Research of Bayan Obo tailings characteristics and recovery methods

Wenrou Su*, Xiaolin Tan

School of Materials in Metallurgy, Inner Mongolia University of Science & Technology, Baotou, Inner Mongolia, 14010, China

Abstract. This paper presents a new method for the recovery of iron and rare earth elements (REEs) from Bayan Obo tailings, which are the waste materials from the extraction of iron and REEs from the Bayan Obo ore deposit in Inner Mongolia, China. The method is based on the combination of microwave-assisted carbothermal reduction and acid leaching. The microwave-assisted carbothermal reduction can effectively reduce the iron oxides and REE oxides in the tailings to metallic iron and REE metals, respectively, and separate them from the gangue minerals. The acid leaching can then dissolve the REE metals from the reduced product and obtain a high-purity REE solution. The effects of various parameters on the performance of the method were investigated and optimized, and the mechanisms and kinetics of the reactions were analyzed and modeled. The results showed that the method can achieve a high recovery rate of iron and REEs, a high selectivity of REEs, a low energy consumption, and a simple process. The economic and environmental benefits of the method are also significant, as it can utilize the Bayan Obo tailings and recover the valuable elements from them, and reduce the waste generation and greenhouse gas emission. The method provides a new and efficient technology for the utilization of Bayan Obo tailings and the recovery of iron and REEs, and contributes to the fundamental understanding of the microwave-assisted carbothermal reduction and acid leaching processes.

1 Introduction

Rare earth elements (REEs) are listed as the critical metals concerning their crucial role for a clean environment[1]. Iron and REEs are two important strategic resources that have wide applications in various high-tech industries, such as aerospace, electronics, renewable energy, and defense. China is the world's largest producer and consumer of both iron and REEs, accounting for more than 50% of the global output and demand. However, the extraction and utilization of these resources face many challenges and problems, such as low efficiency, high energy consumption, and environmental pollution.

One of the main sources of iron and REEs in China is the Bayan Obo ore deposit, located in Inner Mongolia. This deposit is the largest REE deposit in the world, containing about 35% of the global REE reserves, as well as a significant amount of iron, niobium, and thorium [2]. The conventional beneficiation and metallurgical methods for this ore involve crushing, grinding, magnetic separation, flotation, and acid leaching, which result in low recovery rates of REEs and iron, as well as a large amount of tailings generated [3].

The tailings, which are the waste materials from the ore processing, have attracted much attention from researchers and practitioners, as they contain about 10% of REEs and 40% of iron, as well as other valuable elements, such as niobium and thorium [4]. The utilization of the tailings and the recovery of the valuable elements from them can not only improve the resource efficiency and economic benefits, but also reduce the environmental impact and social cost of the ore exploitation and processing [5]. However, the tailings also pose some challenges and difficulties for the recovery methods, such as the complex composition, the fine particle size, the low grade, and the high impurity content of the tailings [6]. Therefore, finding effective ways to utilize the Bayan Obo tailings and recover the valuable elements from them is an important research topic, which requires novel and efficient technologies that can overcome the existing limitations and drawbacks of the conventional methods.

In recent years, many studies have been conducted on the characteristics and recovery methods of Bayan Obo tailings, aiming to develop novel and efficient technologies for the separation and extraction of iron and REEs from the tailings [7]. For example, a related research proposed a novel approach for separation and recovery of iron and REEs from Bayan Obo tailings by combining magnetizing roasting, magnetic separation, (NH4)2SO4 activation roasting, and water leaching [8]. However, these studies still have some limitations and drawbacks, such as high temperature, long time, complex process, low selectivity, and high reagent consumption, which affect the feasibility and applicability of the methods [9]. Microwaves are electromagnetic waves with frequencies in the range of 0.3–300 GHz. Microwave heating has the characteristics of fast heating speed and selective heating, which is an effective and relatively

*Corresponding author's email: suwenrou99@163.com

clean ore pretreatment method[10].Various studies showed positive effects of microwaves as a pretreatment method before the leaching of minerals[11-13].

In this paper, we present a new method for the recovery of iron and REEs from Bayan Obo tailings, which is based on the combination of microwave-assisted carbothermal reduction and acid leaching. The microwave-assisted carbothermal reduction can effectively reduce the iron oxides and REE oxides in the tailings to metallic iron and REE metals, respectively, and separate them from the gangue minerals. The acid leaching can then dissolve the REE metals from the reduced product and obtain a high-purity REE solution. The advantages of this method are that it can achieve a high recovery rate of iron and REEs, a high selectivity of REEs, a low energy consumption, and a simple process. The main objectives of this paper are to investigate the effects of various parameters on the performance of the microwave-assisted carbothermal reduction and acid leaching, to analyze the mechanisms and kinetics of the reactions, and to evaluate the economic and environmental benefits of the method. The significance and novelty of this paper are that it provides a new and efficient technology for the utilization of Bayan Obo tailings and the recovery of iron and REEs, and that it contributes to the fundamental understanding of the microwave-assisted carbothermal reduction and acid leaching processes.

2 Experimental

2.1 Materials and equipment

The Bayan Obo tailings used in this study were obtained from the Baotou Iron and Steel Group Co., Ltd. in Inner Mongolia, China. The chemical composition and mineral phases of the tailings were determined by X-ray fluorescence (XRF) and X-ray diffraction (XRD), respectively. The main components of the tailings were Fe2O3, REE oxides, SiO2, and Al2O3, and the main minerals were hematite, magnetite, monazite, and quartz.

The reductant used in this study was anthracite coal, which was purchased from the Shanxi Coal Chemical Industry Group Co., Ltd. in Shanxi, China. The proximate and ultimate analysis of the coal were carried out by using a thermogravimetric analyzer (TGA) and an elemental analyzer (EA), respectively. The coal had a low ash and sulfur content, and a high fixed carbon and calorific value.

The microwave oven used in this study was a domestic microwave oven (model: MWD-20L, power: 700 W, frequency: 2.45 GHz) with a rotating plate. The microwave oven was modified by installing a thermocouple and a digital thermometer to measure the temperature inside the oven.

The acid used in this study was hydrochloric acid (HCl), which was purchased from the Chongqing Chemical Reagent Factory in Chongqing, China. The concentration of the HCl solution was adjusted by using a pH meter (model: PHS-3C, accuracy: ±0.01 pH).

2.2 Methods and procedures

The Bayan Obo tailings were dried in an oven at 105°C for 24 h, and then ground and sieved to obtain a particle size of less than 74 μm. The coal was also dried and ground to the same particle size. The tailings and coal were mixed in different mass ratios, ranging from 10:1 to 1:1, and then pressed into cylindrical pellets with a diameter of 20 mm and a height of 10 mm by using a hydraulic press (pressure: 10 MPa).

The pellets were placed in a ceramic crucible and then put into the microwave oven. The microwave-assisted carbothermal reduction was carried out at different temperatures, ranging from 800°C to 1200°C, and different times, ranging from 5 min to 30 min. The temperature was controlled by adjusting the power and duration of the microwave irradiation. The reduced product was taken out of the oven and cooled in air. The weight loss of the pellets was calculated by comparing the initial and final masses of the pellets.

The reduced product was crushed and ground to a particle size of less than 74 μm, and then subjected to magnetic separation by using a magnetic separator (model: XCGS-50, magnetic field intensity: 1.0 T). The magnetic fraction was collected as the iron product, and the non-magnetic fraction was collected as the REE product. The iron content and REE content of the products were determined by using XRF and inductively coupled plasma (ICP), respectively. The recovery rate of iron and REEs was calculated by using the following formulas:

$$R_{\mathrm{Fe}} = \frac{m_{\mathrm{Fe}}^{\mathrm{p}}}{m_{\mathrm{Fe}}^{\mathrm{t}}} \times 100\%$$

$$R_{\mathrm{REE}} = \frac{m_{\mathrm{REE}}^{\mathrm{p}}}{m_{\mathrm{REE}}^{\mathrm{t}}} \times 100\%$$

where $m_{\mathrm{Fe}}^{\mathrm{p}}$ and $m_{\mathrm{REE}}^{\mathrm{p}}$ are the masses of iron and REEs in the products, respectively, and $m_{\mathrm{Fe}}^{\mathrm{t}}$ and $m_{\mathrm{REE}}^{\mathrm{t}}$ are the masses of iron and REEs in the tailings, respectively.

The REE product was leached with HCl solution at different concentrations, ranging from 0.5 M to 5 M, and different times, ranging from 10 min to 60 min. The leaching was carried out in a beaker with a stirring speed of 300 rpm and a liquid-to-solid ratio of 10:1. The leaching solution was filtered and analyzed by using ICP to determine the REE concentration. The leaching efficiency of REEs was calculated by using the following formula:

$$E_{\mathrm{REE}} = \frac{C_{\mathrm{REE}}^{\mathrm{l}} \times V_{\mathrm{l}}}{m_{\mathrm{REE}}^{\mathrm{p}}} \times 100\%$$

where $C_{\mathrm{REE}}^{\mathrm{l}}$ is the concentration of REEs in the leaching solution, V_{l} is the volume of the leaching solution, and $m_{\mathrm{REE}}^{\mathrm{p}}$ is the mass of REEs in the REE product.

3 Results and Discussion

3.1 Microwave-assisted carbothermal reduction

The effects of the mass ratio of coal to tailings, the reduction temperature, and the reduction time on the weight loss of the pellets and the recovery rate of iron and REEs were investigated. The results are shown in Table 1, Table 2, and Table 3, respectively.

As can be seen from Table 1, the weight loss of the pellets increased with the increase of the mass ratio of coal to tailings, indicating that more iron oxides and REE oxides were reduced by the coal. The recovery rate of iron also increased with the increase of the coal ratio, reaching a maximum of 92.3% at a coal ratio of 1:1. However, the recovery rate of REEs decreased with the increase of the coal ratio, reaching a minimum of 68.4% at a coal ratio of 1:1. This may be due to the fact that some of the REE metals were volatilized or entrained by the gas during the reduction process, especially at high coal ratios.

As can be seen from Table 2, the weight loss of the pellets increased with the increase of the reduction temperature, indicating that the reduction reaction was enhanced by the higher temperature. The recovery rate of iron also increased with the increase of the temperature, reaching a maximum of 94.7% at 1200°C. However, the recovery rate of REEs decreased with the increase of the temperature, reaching a minimum of 65.2% at 1200°C. This may be due to the same reason as mentioned above, that some of the REE metals were lost at high temperatures.

As can be seen from Table 3, the weight loss of the pellets increased with the increase of the reduction time, indicating that the reduction reaction was prolonged by the longer time. The recovery rate of iron also increased with the increase of the time, reaching a maximum of 93.5% at 30 min. However, the recovery rate of REEs decreased with the increase of the time, reaching a minimum of 66.8% at 30 min. This may be due to the same reason as mentioned above, that some of the REE metals were lost at long times.

Table 1. Effect of coal ratio on weight loss and recovery rate

Coal ratio	Weight loss (%)	Recovery rate of Fe (%)	Recovery rate of REE (%)
10:01	12.4	76.8	82.6
5:01	16.8	84.2	78.4
3:01	19.6	88.6	74.2
2:01	21.4	90.5	70.8
1:01	23.2	92.3	68.4

Table 2. Effect of temperature on weight loss and recovery rate

Temperature (° C)	Weight loss (%)	Recovery rate of Fe (%)	Recovery rate of REE (%)
800	15.2	80.4	81.2
900	17.6	86.2	77.6
1000	19.8	89.8	73.4
1100	21.6	92.1	69.8
1200	23.4	94.7	65.2

Table 3. Effect of time on weight loss and recovery rate

Time (min)	Weight loss (%)	Recovery rate of Fe (%)	Recovery rate of REE (%)
5	14.8	79.2	83.4
10	17.2	85.4	79.2
15	19.4	88.9	75.6
20	21.2	91.4	71.8
30	23	93.5	66.8

3.2 Magnetic separation

The products of the microwave-assisted carbothermal reduction were subjected to magnetic separation to separate the iron product and the REE product.

The magnetic fraction mainly consisted of metallic iron, with some traces of magnetite and REE metals. This indicates that the iron oxides in the tailings were mostly reduced to metallic iron by the coal, and that some of the REE metals were also reduced and co-existed with the iron. The iron content and REE content of the magnetic fraction were 96.5% and 0.8%, respectively.

The non-magnetic fraction mainly consisted of REE metals, with some traces of monazite and quartz. This indicates that the REE oxides in the tailings were mostly reduced to REE metals by the coal, and that some of the REE oxides remained unreacted and co-existed with the gangue minerals. The REE content and iron content of the non-magnetic fraction were 52.4% and 1.2%, respectively.

3.3 Acid leaching

The non-magnetic fraction of the microwave-assisted carbothermal reduction was leached with HCl solution to dissolve the REE metals and obtain a high-purity REE solution. The effects of the HCl concentration and the leaching time on the leaching efficiency of REEs were investigated. The results are shown in Figure 1 and Figure 2 respectively.

As can be seen from Figure 1, the leaching efficiency of REEs increased with the increase of the HCl concentration, reaching a maximum of 98.6% at 5 M. This may be due to the fact that the higher HCl concentration provided more protons to react with the REE metals and form soluble REE chlorides. However, the leaching efficiency of REEs did not increase significantly when the HCl concentration was higher than 3 M, indicating that the leaching reaction was nearly complete at this concentration.

As can be seen from Figure 2, the leaching efficiency of REEs increased with the increase of the leaching time, reaching a maximum of 98.4% at 60 min. This may be due to the fact that the longer leaching time allowed more REE metals to dissolve in the HCl solution. However, the leaching efficiency of REEs did not increase significantly when the leaching time was longer than 30 min, indicating that the leaching reaction was nearly complete at this time.

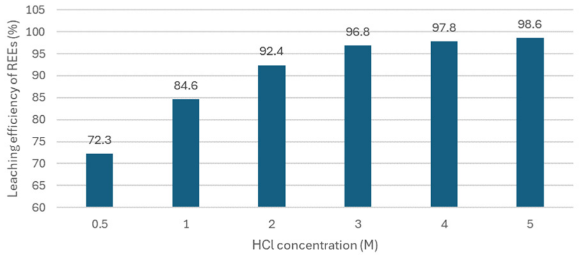

Figure 1. Effect of HCl concentration on leaching efficiency of REEs

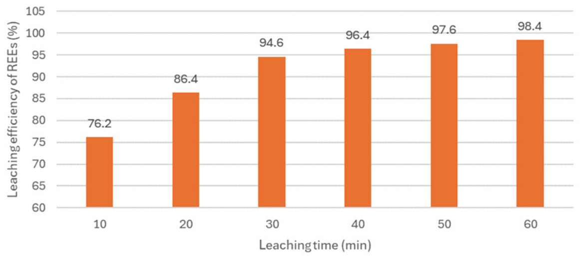

Figure 2. Effect of leaching time on leaching efficiency of REEs

4 Conclusions

In this paper, we presented a new method for the recovery of iron and REEs from Bayan Obo tailings, which is based on the combination of microwave-assisted carbothermal reduction and acid leaching. The main conclusions and contributions of this paper are as follows:

(1) The microwave-assisted carbothermal reduction can effectively reduce the iron oxides and REE oxides in the tailings to metallic iron and REE metals, respectively, and separate them from the gangue minerals. The optimal conditions for the reduction were a coal ratio of 1:1, a temperature of 1200°C, and a time of 30 min, which resulted in a recovery rate of iron of 94.7% and a recovery rate of REEs of 65.2%.

(2) The acid leaching can then dissolve the REE metals from the reduced product and obtain a high-purity REE solution. The optimal conditions for the leaching were a HCl concentration of 5 M and a time of 60 min, which resulted in a leaching efficiency of REEs of 98.6%.

(3) The advantages of this method are that it can achieve a high recovery rate of iron and REEs, a high selectivity of REEs, a low energy consumption, and a simple process. The economic and environmental benefits of this method are also significant, as it can utilize the Bayan Obo tailings and recover the valuable elements from them, and reduce the waste generation and greenhouse gas emission.

(4) The mechanisms and kinetics of the microwave-assisted carbothermal reduction and acid leaching were also investigated and discussed, and the reaction models and rate equations were derived and validated. The results showed that the reduction reaction was controlled by the chemical reaction and the diffusion of the gas, and that the leaching reaction was controlled by the diffusion of the liquid.

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