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Leach of the weathering crust elution-deposited rare earth ore for low environmental pollution with a combination of $(NH_4)_2SO_4$ and EDTA

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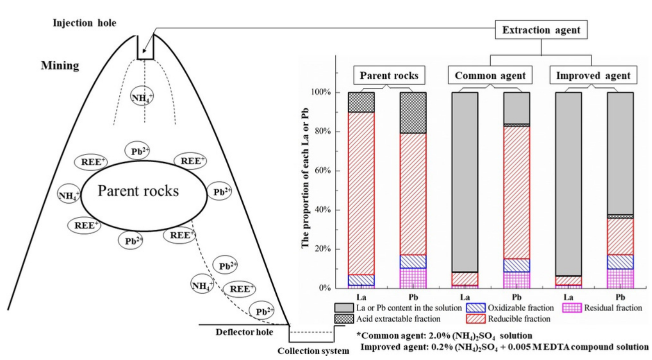
HIGHLIGHTS

- We developed an improved compound agent of $(NH_4)_2SO_4$ and EDTA.
- The extraction efficiency of La reached up to 93.5%, which is consistent with 2.0% $(NH_4)_2SO_4$ solution.
- The extraction efficiency of Pb was 62.3%, which was much higher than that (16.16%) achieve by using 2.0% $(NH_4)_2SO_4$ solution.

GRAPHICAL ABSTRACT



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ABSTRACT

High concentration of ammonium sulfate, a typical leaching agent, was often used in the mining process of the weathering crust elution-deposited rare earth ore. After mining, a lot of ammonia nitrogen and labile heavy metal fractions were residual in tailings, which may result in a huge potential risk to the environment. In this study, in order to achieve the maximum extraction of rare earth elements and reduce the labile heavy metal, extraction effect and fraction changes of lanthanum (La) and lead (Pb) in the weathering crust elution-deposited rare earth ore were studied by using a compound agent of $(NH_4)_2SO_4$-EDTA. The extraction efficiency of La was more than 90% by using 0.2% $(NH_4)_2SO_4$-0.005 M EDTA, which was almost same with that by using 2.0% $(NH_4)_2SO_4$ solution. In contrast, the extraction efficiency of Pb was 62.3% when use 0.2% $(NH_4)_2SO_4$-0.005 M EDTA, which is much higher than that (16.16%) achieved by using 2.0% $(NH_4)_2SO_4$ solution. The released Pb fractions were mainly acid extractable and reducible fractions, and the content of reducible fraction being leached accounted for 70.45% of the total reducible fraction. Therefore, the use of 0.2% $(NH_4)_2SO_4$-0.005 M EDTA can not only reduce the amount of $(NH_4)_2SO_4$, but also decrease the labile heavy metal residues in soil, which provides a new way for efficient La extraction with effective preventing and controlling environmental pollution in the process of mining the weathering crust elution-deposited rare earth ore.

1. Instruction

It is known that the rare earth elements (REEs) contain 17

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elements in the periodic table, including "lanthanides" along with yttrium and scandium. With the rapid development of modern science and technology, the demand for rare earth (RE) is increasing dramatically. RE is widely used in aviation, transportation, electric devices, medical treatments, and many other fields (Chen, 2011; Du and Graedel, 2013), especially, the middle and heavy RE are highly associated with the hi-tech industry and cutting-edge technology products (Wang et al., 2015; Yang and Zhang, 2015). The weathering crust elution-deposited rare earth ore, also named the ion-adsorption rare earth ore, is a typical medium and heavy RE resource (Chi and Tian, 2008), and is widely distributed at seven provinces in southern China (Huang et al., 2015). The REEs in the weathering crust elution-deposited rare earth ore are adsorbed on the clay minerals by ion-exchangeable phase, which accounts for more than 80% of the total amount of RE (Chi et al., 2005), and the weathering crust elution-deposited rare earth ore exists with the accompanying heavy metal elements (Bao and Zhao, 2008).

Currently, 0.5%–2.0% $(NH_4)_2SO_4$ is used in the mining process of the weathering crust elution-deposited rare earth ore. The ion exchange occurs between ammonium ions (NH_4^+) and RE ions, and the mother liquid containing RE ions is formed (Tian et al., 2010, 2013b). The earliest research of the weathering crust elution-deposited rare earth ore mainly has focused on the leaching mechanism and how to improve the extraction efficiency (Moldoveanu and Papangelakis, 2012; He et al., 2016). As the technology matures, the ecological problems (eg, ammonia nitrogen (AN) and heavy metal pollution) caused by mining, have received widespread attention (Li et al., 2013; Chen et al., 2015; Xiao et al., 2015). The problem of AN pollution in soil and water is becoming more and more serious due to the use of high concentration $(NH_4)_2SO_4$. In order to prevent AN pollution, Qiu et al. and Tian et al. optimized the leaching process, to reduce the consumption of $(NH_4)_2SO_4$ (Qiu et al., 2008; Tian et al., 2013a). Xiao et al. showed that $MgSO_4$ was used instead of $(NH_4)_2SO_4$ as an extraction agent, to exact the REEs without AN pollution (Xiao et al., 2015). Yang et al. indicated that there was still lots of AN residue in the tailings after mining the weathering crust elution-deposited rare earth ore, and using KCl solution as a leaching agent instead of water could quickly and effectively solve AN pollution at a wide range of pHs (Yang et al., 2016).

During the leaching process of the weathering crust elution-deposited rare earth ore, high concentration of $(NH_4)_2SO_4$ and the change of the soil environment (such as pH, Eh, etc) can activate toxic heavy metals (such as Pb and Zn) in the weathering crust elution-deposited rare earth ore. It is reported that the heavy metal pollution was very serious in the surrounding soil of the RE mining area (Xu et al., 2015; Pan and Li, 2016). In addition, the enrichment of heavy metals (Pb, Cu, Zn, Cd, Mn, etc) was also found in surface water and groundwater (Hao et al., 2016; Si et al., 2016), according to the result of the investigation of the surrounding soil and water body of RE ore mining areas. The residual heavy metals in tailings may desorb again and contaminate the environment via acid rain (Wen et al., 2012; Tang et al., 2017). Then it can transfer to the human body through the food chain, and ultimately harm human's health (Phan et al., 2013).

It was clear that the previous studies primarily focused on how to reduce AN pollution caused by mining RE. Although a few reports referred to a serious heavy pollution of the surrounding soil and water body of RE ore areas, there has been limited research regarding how to effectively prevent the labile heavy metals in tailings released into the environment. Nowadays, soil washing technology is an important method to effectively remove heavy metals, which can not only permanently remove heavy metals from contaminated soil, but also remove the labile heavy metals in tailings (Zhang et al., 2010). The selection of eluent is the key in the application of the technology, The eluents include inorganic eluent, chelating agent, surfactant and compound agent (Kim and Baek, 2015; Kulikowska et al., 2015; Wu et al., 2015; Luna et al., 2016). Ethylenediaminetetraacetic acid and its salts (EDTA) are most commonly used chelating agents due to their low biodegradability (Tejowulan and Hendershot, 1998), easy to recycle (Nguyen et al., 2015) and less impacts on soil microorganism and enzyme activity compared to other agents (Udovic and Lestan, 2012). Furthermore, EDTA has the most effective chelating ability for different heavy metals, particularly for lead (Qiao et al., 2017). Therefore, $(NH_4)_2SO_4$ combined with EDTA is a improved extraction agent, which could provide a possibility to reduce environmental pollution of mining the weathering crust elution-deposited rare earth ore.

In this paper, a representative weathering crust elution-deposited rare earth ore associating lead, was selected as the research medium, and lanthanum (La) and lead (Pb) were used as targets. The extraction effect and fraction changes of La and Pb were investigated by using $(NH_4)_2SO_4$ solution, EDTA solution and improved extraction agent $(NH_4)_2SO_4$-EDTA, respectively, to efficiently remove the residual toxic heavy metals in tailings and reduce the environmental risk after the mining.

2. Materials and methods

2.1. Materials

The rare earth ore samples were collected from the weathering crust elution-deposited rare earth ore (4–6 m depth), located in the Anyuan city of Jiangxi Province of southern China. The rare earth ore samples were air-dried, crushed, and passed through a 0.425 mm sieve for experimental use. The major mineral composition and basic and basic physical and chemical properties of the soil are displayed in Table 1. EDTA was for short Na_2EDTA selected for use in the experiment. All the chemicals used in this study were of analytical grade and purchased from Beijing Chemical Corp., China. The Pb and La standard solutions were purchased from the National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials (NCATN). Deionized distilled water was used in all the experiments.

2.2. Experimental methods

2.2.1. Batch extraction experiments

In order to extract La and Pb from soil as much as possible, batch extraction experiments were conducted, where several conditions (such as the contact time and concentrations of $(NH_4)_2SO_4$ and EDTA) were studied.

For the effect of $(NH_4)_2SO_4$ or EDTA concentration, soil was

Table 1
The major mineral composition and basic physical and chemical properties of the soil used in the experiment.

Parameters	Soil	
Particle size distribution	Sand (2–0.05 mm)	32.3%
	Silt (0.05–0.005 mm)	48.1%
	Clay (<0.005 mm)	19.6%
Mineral composition	Quartz	86.0%
	Kaolinite	13.0%
	Hematite	1.00%
Physical and chemical properties	pH	4.41
	pH_{PZC}	4.35
	Organic carbon (g/kg)	0.0651
Content	Pb (mg/kg)	109 ± 2.74
	La (mg/kg)	276 ± 2.81