



# Leaching kinetics of rare earth elements and fluoride from mixed rare earth concentrate after roasting with calcium hydroxide and sodium hydroxide



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## ABSTRACT

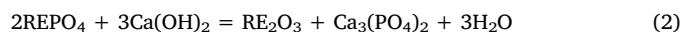
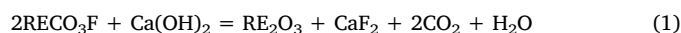
The complex leaching kinetics of rare earth elements and fluoride with a HCl-AlCl<sub>3</sub> solution was investigated for the mixed rare earth concentrate after roasting with calcium hydroxide and sodium hydroxide. The effects of HCl concentration, temperature, reaction time, liquid-solid ratio (L/S), AlCl<sub>3</sub> concentration and stirring speed on leaching kinetics were explored. The results show that the extractions of REEs and fluoride were 86.05% and 90.23%, respectively, under the conditions: 3 mol/L HCl, 0.5 mol/L AlCl<sub>3</sub>, 70 °C, 10 mL/g liquid-solid ratio, 300 rpm stirring speed and 40 min. The XRD and SEM analysis of the samples before and after acid leaching show that the rare earth oxides and fluorite were completely leached. The apparent activation energies of leaching REEs and fluoride were calculated, which were 26.95 kJ/mol for REEs and 20.70 kJ/mol for fluoride. The kinetic data of extractions of REEs and fluoride all fitted a new variant of the shrinking core model, in which both the interfacial transfer and the diffusion through the product layer affected the reaction rate.

## 1. Introduction

The mixed rare earth concentrate from Baotou (shortened as mixed concentrate in the following text) composed of bastnaesite and monazite is an important light rare earth resource (Wu et al., 2004; Chen et al., 2004). Due to its complex composition and phase structure, it is denoted as one of the most difficult decomposing minerals (Huang et al., 2006). At present, the method of sulfuric acid roasting is mainly applied to industrial production for processing the low-grade mixed concentrate (Zhu et al., 2003). But the off-gas of sulfur dioxide and hydrogen fluoride produced in the roasting process, which is difficult to be economically recycled, is seriously limiting its development (Sun et al., 2007). Large quantities of waste water are produced with processing the off-gas through water spray. As the annual treated quantity of mixed concentrate is about 150,000 tons, about 12,000 tons of fluoride is produced and released into atmosphere or ground water.

In recent years, many research works have been done to solve the pollution problem of fluoride (Ma et al., 2010; Wu et al., 2009; Huang et al., 2001). Many researchers deemed that the fluorine element would be converted into fluoride by adding the compounds of alkali metals in the roasting process to avoid the fluorine element into the off-gas (Bautista and Wong, 1989; Zhu et al., 2002; Chen et al., 2004; Xu, 1995). Furthermore, the compounds of alkali metals can promote the decomposition of rare earth minerals containing monazite. The method of adding calcium oxide and calcium chloride in the roasting process

was reported to decompose mixed concentrate (Chen et al., 2010; Wu et al., 2004). But the decomposition ratio is very low, due to the reaction between CaO and mixed concentrate belongs to solid-solid reaction. A new idea of mixing calcium hydroxide-sodium hydroxide and mixed concentrate was proposed (Bian et al., 2014). In the roasting process, sodium hydroxide would be melted down to provide a liquid phase reaction condition, by which the mass transfer between reactants was strengthened and the decomposition reaction was promoted. In addition, the sodium hydroxide played a role of reaction catalyst. The important chemical reactions during the roasting process are provided as follows:

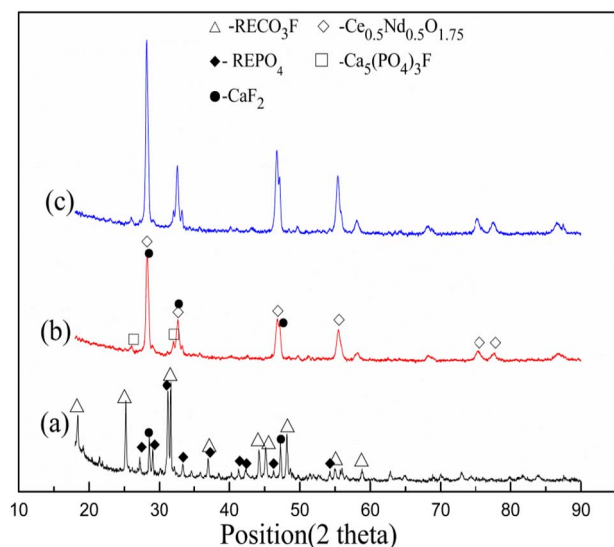


The mixed concentrate after the roasting process is washed by low concentrate of hydrochloric acid (0.5 mol/L) and citric acid (0.05 mol/L) to remove the calcium phosphate. The recovery rate of phosphorus was more than 98%, while the loss rate of REEs was less than 1% by adjusting the pH of the washing solution (Bian, 2008). The purposes of the recovery of phosphorus and separation with REEs were achieved with this process. Then, the rare earth oxide and calcium fluoride in the acid washing products can easily be leached out with a HCl-AlCl<sub>3</sub> solution. The fluorine element in the mixed concentrate finally converted into a stable complex ion [AlF<sub>6</sub>]<sup>3+</sup>, which can be used to produce

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**Table 1**  
Chemical composition of mixed concentrate (a) and sample after acid washing (b).

	RE <sub>x</sub> O <sub>y</sub>	F	P	Ca
(a)	48.94	9.18	3.14	8.90
(b)	57.70	14.40	0.07	15.07



**Fig. 1.** The XRD patterns of samples (a: mixed rare earth concentrate; b: roasted sample, c: roasted sample after acid washing).

cryolite (Akdeniz et al., 1999; Li et al., 2013a; Kumar et al., 2010). Therefore, the problem of fluoride pollution in the decomposition process can be solved effectively, and the fluorine and phosphorus in the mixed concentrate can comprehensively be utilized in this process.

Previous studies (Li et al., 2013b; Li et al., 2016; Zhang et al., 2014;) revealed that the coordination leaching by HCl-AlCl<sub>3</sub> solution for the mixed concentrate was efficient to convert fluorine into [AlF<sub>6</sub>]<sup>3+</sup>, but the extraction of REEs was unsatisfactory, below 70%. Due to that the rare earth oxides are more easily leached than bastnaesite and monazite, the process of coordination leaching for the roasting products of the mixed concentrate and Ca(OH)<sub>2</sub>-NaOH seem to have a potential of leaching REEs and fluoride completely.

This paper aims to reveal the mechanisms of leaching REEs and fluorine from the roasting products of mixed concentrate and Ca(OH)<sub>2</sub>-NaOH, and provide an optimal performance and a scientific reagent consumption. So, the effects of several factors, such as HCl concentration, AlCl<sub>3</sub> concentration, temperature, reaction time, L/S and stirring speed, on the extractions of REEs and fluorine are investigated. The leaching kinetic models of REEs and fluorine are established by the analysis of above factors, and then the apparent activation energies were calculated to compare their leaching behaviors.

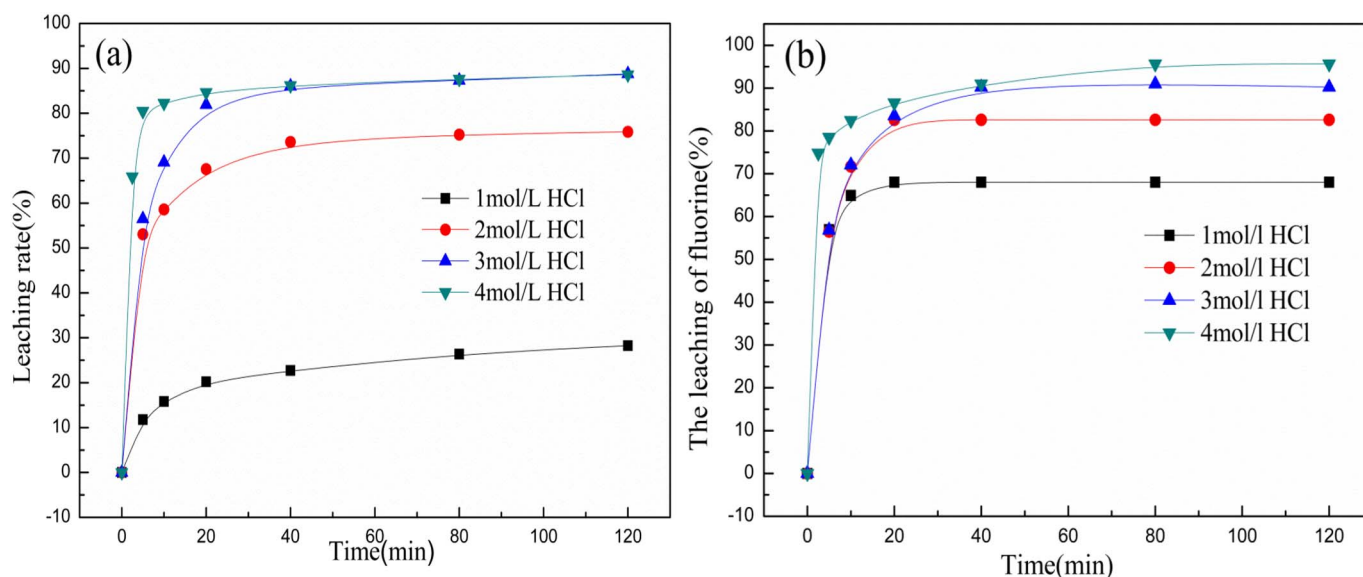
## 2. Experimental

### 2.1. Experimental materials

The mixed concentrate worked in this experiment was from the Baotou in China and was dried at 90 °C for 24 h to remove the free moisture water. The particle size of the mixed concentrate was below 74 μm and the color was gray. The chemical compositions of sample were analyzed and listed in Table 1. The analytical grade reagents were used in the experiment, including hydrochloric acid from Beijing Chemical Works, sodium hydroxide (NaOH), calcium hydroxide (Ca(OH)<sub>2</sub>), aluminium chloride (AlCl<sub>3</sub>) from Tianjin Chemical Reagent No. 3 Factory. And all aqueous solutions were prepared with distilled water.

### 2.2. Procedure

The mixed concentrate was roasted with Ca(OH)<sub>2</sub> and Na(OH)<sub>2</sub> at 700 °C for 30 min in the muffle furnace. The mass ratios of Ca(OH)<sub>2</sub> and Na(OH)<sub>2</sub> to the mixed concentrate were 23.0% and 15.0%, respectively. Then, the roasting product was washed with a hydrochloric acid-citric acid (0.5 mol/L-0.05 mol/L) solution under the conditions: 40 °C, 40 min, 10 mL/g liquid-solid ratio and 300 rpm stirring speed (Bian, 2008). After completion, the solution was rapidly separated by vacuum filtration. The acid washing solution was used to recover phosphate ion, and the filter residue after dried at 60 °C was used to the leaching kinetics experiments of REEs and fluoride. The leaching experiments were performed in a 500 mL three-neck flask glass reactor and a water bath and a mechanical stirrer were employed. Firstly, a certain amount of HCl-AlCl<sub>3</sub> solution was added into the reactor and heated up to a specific temperature. Upon temperature stabilization, 20.0 g filter residue sample was added into the reactor. After a certain period, the leaching solution was separated by vacuum filtration. Leaching slag was dried at



**Fig. 2.** Effect of initial concentration of HCl on the extractions of REEs (a) and fluoride (b) (0.5 mol/L AlCl<sub>3</sub>, temperature 70 °C, 10 mL/g L/S and stirring rate 300 rpm).

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