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Immobilization of rare earth elements of the mine tailings using phosphates and lime

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Abstract

Excessive exploitation of rare earth mines produced a great deal of mine tailings which needs proper treatment. High concentration of the total rare earth elements (REEs) (685.8 ± 48.7 mg/kg) still existed in the mine tailings, which was more than 3 times as much as the average background concentration of China. More importantly, 88.8% of the REEs fractionated in exchangeable fraction under sequential extraction analysis, and 91.7% were leached under TCLP procedure, which indicated a high risk of leaching of REEs into the surrounding environment. Stabilization method was adopted to control the REEs leachability in the mine tailings. Soil incubation experiments were conducted to evaluate the effectiveness of soluble phosphates and lime in immobilizing REEs in the mine tailings. The results revealed that, with the addition of lime, the leachability of REEs reduced by 0.4%-18.3% with the addition of lime at 0.1%-1% (by weight). A more effective immobilization result was obtained with the addition of phosphates, as the REEs leachability reduced by 71.1%-98.4%. The sequential extraction analysis revealed that the lime treatment converted REEs in F1 into F2. In contrast, phosphate treatment converted the REEs into more stable fractions. The mechanism of the efficient immobilization of REEs with the soluble phosphates was described as follow: (1) Cation exchange between free proton or potassium ion and the soil bounded REEs; (2) Complexation and precipitation reactions between phosphate and REEs. In addition, the final pH value after soil incubation also influenced the effect of the immobilization of REEs.

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Keywords: Immobilization; REEs; mine tailings; sequential extraction analysis; phosphates

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1. Introduction

Rare earth elements (REEs) are worthful additives in chemical engineering, military, medicine, agriculture, as well as scientific research. China has been the maximal production and export state of REEs for many years. The U.S. Geological Survey revealed that, in 2013 and 2014, China produced 200 thousand tons of REEs, which accounted for 90.9% of the world's production (Salazar and McNutt, 2014). The excessive exploitation causes massive devastation to the environment. The rural areas close to the mining sites of Ganzhou city of Jiangxi Province (southern China) are typical victims. In these areas, the REEs exist in a type of rare-earth-bearing (ion adsorption) clay. In order to extract the REEs, the clay is either excavated and soaked in ponds, or in-situ soaked using ammonium sulfate as an extractant. The residual clay soil after extraction is then piled to form the mine tailings. According to a local government report, the production of each ton of rare earth would result in 200 m^2 of vegetation destruction, 300 m^2 of surface soil stripping, 2,000 m^3 of mine tailings, and 12 million m^3 of annual soil erosion. In addition, the exposed soil is more susceptible to leaching; the leached REEs will contaminate the ground water and downstream farmland. The exogenous REEs have caused widespread concern because of their accumulation in soil, water as well as biota (Hirano and Suzuki, 1996; Krejčová et al., 2012; Pérez-López et al., 2010; Xu et al., 2012; Zhang et al., 2000). High concentration of REEs in the soils is harmful to the soil ecosystems (Li et al., 2011),and may prohibit the growth of plants (Liang et al., 2005; Thomas et al., 2014). REEs may be also accumulated in organs of human by ingestion, inhalation, and dermal contact, resulting in a chronic toxicity to human cells and an increase of health risks (Li et al., 2013; Tong et al., 2004; Wei et al., 2013; Oliveira et al., 2014). Therefore, there is a demand of a cost-effective technology to control the bioaccessibility and leaching of the REEs in the mine tailings.

Chemical stabilization is a widely applied soil remediation technology to treat heavy metal polluted soils (Guo et al., 2006). Phosphate is one of the most effective reagents in stabilizing heavy metals due to the formation of secondary phosphate precipitates, which are considered stable over a wide variation of geochemical conditions (Cao et al., 2002; Hettiarachchi et al.,2000; Xenidis et al., 2010). Lime and oxides are also useful in immobilizing heavy metals in soils acting as sorbents and precipitators (Lim et al.,2013; Komárek et al., 2013). The solubilities of the phosphates and hydroxides of REEs are rather low, with the solubility product constants of 10^{-20} or lower. Therefore, phosphates and lime are chosen as the remediating reagents for immobilizing REEs. Sequential extraction, proposed by Tessier et al. (1979), is universally used to evaluate the speciation and leachability of heavy metals besides REEs (Cao et al., 2001). Five sequential fractions were defined in this method: the exchangeable fraction (F1), susceptible to changes in ionic composition of water; acid soluble fraction (F2), susceptible to pH changes; reducible fraction (F3), bound with iron and manganese oxides, unstable in reducing conditions; oxidizable fraction (F4), organically bound fraction which may be decomposed under oxidizing conditions and results in a release of the metals into the soil solution; and residual fraction (F5), the least leachable, since stable minerals of the metals are believed to exist (Li et al.,2005; Maiz et al., 2000; Zufiaurreet al., 1998). F1 and F2 are thought to be the most readily leached under moderate altering meteorological and geochemical conditions and they contribute greatly to the bioaccessibility of the metals (Tyler, 2004; Cao et al., 2000).

A Chinese government ad hoc environmental investigation of Jiangxi Province in 2012 showed that until the year of 2012, only in Ganzhou City, there were 302 deserted mines, 191 million tons of mine tailings, and 97.34 square kilometers of land areas influenced at the mining sites. A fair amount of the mine tailings were rampant piled without proper disposal. Due to the weak acid soil environment and rain leaching, the surrounding farmland and groundwater are suffering or under threat of the leaching of REEs at various degrees. A chemical immobilization technique was attempted to control the leaching of the REEs of the mine tailing samples in this study. We hope that it will become available as a cost-effective measure in the future in decreasing the leaching and bioaccessibility of REEs.

2. Materials and methods

2.1 Materials