

Extraction of rare earth elements from fluoride molten salt electrolytic slag by mineral phase reconstruction

Yong Liang^{*}, Yongkang Li, Liyan Xue, Yu Zou

School of Metallurgical and Chemical Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, Jiangxi, China

ARTICLE INFO

Article history:

Available online 30 December 2017

Keywords:

Molten salt electrolysis slag
Rare earth
Sodium silicate
Mineral phase reconstruction
Recovery

ABSTRACT

There is no environmentally efficient process to extract rare earth elements from the slag of fluoride molten salt electrolysis. An extraction method was developed by drawing on the experience of extracting rare earths from gadolinite by hydrochloric acid decomposition. Sodium silicate roasting was used to reconstruct the phases of the rare earth electrolysis slag in a fluoride molten salt. The rare earth fluoride in the slag was transformed into a rare earth silicate that is easily dissolved by acid. A novel process of extracting rare earths from slag by sodium silicate roasting, washing, and acid leaching was developed. The effects of roasting time, mass ratio of sodium silicate to molten salt electrolytic slag, roasting temperature, leaching time, hydrochloric acid concentration, acid leaching temperature, and leaching liquid–solid ratio on the extraction of rare earths were examined. Under conditions of a roasting time of 1.5 h, roasting temperature of 850 °C, mass ratio of 1.5:1, leaching time of 2 h, hydrochloric acid concentration of 4 mol L⁻¹, leaching temperature of 80 °C, and liquid–solid leaching ratio of 12:1, a leaching efficiency of rare earths from the slag of 98.96% was achieved.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Molten salt electrolysis in fluoride salts is commonly used for producing low-melting rare earth elements (REEs) (Zhu, 2014; Xu, 2012a). With ongoing production, various non-REE impurities accumulate in the electrolytic tank, resulting in deterioration of the electrolyte system and upsetting the normal course of the electrolysis process. The waste electrolyte needs to be discharged from the tank and replaced with new electrolyte. Owing to the influence of the electrolysis system itself, the REEs are enriched in the waste electrolyte and form an important secondary resource (Neelameggham et al., 2014; Xu et al., 2010; The research group of Academy of Sciences of sustainable development Chinese, 1993; Interian et al., 2011). The waste electrolyte can contain 10 wt% to 80 wt% of REOs (Liang et al., 2016a): their recovery from the slag is of great significance to the sustainable development of the industry.

The two main methods for the treatment of RE fluoride molten salt electrolytic slag are the acid and alkali methods. The acid method has many disadvantages, such as low recovery of the contained metal, production of HF and other acidic gases, corrosion

of equipment, and environmental pollution (Xiao et al., 2015), so it has been replaced by the alkaline method. The alkaline method involves mixing and roasting alkaline materials with the electrolytic slag. The RE fluorides in the slag are transformed into an RE compound that is readily soluble in an inorganic acid, thereby enabling the REE to be extracted. Lin Jian et al. (2011) mixed and roasted calcium hydroxide with electrolytic slag, and then used 30% hydrochloric acid to dissolve the roasted product to extract the REEs from the slag. Although this method can significantly improve the extraction of REEs, it requires a roasting temperature of 950–1000 °C, which corresponds to a high energy consumption. Calcium fluoride formed in the roasted product is decomposed into fluoride ions that are easily re-combined with RE ions to form an RE fluoride in the subsequent process of acid decomposition, resulting in their incomplete extraction (Liang et al., 2016b). Hu et al. (2015) used sodium hydroxide roasting to transform RE fluoride in an electrolytic slag: at a calcination temperature of 300–500 °C, the RE fluoride was transformed into RE hydroxide and sodium fluoride, but no reference was made to the extent of extraction. In summary, the existing treatment process has low metal recovery and pollutes the environment: a green and efficient method of extracting REE from this source is urgently needed.

The essence of the abovementioned alkali extractions is the transformation of RE fluoride in the slag into an acid-soluble RE compound. The key to the efficient extraction of REE from molten

^{*} Corresponding author. School of Metallurgical and Chemical Engineering, Jiangxi University of Science and Technology, No. 86 Hongqi Avenue, Ganzhou 341000, China.

E-mail address: 245572722@qq.com (Y. Liang).

salt electrolytic slag therefore lies in the reconstruction of the mineral phase of the RE fluoride in the slag. The authors were inspired by the technology used for the hydrochloric acid decomposition of gadolinite. This is a rare earth silicate that is insoluble in water, but can be decomposed by hydrochloric acid, which thereby transforms the REE in the concentrate into a soluble chloride (Xu, 2012b). It was proposed that if the RE fluoride in an electrolytic slag can be transformed into a silicate, then hydrochloric acid leaching can be used to extract the REE.

This study used sodium silicate roasting to treat an RE fluoride molten salt electrolytic slag. The mineral phase of the RE fluoride in the slag was reconstructed by transformation into an RE silicate. The fluorine in the slag was completely converted to sodium fluoride, which was removed by washing with water. Hydrochloric acid was used to leach the washed silicate and extract the REEs from the slag. The effects of roasting temperature and time, the mass ratio, leaching temperature, and hydrochloric acid concentration on the extraction of the REE were systematically investigated.

2. Experimental

2.1. Raw material and reagents

The fluoride molten salt electrolytic slag was provided by a RE refinery in Jiangxi Province, China. Prior to the experiments, the slag was ground to -200 mesh ($<74\ \mu\text{m}$). The amounts and distribution of REE in the slag (the data are given in terms of oxide) are shown in Table 1. X-ray diffraction analysis indicated that the main phases were LaF_3 and $\text{LaO}_{0.7}\text{F}_{1.6}$ (as shown in Fig. 1). Sodium silicate, hydrochloric acid, and other reagents were of analytical grade.

2.2. Experimental method

In a typical experiment, prescribed amounts of slag and sodium silicate were evenly mixed and the mixture roasted in a muffle furnace. After the selected roasting time, the product was washed several times with water and the slurry filtered. The dried filter cake was charged into a three-necked bottle containing a selected concentration hydrochloric acid.

Phase analysis of the raw materials, roasted product, and acid-leached residue were carried out by X-ray diffractometer (X'Pert Powder, PANalytical, Netherlands). The chemical composition of the acid-leached residue was determined by X-ray fluorescence spectrometry (AxiosMAX, PANalytical, Netherlands). Microanalysis of the roasted product after washing was carried out by scanning electron microscopy (SIGMA, Carl Zeiss, Germany) and energy-dispersive spectrometry (X-MaxN 20 mm², Oxford Instruments, UK). The total amounts of rare earth oxides (TREO) and their distribution patterns were analyzed using the oxalate gravimetric method (GB 14635–2008, CHINA) with an inductively coupled plasma emission spectrometer (725-OES, Agilent Technologies, USA).

3. Results and discussion

3.1. Effect of roasting time

The effect of roasting time on the leaching efficiency of REEs and TREO from the acid-leaching residue was investigated using a mass ratio of sodium silicate to molten salt electrolytic residue of 1.5:1, a

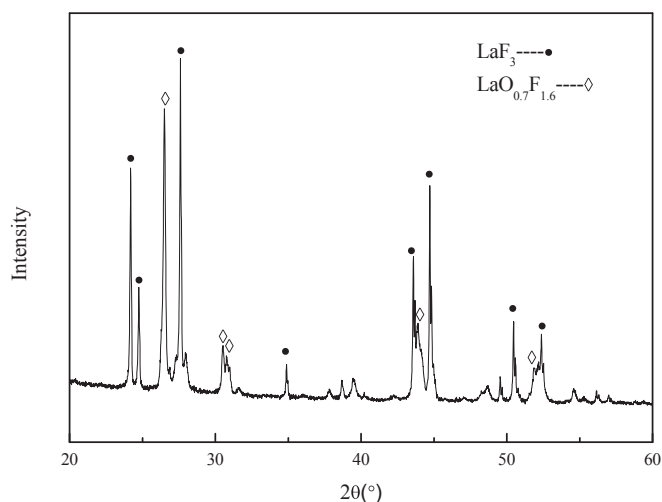


Fig. 1. X-ray diffraction pattern of the experimental raw.

roasting temperature of $850\ ^\circ\text{C}$, leaching time of 2 h, HCl concentration of $4\ \text{mol L}^{-1}$, leaching temperature of $90\ ^\circ\text{C}$, and liquid–solid (L/S) ratio in leaching of 10:1. The results are shown in Fig. 2. The leaching efficiency of the RE increased with time, from 95.23% to 97.93% on increasing the roasting time from 0.5 h to 1.5 h. Correspondingly, the RE content of the acid-leached residue decreased from 7.80% to 3.83%. The leaching efficiency did not significantly change with further increase in roasting time, so an appropriate roasting time was selected as 1.5 h.

3.2. Effect of mass ratio

To test the effect of the mass ratio of sodium silicate to electrolytic slag on the leaching efficiency of REEs and TREO in the acid-leached residue within the range of 1.1:1–1.9:1, the experimental parameters were set as follows: roasting time: 1.5 h; roasting temperature: $850\ ^\circ\text{C}$; leaching time: 2 h; HCl concentration: $4\ \text{mol L}^{-1}$; leaching temperature: $90\ ^\circ\text{C}$; L/S ratio: 10:1. The results are shown in Fig. 3. The leaching efficiency of the REE first increased and then decreased. When the mass ratio was 1.5:1, the leaching efficiency was 97.93%. With time, the leaching efficiency decreased as the amount of sodium silicate increased.

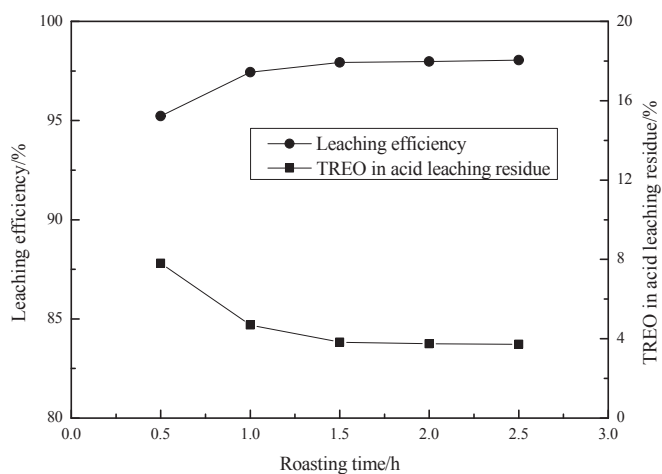


Fig. 2. Effect of roasting time on the leaching efficiency of REEs and the TREO in acid leaching residue. (The mass ratio of sodium silicate to molten salt electrolytic residue 1.5:1, roasting temperature $850\ ^\circ\text{C}$, leaching time 2 h, hydrochloric acid concentration $4\ \text{mol L}^{-1}$, leaching temperature $90\ ^\circ\text{C}$, L/S ratio 10:1).

Table 1
TREO and REO distribution in the experimental raw.

	TREO	La_2O_3	CeO_2	Others
Content/%	77.66	99.61	0.25	0.14

Download English Version:

<https://daneshyari.com/en/article/8098753>

Download Persian Version:

<https://daneshyari.com/article/8098753>

[Daneshyari.com](https://daneshyari.com)