

## Study on extracting aluminum hydroxide from reduction slag of magnesium smelting by vacuum aluminothermic reduction

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Key words: magnesium smelting; aluminum hydroxide; reduction slag;  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ ;

### Abstract

The reduction slag from magnesium smelting by vacuum aluminothermic reduction using dolomite and magnesite as raw materials consists mainly of  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$ . The alumina is more than 67% of the slag and is mainly in the form of  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ . The process of producing aluminum hydroxide from the slag by leaching with a mixture of sodium hydroxide and sodium carbonate was studied. This showed that the leaching rate of alumina is more than 86% when leaching temperature is  $95^\circ\text{C}$ , and  $L/S$  is 5, and leaching time is 2h. The magnesia-alumina spinel which generated in the reduction process and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  which is generated in the leaching process, are the two main causes of loss of alumina. The chemical composition of aluminum hydroxide products obtained after carbonation precipitation can meet the quality standard of the alumina plant.

### Introduction

A new magnesium production method has recently been introduced, which is based on two steps, the first of which is producing magnesium with vacuum aluminothermic reduction, and the second step is the extraction of aluminum hydroxide from the reduction slag. Figure 1 gives the flowchart of the new magnesium production method. The process of producing magnesium uses dolomite and magnesite as materials and aluminum powder as the reductant. After the reduction process, magnesium and a reduction slag can be obtained. The main phase of the reduction slag is  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ . The content of  $\text{Al}_2\text{O}_3$  is more than 67% and the content of  $\text{SiO}_2$  is below 1%. For a mass ratio of  $\text{Al}_2\text{O}_3$  to  $\text{SiO}_2$  is more than 60, the slag is suitable for leaching to produce aluminium hydroxide. This paper describes the study of extracting aluminum hydroxide from the reduction slag of this magnesium smelting process.

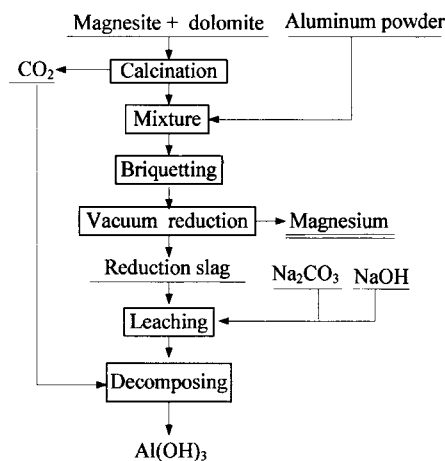
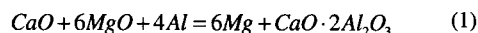


Figure 1 The flowchart of the new magnesium production method

### Experimental

#### Materials

The experimental materials is a reduction slag of magnesium smelting using dolomite and magnesite as materials and aluminum powder as reductant, the addition of materials and reductant follows the reaction equation (1). The magnesium smelting experiment was carried out at  $1140^\circ\text{C}$ , and the aluminum power excess is 5%. The chemical composition of the reduction slag is listed in Table1 and Figure 2 shows the XRD pattern of the reduction slag.



MgO	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Al	Fe <sub>2</sub> O <sub>3</sub>
6.13	20.86	0.89	67.54	3.50	1.08

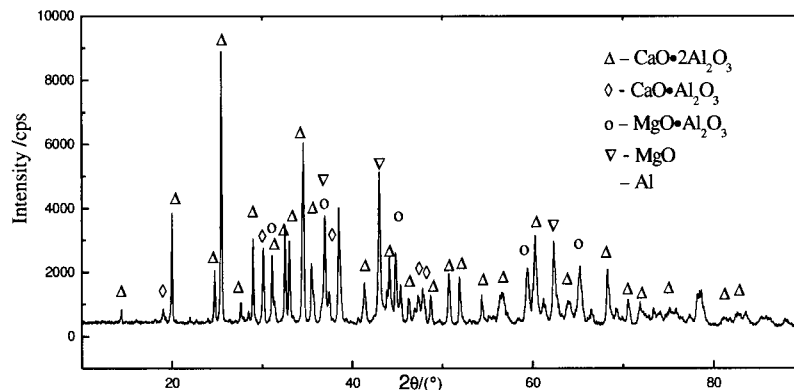
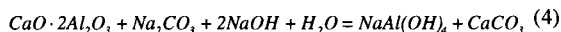
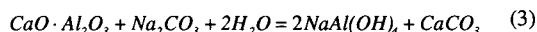
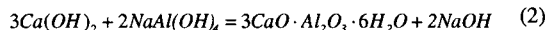


Figure 2 The XRD spectra of reduction slag

As shown in Table 1 and Figure 2, the main phase of the reduction slag is  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ , and there are also small amounts of  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ ,  $\text{MgO} \cdot \text{Al}_2\text{O}_3$ ,  $\text{MgO}$  and Aluminum powder. The main chemical composition is  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ , unreacted  $\text{MgO}$  and  $\text{Al}$ .

#### Experimental principle

Alumina in the reduction slag is mainly in the form of  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ , and it cannot be leached by a sodium hydroxide solution because in the leaching process, the  $\text{CaO}$  of the reduction slag would react with sodium hydroxide to form  $\text{Ca}(\text{OH})_2$  which would then react with  $\text{NaAl}(\text{OH})_4$  to form tricalcium hydroaluminate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ ) [1,2] (equation 2). Because tricalcium hydroaluminate is stable in sodium hydroxide solution [3], a lot of  $\text{Al}_2\text{O}_3$  entering into the leaching process is lost. The  $\text{CaO}$  of the reduction slag would react with sodium carbonate prior to sodium hydroxide to form  $\text{CaCO}_3$  which has lower solubility and is more stable than  $\text{Ca}(\text{OH})_2$ . The formation of  $\text{CaCO}_3$  inhibits the formation of tricalcium hydroaluminate and reduces the loss of  $\text{Al}_2\text{O}_3$  [4]. The leaching principle of  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$  and  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  are listed as follows [5, 6]:



In the leaching process, elemental  $\text{Al}$  (unreacted aluminum powder) in the reduction slag can react with sodium hydroxide and also with sodium carbonate, but the reaction rate of elemental  $\text{Al}$  with sodium hydroxide is much faster than with sodium carbonate, so most of the elemental  $\text{Al}$  react with sodium hydroxide. Elemental  $\text{Al}$  is fully solution in the leaching solution.



#### Experimental Method

The leaching experiments were carried out in a constant temperature water bath, and used an Erlenmeyer flask which is sealed with a condenser and stirred with a magnetic rotor. Before the experiments began, the leaching solution of mixed  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$  was heated to a given temperature, then added into the reduction slag. After leaching for a given time, the leaching solution was filtered rapidly and washed three times by hot deionized water, and the alumina concentration of the filtrate was measured by chemical titration, and the alumina leaching rate of reduction slag was calculated.

The filtrate without the wash liquid was a sodium aluminate solution, and it was decomposed by carbonation in the water bath at  $80^\circ\text{C}$ . The finish of decomposition was determined by the decomposed rate. When the decomposition reached 90%, it was stopped, filtered and aluminum hydroxide could be obtained.

#### Results and discussions

In the reduction slag, the aluminium is present in two main species, one is the alumina which exists in  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$  and  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ , the other is elemental  $\text{Al}$  (unreacted aluminum powder). The elemental  $\text{Al}$  can enter into the leaching solution completely and alumina can not. To distinguish the two parts, the alumina leaching rate was described as the leaching rate of alumina and the aluminum leaching rate was described the leaching rate of element aluminum. The conditions effecting the alumina leaching rate are mainly leaching temperature, leaching time, the content of sodium hydroxide and sodium carbonate.

##### Effect of leaching temperature on alumina leaching rate

The results of effect of leaching temperature on alumina leaching rate are shown in Figure 3, and the experiments were carried out under the conditions of leaching L/S 5, leaching time

2h, content of sodium hydroxide 100g/L, and content of sodium carbonate 120g/L.

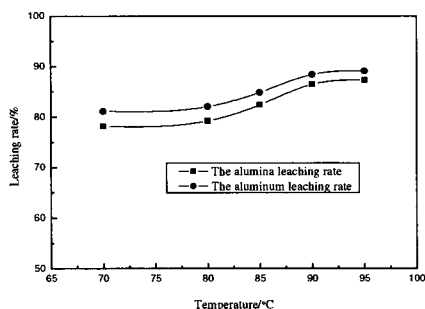


Figure 3 Effect of leaching temperature on the alumina leaching rate

The effect of leaching temperature on the alumina leaching rate is very notable, the leaching rate of alumina in the reduction slag increases with increasing leaching temperature and levels off when the leaching rate reaches 90°C.

#### Effect of leaching time on alumina leaching rate

The results of effect of leaching time on alumina leaching rate are shown in Figure 4, and the experiments were carried out under the conditions of leaching L/S 5, leaching temperature 95°C, the content of sodium hydroxide 100g/L, and content of sodium carbonate 120g/L.

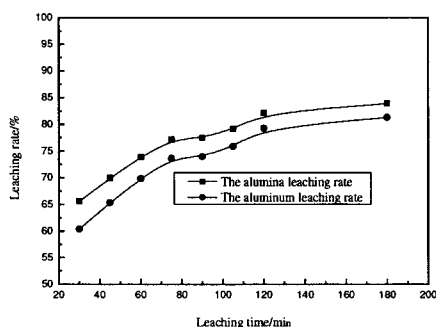


Figure 4 Effect of leaching time on the alumina leaching rate

As shown in Fig.4, the leaching rate of alumina in reduction slag increases with the extension of leaching time and levels off when the leaching time extends 2h.

#### Effect of the content of sodium carbonate on alumina leaching rate

The results of effect of the content of sodium carbonate on alumina leaching rate are shown in Figure 5, and the experiments were carried out under the conditions of leaching L/S 5, leaching

temperature 95°C, leaching time 2h, content of sodium hydroxide 100g/L

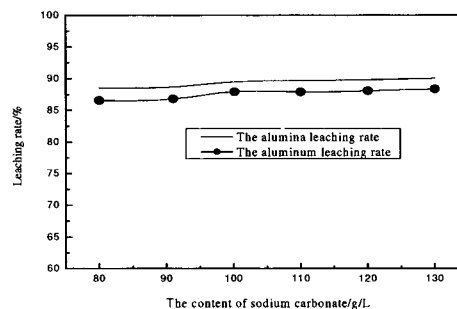
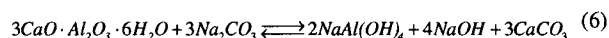


Figure 5 Effect of content of sodium carbonate on the alumina leaching rate

It can be seen from Figure 5 that the content of sodium carbonate has little effect on the alumina leaching rate when the content of sodium carbonate is between 80 and 130 g/L, especially over 100 g/L. In the leaching process of the reduction slag, there are at least five reactions in the leaching solution, they are the formation of sodium aluminate (equations 3, 4 and 5), the formation of tricalcium hydroaluminate (equation 2) and the decomposition of tricalcium hydroaluminate (equation 6). There are two main roles of sodium carbonate, one is reaction with CaO to form CaCO<sub>3</sub>, the other is decomposing tricalcium hydroaluminate [7,8].

The content of sodium carbonate depends on two factors, one is that the content of sodium carbonate must exceed the theoretical amount to avoid the forming of tricalcium hydroaluminate and the theoretical amount is about 80g/l when the L/S is 5, the other aspect is that since the decomposition of tricalcium hydroaluminate is a reversible reaction, thus the higher the content of sodium the better in order to decompose tricalcium hydroaluminate. According to the results shown in Fig.4, the optimal content is 100 g/L.



#### Effect of the content of sodium hydroxide on alumina leaching rate

The effect of the content of sodium hydroxide on alumina leaching rate is shown in Figure 6. The experiments were carried out under the conditions of leaching L/S 5, leaching temperature 95°C, leaching time 2h, content of sodium carbonate 100g/L.

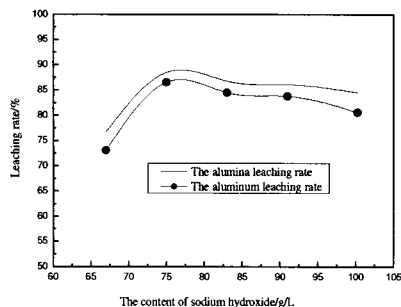


Figure 6 Effect of content of sodium hydroxide on the alumina leaching rate

As shown in Figure 6, the content of sodium hydroxide has great effect on the alumina leaching rate. The alumina leaching rate increases at first, and then decreases with the increase of sodium hydroxide concentration, and there is a maximum at a content of 75g/L.

#### Phase analysis of Leaching slag

The main chemical composition of the leaching slag is listed in table 2, and the XRD pattern of the leaching slag was analysed in Figure 7.

Al <sub>2</sub> O <sub>3</sub>	MgO	CaCO <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	others
17.88	6.38	70.53	2.81	0.79	1.61

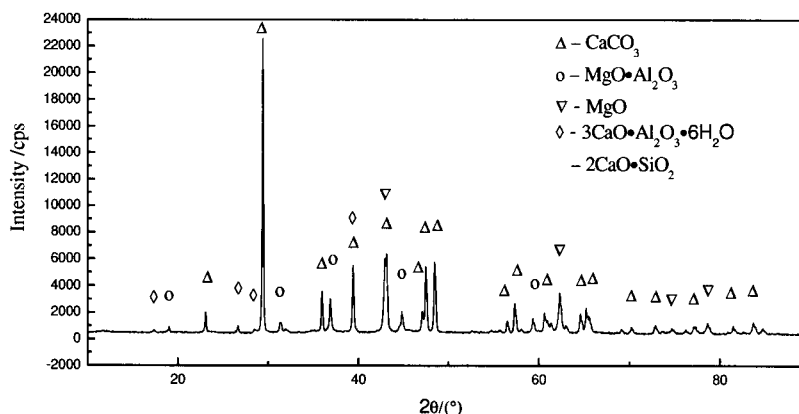


Figure 7 The XRD of the leaching slag

As shown in Figure 7 and Table 2, the main phase of the leaching slag is calcium carbonate, and there are some other phases such as magnesia-alumina spinel (MgO·Al<sub>2</sub>O<sub>3</sub>), tricalcium hydroaluminate (3CaO·Al<sub>2</sub>O<sub>3</sub>·6H<sub>2</sub>O), and calcium silicate (2CaO·SiO<sub>2</sub>). It is also found that the CaO·2Al<sub>2</sub>O<sub>3</sub> and CaO·Al<sub>2</sub>O<sub>3</sub> are decomposed completely.

In the sodium aluminate solution which result from leaching of the reduction slag, the alumina concentration is 120-150g/L, and SiO<sub>2</sub> concentration is 0.2-0.3 g/L, and the ratio of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> is more than 500. Since the A/S is high, the sodium aluminate solution can be decomposed by carbonation without desilication process. The composition of the aluminum hydroxide obtained is shown in Table 3.

		Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O
the national standards of china	AH-1	64.5	0.02	0.02	0.4
	AH-2	64.0	0.04	0.04	0.5
	AH-3	63.5	0.06	0.06	0.6
Al(OH) <sub>3</sub> of this project		64.3	0.03	0.01	0.43

The chemical composition of the aluminum hydroxide products used reduction slag of magnesium smelting as materials can meet the quality standard of the alumina plant. In addition, the

sodium aluminate solution is suitable to producing high added value non-metallurgical alumina.

### Conclusions

(1) The main phase of the reduction slag from magnesium smelting by vacuum aluminothermic reduction is  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ , and the  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$  can be decomposed completely by leaching with alkali solution to form  $\text{CaCO}_3$  and sodium aluminate solution.

(2) The leaching rate of alumina from the slag is more than 86% and the leaching rate of element aluminum is more than 90% when the reduction slag leached at 95 °C for 2h. The magnesia-alumina spinel which is generated in the reduction process and  $3\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$  which is generated in the leaching process were the two main pathways which caused loss of alumina.

(3) Aluminum hydroxide conforming to the national standards of China could be produced after carbonation precipitation.

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