

## IRON RECOVERY FROM RED MUD BY REDUCTION ROASTING-MAGNETIC SEPARATION

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### Abstract

This work provided an effective method for comprehensive utilization of red mud, which mainly focused on the first step of recovering iron from a high iron content red mud by reduction roasting-magnetic separation. During the reduction, iron oxides were reduced to metallic iron with the aid of sodium sulfate and sodium carbonate. Effects of the dosages of sodium sulfate and sodium carbonate, roasting temperature and roasting time on the metallization ratio of iron of roasted product, total iron grade and iron recovery of magnetic concentrate were primarily investigated. In the presence of 6% Na<sub>2</sub>SO<sub>4</sub>, 6% Na<sub>2</sub>CO<sub>3</sub> and optimal reduction roasting-magnetic separation conditions: roasting temperature of 1050 °C, roasting time of 60 min, magnetic separation feed fineness of 90% passing 74 μm and magnetic field intensity of 0.1 T, a magnetic concentrate containing 90.12% iron with iron recovery of 94.95% was obtained from a red mud containing 48.23% total iron, 7.71% Al<sub>2</sub>O<sub>3</sub> and 7.69% SiO<sub>2</sub>.

### Introduction

A vast amount of solid waste i.e. red mud is produced from Bayer process for alumina extraction from bauxite[1]. Approximately 0.8-1.5 tons of red mud is generated per ton of alumina produced depending on the original properties of the bauxite and the operating conditions[2]. Due to the increasing alumina production and high-aluminum-content bauxite depletion, the annual output of the red mud is continuously increasing. At present, about 70 Mt of red mud is produced annually in the worldwide[3]. It is estimated that the accumulative total pile of stock of red mud will reach 350 Mt by 2015 in China[4].

The major constituents of red mud are crystalline hematite (Fe<sub>2</sub>O<sub>3</sub>), boehmite (γ-AlOOH), quartz (SiO<sub>2</sub>), sodalite (Na<sub>4</sub>Al<sub>3</sub>Si<sub>3</sub>O<sub>12</sub>Cl) and gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O)[5]. Red mud obtained from the Bayer process contains high amount of Fe<sub>2</sub>O<sub>3</sub> (>30%) and Al<sub>2</sub>O<sub>3</sub> (>15%)[6], and the iron content in the mud is high (above 50% as an oxide) when its content in the feed is high (near or above 20% as oxide)[7]. In the viewpoint that red mud usually contains high iron content which could be regarded as an iron-bearing material, extensive works have been carried out in order to recover iron from red mud[8]. In terms of the methodology, the processes of iron recovery can be classified into three categories: 1) magnetic separation[9, 10]; 2) smelting[11, 12]; 3) solid state reduction [13, 14].

The results of direct application of magnetic separation on red mud are unsatisfied due to the complex mineralogy and fine dissemination of iron-bearing minerals. Smelting approach is high energy consumption and capital cost, and also bears the disadvantage of blending with high grade iron ore before charged into the blast furnace[15]. In the solid state reduction method, iron minerals are converted to metallic iron which can be separated magnetically under more mild condition. Moreover, the comparatively higher cost of reducing iron oxides to metallic iron can be compensated by the value-added product of metallic iron which can be charged into electric furnace for steelmaking, compared to the direct magnetic separation of hematite from red mud. In the other hand, this method still suffers from the disadvantage of making the separation of the reduced mass from the rest of the product difficult. Thus, the product is highly contaminated with the gangue material as the metallic iron is obtained in a very fine form.

Therefore, the behavior investigation of metallic iron grains is significant to the availability of solid state reduction method

[16]. This work mainly focused on the first step of recovering iron from a high iron content red mud by reduction roasting-magnetic separation with the aid of sodium sulfate and sodium carbonate.

## Experimental

### Materials

**Red mud.** The red mud sample used in this research was taken from Shandong aluminum company, China, and its chemical composition is presented in Table I. As seen from Table I, the red mud contains 48.23% total iron, 7.71%  $Al_2O_3$  and 7.69%  $SiO_2$ . XRD analysis indicates it mainly consists of goethite ( $FeO(OH)$ ), hematite ( $Fe_2O_3$ ) and quartz ( $SiO_2$ ).

Table I. Chemical composition of high-iron-content red mud

Composition	Mass/%
$Fe_{total}$	48.23
$Al_2O_3$	7.31
$SiO_2$	7.96
$TiO_2$	1.42
$Na_2O$	1.35
S	0.10
P	0.08
LOI*	10.28

\*LOI: loss on ignition

**Reductant.** Lignite was used as the reducing agent. Its proximate analysis and ash chemical composition is shown in Table II.

Table II. Proximate analysis of lignite /wt.%

Proximate analysis*				Main chemical composition of ash			
$M_{ad}$	$A_d$	$V_{daf}$	$F_{cad}$	CaO	MgO	$Al_2O_3$	$SiO_2$
6.91	5.31	35.15	52.63	3.36	0.63	32.16	45.46

\* $M_{ad}$ : Moisture;  $A_d$ : Ash content;  $V_{daf}$ : Volatile content;

$F_{cad}$ : Fixed carbon content

**Additives.** Sodium carbonate and sodium sulfate were used as additives. Both of them were of analytical grade.

### Methods

Red mud was dried and thoroughly mixed with a given mass proportion of additives ( $Na_2SO_4$  and  $Na_2CO_3$ ) and water. Each 2 g of the mixture was compressed into a cylinder with diameter of 10 mm and height of 10 mm. Lignite was crushed and screened to a size range of 0.5-2.0 mm and used as the reductant. After drying, about 30 g dry red mud cylinders were mixed with an excessive amount of lignite to ensure the sufficient reducing atmosphere. The mixtures of red mud cylinders and lignite were charged into a cylindrical heat-resistant stainless steel pot. Then, the pot was put into a vertical resistance furnace (Figure 1) and roasted for a given period. After roasting, the reduced cylinders were cooled to room temperature in the pot isolated from atmospheric oxygen. A 20 g sub-sample of the cooled cylinders was ground to about 90 wt.% passing 74  $\mu m$  in an XMQ  $\Phi 240 \times 90$  ball mill. The slurry was then separated in an XCGS-73 Davies Magnetic Tube using a magnetic field intensity of 0.1 T.

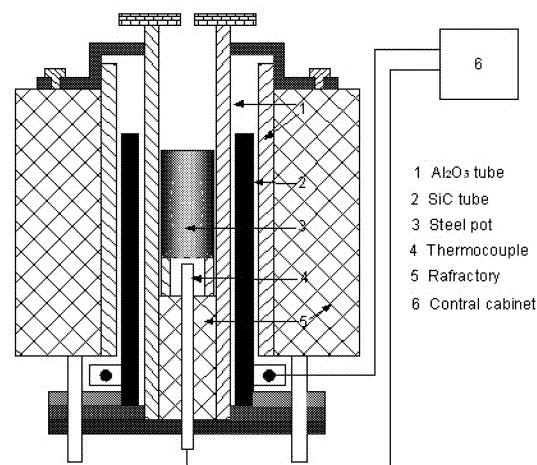


Figure 1. Schematic diagram of the vertical resistance furnace

## Results and Discussion

### Reduction Roasting-Magnetic Separation of Red Mud in the Absence of Additives

The reduction and separation results in the absence of additives are shown in Figure 2 and Figure 3. As shown in Figure 2, all the indexes increased significantly with the increasing roasting temperature from 750 to 1050  $^{\circ}C$ , while kept approximately constant as the temperature further

increased to 1100 °C. Likewise, as seen from Figure 3, the indexes also increased with the prolonged roasting time, and reached a maximum at the roasting time of 60 min.

It is noteworthy that iron metallization ratio of reduced cylinders in the absence of additives maintained at a low level (< 80%), suggesting that the reduction of iron oxides is not sufficient. The limited reduction of iron oxides during roasting in the absence of additives would affect adversely on the quality and yield of magnetic concentrate.

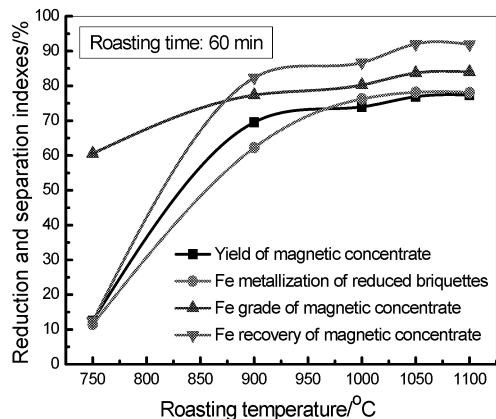


Figure 2. Reduction and separation indexes of red mud as the function of roasting temperature in the absence of additives

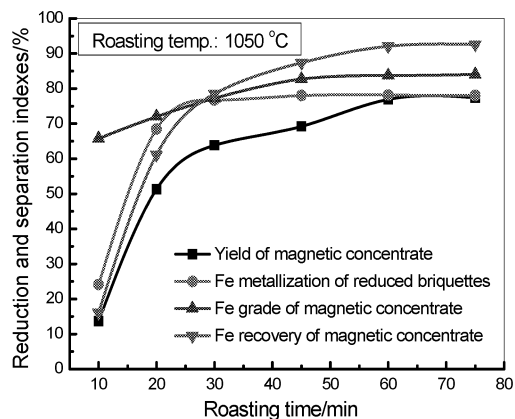


Figure 3. Reduction and separation indexes of red mud as the function of roasting time in the absence of additives

#### Reduction Roasting-Magnetic Separation of Red Mud in the Presence of Additives

Effects of Sodium Salts. As indicated from Figure 2 and Figure 3 that iron metallization ratio of reduced cylinders in the absence of additives was limited at a low level less than 80%. Thus, sodium carbonate and sodium sulfate were used as

additives to enhance the reduction of red mud. Under the conditions of roasting temperature of 1050 °C, roasting time of 60 min, magnetic separation feed fineness of 90% passing through 74 μm and magnetic field intensity of 0.1 T, the effects of sodium carbonate and sodium sulfate used alone or in combination are presented in Figures 4-6.

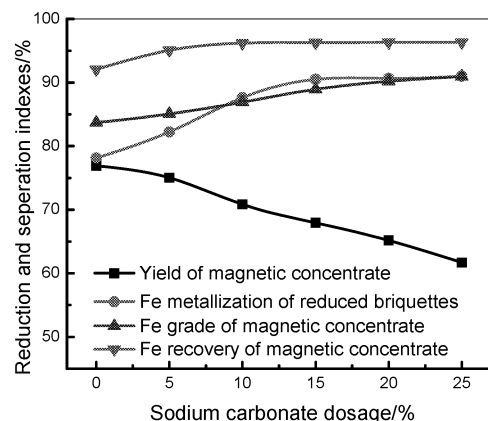


Figure 4. Effect of sodium carbonate dosage (roasting temperature: 1050 °C; roasting time: 60 min)

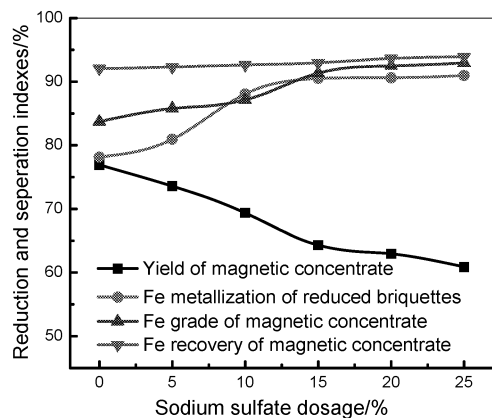
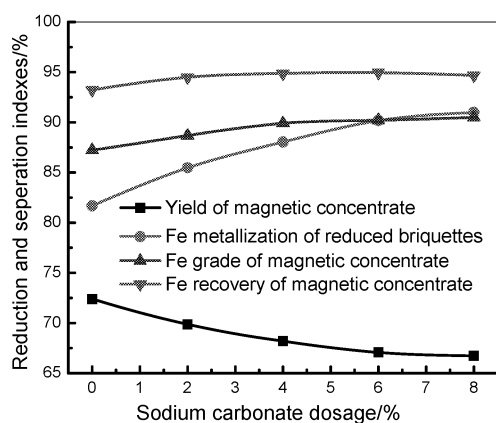


Figure 5. Effect of sodium sulfate dosage (roasting temperature: 1050 °C; roasting time: 60 min)

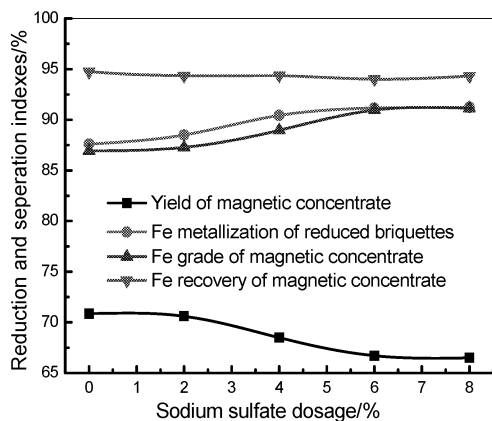
Figure 4 and Figure 5 show effects of sodium carbonate dosage and sodium sulfate dosage in the range of 0 to 25% on the reduction and separation indexes of red mud, respectively. The results show that Fe metallization ratio in reduced cylinders, Fe grade and Fe recovery of magnetic concentrate gradually increased with either the increasing sodium carbonate dosage or the increasing sodium sulfate dosage, whereas the yield of magnetic concentrate decreased. Compared with those in the absence of additives, the results were improved obviously in the presence of either sodium

carbonate or sodium sulfate. Iron metallization of reduced cylinders went up from 78.2% to 87.6% with the addition of 10% sodium carbonate, and from 78.2% to 88.1% with the addition of 10% sodium sulfate. This suggests that the reduction of red mud can be enhanced by either sodium carbonate or sodium sulfate, leading to the improvement of iron grade and recovery in the magnetic concentrate.

Taking into account that the reduction and separation indexes were improved by using sodium carbonate and sodium sulfate alone, the combinational effects of sodium carbonate and sodium sulfate were investigated further, and the results are shown in Figure 6.



(a) sodium sulfate dosage: 10%

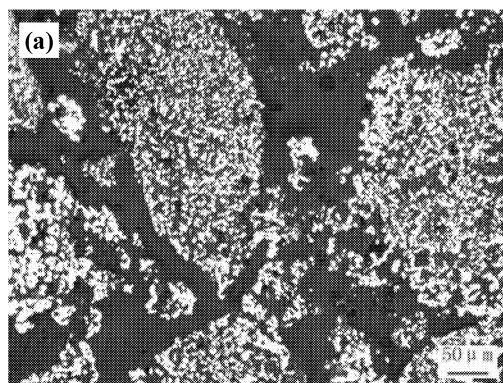


(b) sodium carbonate dosage: 6%

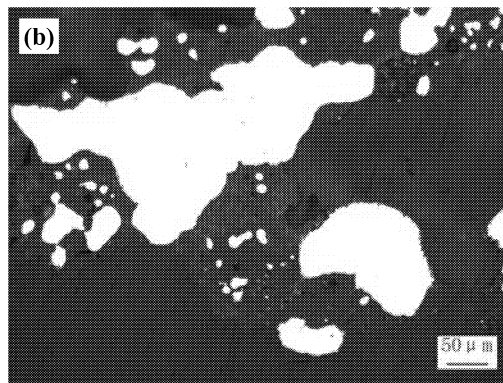
Figure 6. The combinational effect of sodium carbonate and sodium sulfate (roasting temperature: 1050 °C; roasting time: 60 min)

The results in Figure 6 confirm that the enhancing effects of sodium carbonate and sodium sulfate used in combination were more significant than those used alone. Fixing the sodium

carbonate dosage at 10%, the reduction and separation indexes as the function of sodium carbonate dosage are presented in Figure 6a. Figure 6(a) shows that Fe metallization, Fe grade and Fe recovery gradually increased when sodium sulfate ratio increased from 0 to 6%, and then leveled off with the further increase of sodium sulfate dosage from 6% to 8%. Subsequently, the effect of sodium sulfate dosage in the combination of 6% sodium carbonate was also investigated in Figure 6(b). Therefore, the optimal additive dosages of 6% sodium carbonate in combination with 6% sodium sulfate were determined.



(a) Without additives



(b) 6% Na<sub>2</sub>CO<sub>3</sub> + 6% Na<sub>2</sub>SO<sub>4</sub>

Figure 7. Microstructure of reduced red mud cylinders at 1050 °C for 60min (metallic iron particles are in white color)

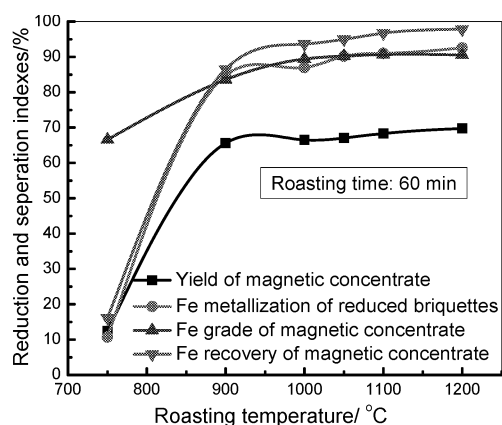
The microstructures of cylinders reduced at 1050 °C for 60min in the absence and presence of additives are presented in Figure 7. Figure 7(a) shows clearly that the metallic iron particles are finely disseminated with size of 1-5 μm in the absence of additives. The scattered distribution of metallic iron particles with such a small size leads to the unsatisfied

separation of metallic iron from gangues. By contrast, the presence of 6% Na<sub>2</sub>CO<sub>3</sub> and 6% Na<sub>2</sub>SO<sub>4</sub> enhances the growth of metallic iron grains obviously to obtain a size of about 100 $\mu$ m (see in Figure 7(b)).

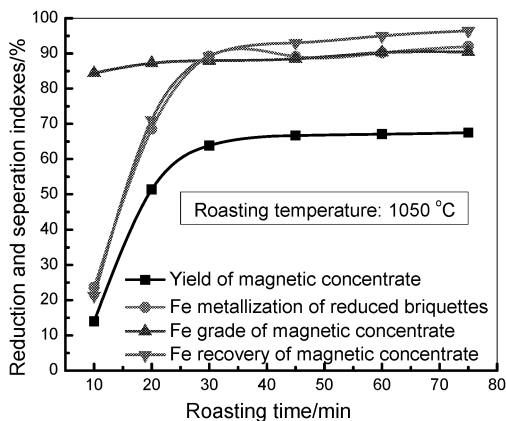
It can be concluded that sodium sulfate and sodium carbonate can promote the aggregation of metallic iron particles during reduction roasting, which is favorable for the downstream magnetic separation. Therefore, the separation indexes of reduced red mud cylinders as shown in Figure 2-6 are improved by the addition of sodium sulfate and sodium carbonate. Taken in comparisons, sodium sulfate plays a more important role in the metallic iron grain growth than sodium carbonate. In view of that an excessive amount of sodium sulfate would be detrimental to the quality of magnetic concentrate leading to high sulfur content; therefore the combinational use of 6% Na<sub>2</sub>CO<sub>3</sub> and 6% Na<sub>2</sub>SO<sub>4</sub> is preferential.

Effects of Roasting Temperature and Time. The reduction and separation results as the function of roasting temperature and roasting time in the presence of 6% Na<sub>2</sub>CO<sub>3</sub> and 6% Na<sub>2</sub>SO<sub>4</sub> are shown in Figure 8

As shown in Figure 8, with the increasing roasting temperature and time, approximately all the indexes increased. Reduction and separation indexes increased rapidly as roasting temperature increased from 750 to 900 °C and then increased slightly. When roasting temperature further increased beyond 1050 °C, the indexes leveled off. With regard to roasting time, reduction and separation indexes increased with the prolonged roasting time. When roasting time exceeded 60 min, these indexes kept approximately constant. In the viewpoint of energy consumption, roasting temperature of 1050 °C and roasting time of 60 min were recommended, and a magnetic concentrate containing 90.12% iron with iron recovery of 94.95% was obtained.



(a)



(b)

Figure 8. Effects of roasting temperature (a) and roasting time (b) in the presence of 6% Na<sub>2</sub>CO<sub>3</sub> and 6% Na<sub>2</sub>SO<sub>4</sub>

## Conclusions

By reducing iron oxides from a red mud for magnetic separation of metallic iron, the total volume of mud slurry will be reduced for the downstream alumina extraction. The first step of recovering iron from a high iron content red mud by reduction roasting-magnetic separation was mainly investigated, and the following conclusions are obtained.

- (1) The optimal roasting-magnetic separation conditions: roasting temperature of 1050 °C, roasting time of 60 min, sodium sulfate dosage of 6% and sodium carbonate dosage of 6%. Under the optimal conditions, a magnetic concentrate containing 90.12% iron with iron recovery of 94.95% was obtained from a red mud containing 48.23% total iron, 7.71% Al<sub>2</sub>O<sub>3</sub> and 7.69% SiO<sub>2</sub>.
- (2) The combined use of sodium carbonate and sodium sulfate is able to intensify the reduction of iron oxides and also promotes the growth of metallic iron grains during the reduction roasting. Thus, the magnetic separation of metallic iron from gangue materials is enhanced.

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