements on silica gel
514 modified with diglycol amic acid. *Hydrometallurgy* **2015**, *152*, 178-182.
- 515 (22) Anastopoulos, I.; Bhatnagar, A.; Lima, E. C. Adsorption of rare earth metals: A review of recent
516 literature. *J. Mol. Liq.* **2016**, *221*, 954-962.
- 517 (23) Ngwenya, B. T.; Magennis, M.; Olive, V.; Mosselmans, J. F. W.; Ellam, R. M. Discrete site
518 surface complexation constants for lanthanide adsorption to bacteria as determined by experiments
519 and linear free energy relationships. *Environ. Sci. Technol.* **2010**, *44*, 650-656.
- 520 (24) Jia, J. T.; Zhang, Y. W.; Wu, S.; Liao, C. S.; Yan, C. H.; Liu, J. Y.; Deng, G. M.; Rui, X. B.
521 Distribution and separation of aluminum in the rare earth solvent extraction separation processes(I).
522 *Chin. Rare Earths* **2001**, *22*, 10-13.
- 523 (25) Tian, J.; Yin, J. Q.; Chen, K. H.; Rao, G. H.; Jiang, M. T.; Chi, R. A. Extraction of rare earths
524 from the leach liquor of the weathered crust elution-deposited rare earth ore with non-precipitation.

-
- 525 *Int. J. Miner. Process.* **2011**, 98, 125-131.
- 526 (26) Chi, R. A.; Xu, J. M.; He, P. J.; Zhu, Y. J. Recovering RE from leaching liquor of rare earth ore
527 by extraction. *T. Nonferr. Metal. Soc.* **1995**, 5, 36-40.
- 528 (27) Xie, F.; Zhang, T. A.; Dreisinger, D.; Fiona, Doyle. A critical review on solvent extraction of
529 rare earths from aqueous solutions. *Miner. Eng.* **2014**, 56, 10-28.
- 530 (28) Li, D. Q.; Liu, D. C. Mechanism on extracting aluminium from an acid solution by primary
531 amine N1923. *Nonferr. Metal. (Extr. Metall.)* **1988**, 3, 29-31.
- 532 (29) Li, Y. X.; Chen, Z. J. Extraction of Lanthanum from the neutral sulfate aqueous solution by
533 N1923. *Chin. Rare Earths* **1992**, 6, 34-37.
- 534 (30) Wang, Y. Rare earths enrichment and ammonium removing from low concentration of rare
535 earths solution. Ph.D. Dissertation, Nanchang University, Nanchang, JX, 2015.
- 536 (31) Huang, K.; Liu, H. Z.; Tao, A. Z. A kind of large-phase-ratio liquid-liquid two-phase extractor
537 for continuous and countercurrent extraction. China Patent 201110404565.2, December 07, 2011.
- 538 (32) Huang, K.; Xiao, C. X.; Liu, H. Z. A kind of large-phase-ratio extraction device for organic
539 liquid film on bubble surface. China Patent 201410007908.5, January 01, 2014.
- 540 (33) Huang, K.; Liu, J.; Wu, H. Z.; Liu, H. Z. A kind of bubble-assisted organic film generator. China
541 Patent 201410023670.5, January 20, 2014.
- 542 (34) Huang, K.; Xiao, C. X.; Zheng, H.; Liu, H. Z. A kind of extraction device and method for
543 generating organic liquid film covered bubbles in aqueous solution. China Patent 201410006753.3,
544 January 07, 2014.
- 545 (35) Huang, K.; Liu, J.; Wu, H. Z.; Liu, H. Z. A new bubbling extraction tower: toward liquid-liquid

-
- 546 solvent extraction at large aqueous-to-oil phase ratios. *AIChE J.* **2015**, *61*, 3889-3897.
- 547 (36) Liu, J.; Huang, K.; Wu, H. Z.; Liu, H. Z. A feasible strategy for calculating the required mass
- 548 transfer height of a new bubbling organic liquid membrane extraction tower directly based upon the
- 549 experimental kinetic data. *Ind. Eng. Chem. Res.* **2016**, *55*, 4426-4434.
- 550 (37) Zhang, L. The preparation of composite sulfates using high concentrations chloride wastewater
- 551 and its application in extraction of ion-type rare earth. Ph.D. Dissertation, Nanchang University,
- 552 Nanchang, JX, 2015.
- 553
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Table of Contents graphic (TOC Art)

Synopsis: A new approach was suggested for enrichment of low concentration rare earths from the in-situ leaching solutions of ion-adsorption ores.