



Recovery of iron from red mud by selective leach with oxalic acid



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ABSTRACT

The recovery of iron from red mud by selective leach with oxalic acid was studied. In order to reduce the cost of iron recovery, the red mud was washed with diluted hydrochloric acid before it was leached. Experiment results showed that after washing with 3 mol/L HCl under L/S ratio 2:1 mL/g at room temperature for 1 h, the loss of oxalic acid in the leached residue was decreased from about 17% to less than 1%. Under the conditions of washed red mud/H₂C₂O₄·2H₂O/H₂SO₄ mass ratio 3:3:2 with L/S ratio 16:1 mL/g at 95 °C for 1.5 h, the leach ratio of iron was 94.15%, while that of aluminum was 21.12% and, the content of iron was 0.69% in the leached residue. After reducing with iron scraps at 50 °C for 60 min, the iron in the leached solution was completely changed into the precipitate of FeC₂O₄·2H₂O. Then the FeC₂O₄·2H₂O was turned into FeSO₄·H₂O and H₂C₂O₄ in 9 mol/L H₂SO₄ under the conditions: with L/S ratio 5:1 mL/g at 50 °C stirring for 20 min. By filtering the supernatant immediately, the product of FeSO₄·H₂O was obtained and, the crystal of H₂C₂O₄·2H₂O was formed by cooling the filtrate at room temperature.

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1. Introduction

Red mud (bauxite residue) is a solid waste produced in the process of alumina extraction from bauxite. Depending upon the quality of the raw material processed and alumina extraction efficiencies, approximately 1–2.5 tons of red mud are generated per ton of alumina produced (Paramguru et al., 2005). More than 70 million tons of red mud is discharged to the environment every year all over the world, which causes serious disposal problems for the environment due to its high alkalinity and complex chemical compositions (Liu et al., 2009). Many attempts have been made to find environmental methods to deal with red mud, such as valuable metal recovery from red mud (Ghosh et al., 2011; Tsakiridis et al., 2011; Wang et al., 2013), refractory materials and ceramic production (Guo et al., 2014; Pérez-Villarejo et al., 2012), and catalysts for waste gas and liquid cleaning (Bertocchi et al., 2006; Liu et al., 2011; Poulin et al., 2008). To produce refractory materials, the iron must be removed from red mud due to the fact that high content of Fe₂O₃ can cause low fire resistance of refractory materials (Liu et al., 2008). Many processes have been proposed to remove iron from red mud, such as reduction roasting with adding sodium slag followed by magnetic separation (Zhu et al., 2012), reduction sintering with carbon followed by leaching and magnetic beneficiation (Li et al., 2009) and magnetic separation after co-roasting with pyrite (Liu et al., 2014). However, not only high temperature is needed in the above processes but also high demands are required for chemical reactor. Compared with the pyrogenic processes, oxalic acid was found to have a better performance in iron

removal due to its strong acidity and chelating ability to iron ions (Ambikadevi and Lalithambika, 2000; Taxiarchou et al., 1997; Veglió et al., 1998). By ultraviolet irradiation assistance, the iron in the leached solution was changed from Fe(III) into Fe(II), and the precipitate of FeC₂O₄·2H₂O was formed (Yu et al., 2012). It was found that more than 30% of oxalic acid was decomposed during the irradiation, which made the cost too high to be used in industry. Recently, we found that the iron in the leached solution can be precipitated in the form of FeC₂O₄·2H₂O by reducing with iron scraps (Wang et al., 2014).

In view of the above, the motivation for this study was the need to reduce the cost of the recovery of iron from red mud and to make the reuse of oxalic acid in the process. The present work investigated the selective leach of iron from red mud with oxalic acid and, the reduction of iron in the leached solution with iron scraps to form the precipitate of FeC₂O₄·2H₂O, as well as the separation of oxalic acid and iron from the precipitate with sulfuric acid.

2. Experimental

2.1. Materials and analysis

The red mud used in this study was taken from Guizhou Branch of CHALCO, of which the mesh size ranges from 10 μm to 100 μm and 80% is less than 40 μm. Oxalic acid, sulfuric acid, hydrochloric acid, nitric acid, acetic acid, sodium acetate, potassium permanganate, iron scraps and 1,10-phenanthroline were used in the experiments. The mesh size of the iron scraps ranges from 100 μm to 150 μm. Except iron scraps, all the reagents were of analytical grade. The compositions of red mud and iron scraps were listed in Table 1. The XRD patterns of the

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Table 1

Experimental results of iron recovery from red mud by selective leaching with oxalic acid, %.

Elements	O	Al	Ca	Si	Na	Fe	Ti	K	Cl
Red mud	38.65	13.89	13.73	12.26	7.81	5.38	3.1	2.27	–
Iron scraps	0.13	0.03	–	0.01	–	97.85	–	–	–
Washed red mud	41.13	17.48	4.96	15.38	2.14	7.58	4.09	1.16	0.85
Leached residue	44.48	20.97	6.44	18.45	1.15	0.69	5.02	0.82	0.24
Ferrous oxalate	44.46	0.14	–	0.11	0.12	30.98	–	0.09	–

red mud are shown in Fig. 1. As can be seen, there are six main crystal mineral phases, namely, calcium aluminosilicate hydrate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot 4\text{H}_2\text{O}$), quartz (SiO_2), calcite (CaCO_3), sodium aluminosilicate ($\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 1.7\text{SiO}_2\cdot 2\text{H}_2\text{O}$), hematite (Fe_2O_3) and calcium titanate (CaTi_2O_4).

The concentration of oxalate group was titrated with potassium permanganate. Bivalent iron chemical analysis was based on spectrometric method using 1,10-phenanthroline as complexing agent. Total iron, calcium, aluminum, sodium and so on were determined by inductively coupled plasma (ICP) emission spectroscopy with a PS-6 PLASMA SPECTROVAC, BAIRD (USA). The X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex diffractometer with $\text{Cu K}\alpha$ X-ray radiation at 35 kV and 20 mA.

2.2. Experimental procedure

The experiments were performed according to the flow sheet as shown in Fig. 2. A pre-determined weight of the red mud was washed with diluted hydrochloric acid under stirring to remove the soluble Ca, Na and K. Then the washed red mud was leached with oxalic acid solution to extract iron. After the required contact time, the supernatant was vacuum filtered, and the leached residue was submitted to successive rinsing with water until the filtrate was colorless, before it was dried and analyzed for iron and other element contents.

The Fe(III) containing in the filtrate was reduced with iron scraps to form the precipitate of $\text{Fe}_2\text{O}_4\cdot 2\text{H}_2\text{O}$. After required reaction time, the precipitate was separated by filtration. The contents of ferric iron and ferrous iron, as well as the oxalate group in the solution before and after reduction were analyzed respectively.

All of the precipitates obtained under different conditions were mixed by stirring in water, and then filtrated and dried. In order to separate of oxalic acid and iron, the precipitate was decomposed in 9 mol/L

H_2SO_4 under heating and stirring to form the precipitate of $\text{FeSO}_4\cdot\text{H}_2\text{O}$. After required reaction time, the suspension was filtered immediately, and the filtrate was submitted to be cooled to crystallize oxalic acid. The obtained oxalic acid was reused in the leach and, the crystallized solution was returned to the decomposition.

3. Results and discussion

3.1. Red mud pretreatment

It was found that with oxalic acid to direct leach the iron from red mud, the loss of it in the leached residue was about 17%. To reduce the cost, the red mud was washed with acid solutions before it was leached. Fig. 3 shows the loss ratio of oxalic acid in the leach after washing with different mineral acid solutions. As seen, the loss of oxalic acid in the leached residue was reduced to less than 1% after washing with the diluted solution of HCl or HNO_3 . This is due to the solution of HCl or HNO_3 that can turn the calcite (CaCO_3) existing in red mud into soluble CaCl_2 or $\text{Ca}(\text{NO}_3)_2$, while with H_2SO_4 solution it was changed into CaSO_4 at first, then the CaSO_4 was further changed into CaC_2O_4 in the leaching with oxalic acid. But only diluted HCl solution was chosen as the washing liquid as its cost is relatively low.

Fig. 4 is the XRD patterns of the washed red mud obtained by washing the red mud in 3 mol/L HCl with L/S ratio 2:1 mL/g at room temperature for 1 h. As seen from Fig. 4, there are five main crystal mineral phases, namely, calcium aluminosilicate hydrate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot 4\text{H}_2\text{O}$), quartz (SiO_2), sodium aluminosilicate ($\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 1.7\text{SiO}_2\cdot 2\text{H}_2\text{O}$), hematite (Fe_2O_3) and calcium titanate (CaTi_2O_4). Comparing to Fig. 1, it can be seen that after washing, the calcite (CaCO_3) phase disappeared. The composition of the washed red mud is listed in Table 1 as well. From Table 1, it can be seen that after washing, the contents of Ca, Na and K were reduced, while that of Al, Si and Ti were concentrated.

3.2. Leach iron

3.2.1. Effect of oxalic acid addition

The effect of oxalic acid addition on the leach ratio of iron was studied under the conditions of adding pre-determined weigh of $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ to per 15 g washed red mud with L/S ratio 14:1 mL/g at 95 °C for 2 h. The experimental results were showed in Fig. 5. As can be seen, with the addition increase from 10 g to 30 g, the leach ratio of iron increased from 49.86% to 96.63%, and that of aluminum increased from 5.15% to 71.22%. This indicates that single using oxalic acid as leaching agent, will inevitably cause a large number of aluminum into the leach solution. Thus, it perhaps is an advisable choice to add other addition agent into the solution to make iron leached from it selectively.

3.2.2. Effect of H_2SO_4 addition

Theory analysis results show that mineral acids can be chosen as the addition agent because the complex stability constants of ferric oxalate (2.5×10^9 , 1.6×10^{16} , 1.6×10^{20}) are greater than that of aluminum oxalate (1.8×10^7 , 1.0×10^{13} , 2.0×10^{16}) (Dean, 1985), and proper increase H^+ concentration in the solution is favorable to the dissolution of Fe_2O_3 . Exploratory experiments found that H_2SO_4 , HCl and HNO_3 are all effective addition agents for iron selective leaching, and H_2SO_4 was chosen as the addition agent in the following experiments as its volatility is less than that of HCl or HNO_3 in the solution.

Fig. 6 is the experimental results obtained under the conditions of adding 15 g $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ into per 15 g washed red mud with L/S ratio 14:1 mL/g at 95 °C for 2 h. As seen, with H_2SO_4 addition increase from 0 to 10 g, the leach ratio of iron increased from 70.42% to 92.56%, while that of aluminum increased from 15.76% to 22.25%. Further increase in the addition, the leach ratio of iron maintained almost the same. Hence, the mass ratio of 3:3:2 for the washed red mud/ $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ was chosen as the optimal charge ratio.

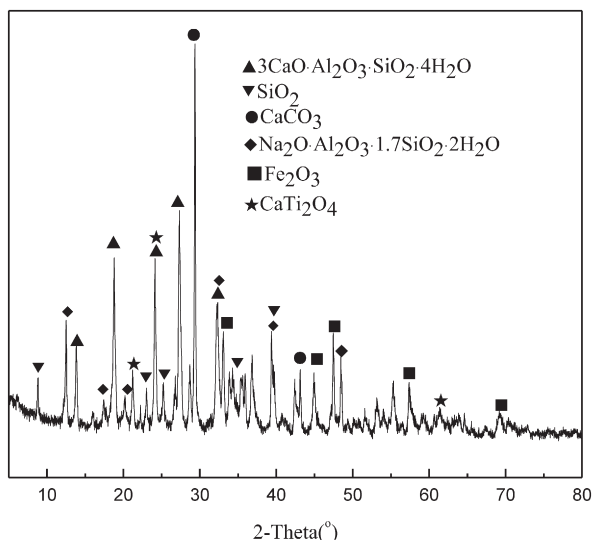


Fig. 1. XRD patterns of red mud.

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