



Effects of organic acids on the leaching process of ion-adsorption type rare earth ore[☆]

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ABSTRACT

To examine the activation of organic acids on the leaching process of ion-adsorption type rare earth ore (IRE-ore), the leaching behavior of rare earth (RE) and zeta potential of IRE-ore were investigated in the absence and presence of carboxylic acids. The results show that all the tested organic acids (acetic acid, malonic acid, citric acid, tartaric acid, succinic acid, and malic acid) can promote RE extraction. At relatively high concentrations of organic acids, the activation efficiency of organic acids on RE extraction is generally consistent with their complexation ability; whereas at their low concentrations, the change of zeta potential on the IRE-ore surface with organic acid concentration and pH has a close association with RE extraction, which indicates that organic acids can impact the surface electrical property of IRE-ore via their adsorption/desorption, and thereby increase/decrease the affinity of RE ions to IRE-ore. Therefore the influence of organic acids on the IRE-ore surface electrical property also plays an important role in RE extraction in addition to their complexation with RE ions.

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1. Introduction

The *in situ* leaching process has been widely used to extract rare earth (RE) from ion-adsorption type rare earth ore (IRE-ore) owing to the ionic presence of RE in the ore.^{1,2} During leaching, RE ions contained in IRE-ore can be replaced by other cations from the leaching solution via ion-exchange reaction.^{3,4} The performance of leaching agent is a critical factor contributing to product quality, RE recovery and even environmental impact.⁵ Many studies have been focused on the choice of leaching agents to promote the leaching performance of IRE-ore. Subsequently, many leaching agents including some single leaching systems (ammonium salt,^{6–8} magnesium sulfate,^{9,10} ammonium citrate¹¹) as well as some mixed leaching systems (sesbania gum,¹² tartrate,¹³ acetate¹⁴ and ferrous sulfate¹⁵ assisted reagents) have been proposed to extract RE from IRE-ore.

Organic acids or salts are usually taken as leaching agents or assisted reagents to promote the leaching process of IRE-ore. They

have two advantages in chemical leaching process.¹⁶ One is their excellent complexing ability with RE³⁺ in the solution. Here, a force arises to pull RE³⁺ far away from the surface of IRE-ore and also the RE re-adsorption decreases during leaching. The other advantage is that the leaching solution can be buffered via the addition of organic acids or salts by which Al³⁺, Fe³⁺ and other undesired ions can be prevented from entering the leaching solution.

Meanwhile, the migration of heavy metal ions in soil is often investigated in the presence of common organic acids. The results revealed that organic acids could accelerate transportation and transformation of heavy metal ions in soil.¹⁷ Some researchers attributed this effect to the release of metal ions to the complexation of organic anions,¹⁸ and others pointed out that the pH of the leaching solution system affected by dissociation of organic acids is decisive to metal desorption.^{19,20} Despite the controversy of these activated mechanisms, the activation to desorption of metal ions can be applied to the development of IRE-ore leaching process.

Based on the current theory, we selected some organic acids as leaching-aid reagents to activate RE leaching from IRE-ore. The zeta potential was measured in the IRE-ore suspension system, and the activation mechanism of these organic acids in the leaching process of IRE-ore was illustrated.

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2. Materials and methods

2.1. Experiment sample and reagents

All chemical reagents were of analytical grade. A typical heavy IRE-ore with a high amount of Y sampled from the Longnan rare earth ore area was used. RE is mainly distributed in the fraction (<0.076 mm) of the IRE-ore.^{14,21} To ensure homogeneity of the IRE-ore sample, it was passed through a 60-mesh sieve before leaching. Its size distribution and the corresponding RE content are listed in Table 1.

The clay fraction (<2 μm) of the IRE-ore was used in the measurement of ζ potential. The sample was separated from IRE-ore by sedimentation based on Stokes sedimentation velocity formula.²² After dialysis and drying, the sample was dispersed into 0.5 g/L suspension with a certain content of organic acid, and the pH of the suspension was adjusted by 0.1 mol/L HCl or 0.01 mol/L NaOH.

2.2. Leaching experiments

The leaching experiments were conducted in a batch reactor. 0.3 mol/L ammonium chloride was used as a main leaching reagent, and a small amount of acetic acid, citric acid, malonic acid, succinic acid, malic acid or tartaric acid was added as a leaching-aid reagent. All organic acids were of low molecular weight as well as low toxicity (Table 2). The amount of the added organic acids was measured via the concentration of carboxylic acid groups (C-COOH) contained in the organic acids.

Next, 3.000 g of the IRE-ore samples was weighed and placed into 50 mL polypropylene centrifuge tube, and a mixed leaching solution was then trickled into the tube. The pH of leaching solution was pre-adjusted by 0.1 mol/L HCl or 0.01 mol/L NaOH. All leaching processes used a fixed weight ratio of solid and liquid at about 1:10. After shaking and equilibrating in a water bath at 25 ± 2 °C for 2 h, the leaching solution was separated by centrifugation at 5000 rpm for 10 min. RE extraction (RE extraction amount per unit mass IRE-ore) was calculated based on determination of the leaching amount of RE by single-channel scanning coupled plasma emission spectrometry (ULTIMA 2, France).

2.3. Zeta potential measurements

The ζ potentials were determined by micro-electrophoresis apparatus (JS94H2, China) after the suspensions of IRE-ore clay fraction were ultra-sonically dispersed for about 30 min and rested for at least 12 h to reach solution equilibrium. When measured, the suspension was shaken well and swiftly transferred to an electrophoresis cup. Then the electrophoretic mobility was calculated within the limits of the computer screen after applying voltage to two electrodes. This process was repeated at least five times to acquire average value. All tests were conducted at 25 ± 0.5 °C and the measurement error was within 2 mV.

3. Results and discussion

3.1. Effect of equilibration time on the leaching process of IRE-ore

The effect of equilibration time on the leaching process of IRE-ore is shown in Fig. 1 in the absence and presence of acetic acid,

Table 1
The content of REO in different size fraction of IRE-ore.

Particle size (mesh)	-60	+60	Total
Mass percent (wt.%)	48.7	51.3	100
REO content (wt.%)	0.06	0.15	0.107

malonic acid and citric acid without pH adjustment. All leaching processes reach equilibrium within the first 1 h, and RE extraction in an additive-free system (no addition of any organic acid) takes less time (about 10 min) than any organic acid system to reach a maximum. The main reason is that the ion-exchange reaction due to electrostatic force is relatively simple, and can proceed rapidly in the additive-free system. In these organic acid systems, specific adsorption of organic anions on IRE-ore and H⁺ dissociated from organic acids may be involved in kinetic reaction besides electrostatic adsorption. This implies a longer time to reach equilibrium²³ and the leaching time was determined to be 1 h in the following experiments.

Meanwhile, in acetic, malonic and citric acid systems, there is an obvious promotion to RE extraction compared to the additive-free system (Fig. 1). RE extraction follows the order: citrate acid > malonic acid > acetic acid > additive-free.

3.2. Effect of organic acids concentration on the leaching process of IRE-ore

Fig. 2 shows the relation between RE extraction and the concentration of organic acids (acetic acid, malonic acid, citric acid, tartaric acid, succinic acid, and malic acid). Versus RE extraction (about 9.66 mmol/kg) in the additive-free system (Fig. 1), all tested organic acids stimulate RE extraction within the experimental concentration (C-COOH: 0.1–10.0 mmol/L). In the use of malonic acid, citric acid, tartaric acid and malic acid, the RE extraction firstly increases rapidly with increasing carboxyl group concentrations. At the carboxyl group concentration above 2.0 mmol/L, RE extraction curves become gentle and the sequence of RE extraction is generally in accordance with that of the complexing ability of organic acids with RE ions. Previous researches also suggested that poly-nuclear complexes of RE ions with short-chain organic acids can contribute to RE mobility in clay minerals,^{24,25} and this may be one of the essential minerogenetic mechanism of IRE-ore.²⁶ Thus, RE extraction may be dominated by coordination activation of organic acids at relatively high concentrations (C-COOH > 2.0 mmol/L).

However, abnormal variations were observed in succinic acid and acetic acid systems. The RE extraction curve has a sharp peak in the succinic acid system at a very low concentration (C-COOH < 1.0 mmol/L). It even surpasses that in the citric acid system during peak intervals. The RE extraction curve is a wide downward parabola across the concentration regime. The acetic acid has a stronger effect on RE extraction than tartaric acid even if the latter has a stronger complexation with RE³⁺. Thus, the complexation of organic acids cannot explain the two exceptional activation cases.

Eu(III) is stable in a water solution in absence of strong reductants.²⁷ It has a similar physico-chemical property with the other RE. The complexation and hydrolysis constants of Eu³⁺ and Y³⁺ are listed in Table 3.^{28–30} As a representative of RE complexation with organic acids, the Eu(III) species distribution in additive-free, acetic acid, malonic acid and citric systems was calculated using Phreeqc software and displayed in Fig. 3. When the pH ranges from 3.0 to 7.0, the acetic acid has only a minor impact on distribution of Eu(III) species in the solution. This indicates that the complexation of acetic acid with RE³⁺ can be ignored during the leaching process of IRE-ore. The monodentate complexes, Eu-malonate⁺ and Eu-citrate⁰, are present in the malonate acid and citrate acid systems, respectively. They increase with increasing pH due to more dissociated organic anions from organic acid molecule at higher pH. At pH values of up to 4.5, the Eu-citrate⁰ gradually becomes the dominant species in the citric acid system. In general, larger complexing ability leads to a more monodentate complex. These monodentate complexes such as Eu-malonate⁺ and Eu-citrate⁰ are barely absorbed on the surface of the IRE-ore due to weak

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