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Green recovery of potassium and aluminum elements from alunite tailings using gradient leaching process

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ABSTRACT

In this work, a gradient leaching process is proposed to treat alunite tailings in order to recover potassium and aluminum. Thermodynamic analysis on the reactions of alunite tailings with potassium hydroxide in the leaching process over the temperature range of 30–120 °C is accomplished. In the gradient leaching process, the main mineral of potassium alunite from alunite tailings is extracted into the concentrated potassium hydroxide solution, while kaolinite and quartz are still remained in the leaching residues. The proposed leaching process is demonstrated to be feasible based on the leaching ratio of potassium, aluminum, silicon elements in the leaching solution by ICP-OES and the mineralogical characterizations of the leaching residues by XRD, IR and Raman spectrometers. Furthermore, the gradient leaching conditions, such as alkali-to-ore mass ratio, leaching temperature, leaching time and potassium hydroxide concentration, are optimized using the response surface method to recover potassium and aluminum from alunite tailings as many as possible and to extract silicon as small as possible. Under the optimal leaching conditions of alkali-to-ore mass ratio 3.3, temperature 81.8 °C, time 41.6 min, and potassium hydroxide concentration 53.9 wt%, the leaching ratio of potassium and aluminum reaches 99.5% and 84.0%, and the leaching ratio of silicon is controlled in 5.6%, respectively. All the obtained results could contribute to affording a green and closed-loop recovering process for potassium and aluminum elements from alunite tailings.

1. Introduction

Five to fourteen billion tons of mine tailings per year worldwide will be discharged from the contemporary mining industry (Lu and Wang, 2012; Mudd and Boger, 2013; Jones and Boger, 2012). It is expected that the amount of tailings discharged during the mineral processing steps will increase in future years due to the declining ore grades, the mining of more complex ores, and changes to processing technology (Mudd, 2010). For example, in copper mining, the amount of tailings usually accounts for 95–99% of the input copper ore (Beylot and Villeneuve, 2017; Edrakai et al., 2014). Through the flotation of the copper tailings, a large amount of alunite tailings can be obtained in China, which contain abundant potassium alunite with associated kaolinite (dickite) and quartz. Considering the wide application and gradual supply risk of the potassium and aluminum resources, alunite tailings will be the potential second mine resources. However, up to now, most of tailings, also including alunite tailings, are discarded, landfilled and backfilled, paste and thickened disposed, or stockpiled as waste materials (McLellan et al., 2009; Adiansyah et al., 2015; Reid et al., 2009; Deschamps et al., 2011; Driussi and Jansz, 2006; Franks et al., 2011). Discarding alunite tailings as waste is not only the loss of valuable resources, but also brings serious environmental impacts and ecological damages such as acid drainage, soils contamination, underground water pollution and potential danger (Dudka and Adriano, 1997; Moreno and Neretnieks, 2006; Kefeni et al., 2017; Kossoff et al., 2014).

Alunite tailings contain abundant potassium alunite with associated kaolinite (dickite) and quartz, being potential K and Al resources. A green and efficient recovery from alunite tailings is necessary to convert the useless tailings into high-value potassium and aluminum resources, meanwhile, to solve the problem of tailings disposal (Dodson et al., 2012). Previously, many

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investigations have been focused on the valuable resources recycle from alunite ores (Kucuk and Yildiz, 2006; Adams, 1935; Özdemir and Cetisli, 2005; Ozacar and Sengil, 1999; Mohammadi and Salarirad, 2013). A hydrometallurgical method is generally used. In the traditional hydrometallurgical process, several operation units are known as fundamental stages, including preconcentration, calcination, acid or alkaline leaching, and crystallization (Luo et al., 2017). However, the traditional process is commonly associated with high costs and energy consumptions due to the high temperature (above 900 °C) involved in the calcination units (Kucuk and Yildiz, 2006; Adams, 1935). Besides, this process could produce large amount of toxic gases, such as SO_2 and SO_3, and thus it needs serious actions to avoid pollution to the environment. While in contrast, only few previous works are focused on recycling from alunite tailings owing to their complicated composition and structure. Zhao et al. (2015) developed an acid calcination-water leaching method to treat associated alunite tailings. The tailings were first calcined at 300 °C by 30% H_2SO_4 solution with the liquid-solid ratio of 2:1, and then were leached at 80 °C in aqueous solution with the liquid-solid ratio of 10:1. The leaching efficiency of aluminum and potassium reached 87.2% and 85.3%, respectively.

In view of the principles of Green Engineering and the goals of a circular economy (Anastas and Zimmerman, 2003; Hunt et al., 2015; Clark et al., 2016; Sheldon, 2016), we propose a green gradient leaching process using highly concentrated KOH solution to recovery potassium and aluminum resources from alunite tailings, in terms of both energy conservation and polluted-substance control. The concentrated KOH media (above 50 wt%) characterized by higher reactivity and higher ionic strength (Liu et al., 2012), has been successfully applied in the treatment of mineral slags to extract valuable metal resources, Cr, Ti, V et al. (Sun et al., 2009; Zheng et al., 2006; Xu et al., 2005; Chen et al., 2014; Zhou et al., 2005). It needs attention that a high concentration of dissolved silicon in the alkaline leaching process will increase leach liquor viscosity and surface tension, induce difficult pulp filtration (Banza et al., 2002), and even result in recovery decline of potassium and aluminum products due to formation of desilication products (aluminosilicates) (Croker et al., 2008; Ma et al., 2012). Although the traditional desilicication method utilizing desilication agents such as calcium oxide and calcium carbonate is generally adopted (Whittington, 1996), it is not effective since the desilication products are not stable in the high alkali solution (Barnes et al., 1999; Whittington and Fallows, 1997; Whittington et al., 1998).

There are mainly potassium alunite, kaolinite and quartz in alunite tailings, but the stabilities of crystal structures of these minerals in the highly concentrated KOH solution are very different, which result in that potassium alunite decomposes firstly, kaolinite decomposes secondly, and quartz decomposes lastly. As known, kaolinite and quartz contain the amount of silicon, and the removal of silicon from solution is difficult if kaolinite and quartz are decomposed. Therefore, the proposed gradient leaching process actually means that potassium alunite from alunite tailings is selectively extracted in the highly concentrated KOH solution at the given leaching condition, while other impure minerals, such as kaolinite and quartz, are still remained in the leaching residues. Up to now, no similar reports are found in literature.

In this work, the gradient leaching process of potassium alunite from alunite tailings is developed, which is beneficial to controlling a low dissolved concentration of silicon and keeping the high leaching ratio of potassium and aluminum. The proposed gradient leaching process is investigated thermodynamically and experimentally, and the gradient leaching conditions are optimized using the response surface method.

2. Experimental

2.1. Material and methods

The average particle size of alunite tailings was measured as 37.25 μm, which could be used directly for the leaching reaction with potassium hydroxide. The chemical reagent potassium hydroxide was of analytical grade (Sinopharm Chemical Reagent Co. Ltd., China), and was used without further treatment. The deionized water was used to prepare solutions in all experiments. The major elements of alunite tailings were determined using the inductively coupled plasma optical emission spectroscopy (ICP-OES, Spectra ARCOS, Germany) following a Na_2O_2/NaOH fusion and a HCl acidification. Total sulfur content of alunite tailings was determined by a Kulun sulphur tester (CLS-2, China). The mineralogical analysis of alunite tailings was performed using X-ray diffraction analysis (D8 Advance, Bruker, Germany), FTIR spectrometer analysis (Nicolet 6700, Thermo Fisher Scientific, USA), Raman spectrometer analysis (DXR, Thermo Fisher Scientific, USA), and SEM-EDS (Quanta 250 and TEAM Pegasus, USA), respectively.

2.2. Experimental apparatus and procedure

The batch reactor used in this work was a 500 mL stainless steel container equipped with a thermocouple, a water-cooled condenser, and a magnetic stirrer. The temperature was controlled by a programmable temperature controller with a precision of ±0.5 °C, while the stirring rate was regulated by a stirrer speed regulator with a precision of ±5 rpm.

All the experiments of alunite tailings leaching by potassium hydroxide solution were conducted as follows. For each run, a certain amount of KOH solution that includes the solute KOH and the solvent water, with KOH concentrations of 30–70%, was added into the flask and heated to a given temperature in a range of 10–130 °C. At the steady stage, a certain amount of the alunite tailings, corresponding to different alkali to ore mass ratios, was added into the container to start the leaching process. The leaching process lasted for a certain time under a constant stirring condition of 700 rpm, from 5 to 65 min. Then the slurry was quickly filtered under a vacuum once the desired time was reached. The filter residue was washed with distilled water for three times and then dried at 100 °C for 12 h. The mineralogical analysis of residues was also determined using XRD, FTIR spectrometer analysis, and Raman spectrometer analysis, respectively. Aluminum and silicon contents of the leach liquor, and potassium content of the washed residue were analyzed via ICP-OES. All experimental data were the average of three parallel experiments. The leaching ratio of potassium (X_K) was calculated using Eq. (1), while the leaching ratio of aluminum and silicon (X_{Al} or X_{Si}) were calculated using Eqs. (2) and (3).

$$X_K = (1 - [K]_r/[K]_0) \times 100 \tag{1}$$

$$X_{Al} = [Al]_f \Big/ [Al]_0 \times 100 \tag{2}$$

$$X_{Si} = [Si]_f \Big/ [Si]_0 \times 100 \tag{3}$$

where $[K]_r$ and $[K]_0$ were the mass of potassium in the residue and in the alunite tailings, $[Al]_f$ and $[Al]_0$ were the mass of aluminum in the leach liquor and in the alunite tailings, $[Si]_f$ and $[Si]_0$ are the mass of silicon in the leach liquor and in the alunite tailings, respectively.