

Study on the effect of Si and silicide on leaching Al₂O₃ from magnesium smelting reduction slag

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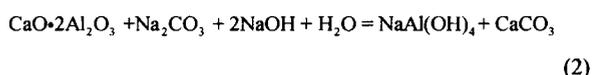
Key words: magnesium smelting; calcium silicate; sodium aluminosilicate hydrate; alumina leaching;

Abstract

The main phases of the reduction slag from magnesium production by vacuum aluminothermic reduction using dolomite and magnesite as materials and using Al-Si alloy as reductant are CaO·2Al₂O₃ and 2CaO·SiO₂. It also has amount of unreacted Si. The Al₂O₃ content of reduction slag is about 55% and SiO₂ is about 10%. When leaching Al₂O₃ with a mixture solution of sodium hydroxide and sodium carbonate, Si and SiO₂ would enter into leaching solution and has a negative effect on Al₂O₃ leaching. The effect of Si and silicide on leaching Al₂O₃ from magnesium smelting reduction slag was studied in laboratory. The results show that total Si and partial SiO₂ would enter into leaching solution and react with NaAl(OH)₄ to form (Na₂O·Al₂O₃·SiO₂)₆·27H₂O which is present in leaching residue and makes a loss of Al₂O₃.

Introduction

A new magnesium production method using calcined dolomite and calcined magnesite as raw materials and aluminum powder as the reductant was invented in China[1,2], 2010. The new method is based on two steps, the first step is producing magnesium with vacuum aluminothermic reduction, and the second step is extracting alumina from the reduction slag. The reduction principle of the new method is listed in formula 1. The main phase of the reduction slag is CaO·2Al₂O₃ and CaO·2Al₂O₃ can be leached by a mixture solution of sodium hydroxide and sodium carbonate (The principle listed in formula 2). Since the content of Al₂O₃ in the reduction slag is more than 67% and the content of SiO₂ is below 1%, SiO₂ has a little effect on Al₂O₃ leaching rate and leaching process[3].



Cycling aluminum mostly exists in aluminum alloys. There are a large number of cycling aluminum alloys in the world every year, and the most is Al-Si alloy. Both aluminum and

silicon can be used as reductant in MgO reduction process. So producing magnesium by vacuum metallothermic reduction using dolomite and magnesite as raw materials and using cycling Al-Si alloy powder as reductant is feasible[4,5]. The reduction slag using Al-Si as reductant conclude about 60% aluminum oxide, some SiO₂ and Si. The reduction slag is suitable to leaching Al₂O₃ but SiO₂ may have a great effect on Al₂O₃ leaching rate and leaching process. This paper describes the effect of Si and silicide on leaching Al₂O₃ from reduction slag by using Al-Si alloy as reductant.

Experimental

Materials

The experimental materials are reduction slag of magnesium smelting using calcined dolomite and calcined magnesite, and Al-Si alloy powder as reductant. When producing magnesium Al-Si alloy as reductant, although aluminum and silicon in the alloy can both reduce MgO into Mg, the chemical reaction activity of aluminum is better than silicon and reduction temperature is lower than silicon, so in the reduction process, the MgO will be reduced by aluminum first and then be reduced by silicon. When the reductant is higher than the recommended, there would be some unreacted silicon remains in the reduction slag. In the reduction process, aluminum reduces MgO follows the reaction equation (1) and silicon reduces MgO follows the reaction equation (3)[6].



The reduction experiments were carried out at 1200°C, and reductant excess is 5%. The reduction ratio of MgO is 88-90%. The chemical composition of the reduction slag is listed in Table1 and Figure 1 shows the XRD pattern of the reduction slag. In table 1, the content of unreacted aluminum and unreacted silicon include in Al₂O₃ and SiO₂.

Table1 The chemical composition of reduction slag (%)

MgO	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃
9.82	29.61	8.96	53.30	0.58

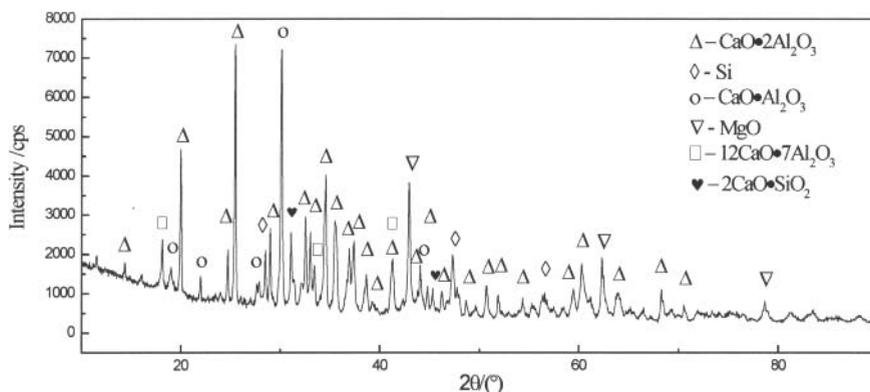
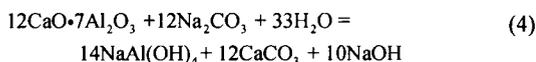
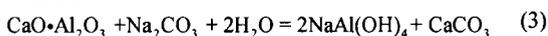


Fig.1 The XRD pattern of the reduction slag

As shown in Table 1 and Figure 2, the main phases of the reduction slag is $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ and $\text{CaO}\cdot \text{Al}_2\text{O}_3$, and there are also small amounts of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$, MgO , $2\text{CaO}\cdot \text{SiO}_2$ and silicon. There are a lot of silicon unreacted and all aluminum took part in the reduction reaction.

Experimental principle

Alumina in the reduction slag is in the form of $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$, $\text{CaO}\cdot \text{Al}_2\text{O}_3$ and $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$. Alumina in $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ can be leached by a mixture solution of sodium hydroxide and sodium carbonate (equation 2), alumina in $\text{CaO}\cdot \text{Al}_2\text{O}_3$ and $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ can be leached by sodium carbonate (equation 4 and 5) [7, 8]. In the present experiments, the mixture solution of sodium hydroxide and sodium carbonate was used as leaching solution.



In reduction slag, silicon was mainly in the form of $2\text{CaO}\cdot \text{SiO}_2$ and elemental silicon (unreacted silicon), when leaching Al_2O_3 from reduction slag, all elemental silicon and part of $2\text{CaO}\cdot \text{SiO}_2$ would be react with sodium hydroxide (equation 6 and 7) and dissolve in leaching solution. The saturation solubility of SiO_2 is lower than 1g/l , so the silica of leaching solution is supersaturated and unstable, it would be precipitated and make some Al_2O_3 lost.

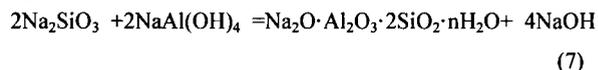


Experimental Method

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 NaOH and Na_2CO_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. Alumina concentration of leaching solution were measured by chemical titration and silica concentration was analysed by spectrophotometer, and the alumina leaching rate of reduction slag was calculated.

3.Results and discussions

The element silicon in the reduction slag present in two main species, one is calcium silicate and the other is elemental Si (unreacted silicon). Elemental Si come from the reductant Al-Si alloy and it will enter into leaching solution completely. Calcium silicate come from two ways, one come from raw materials of reduction process which has lower activity and almost do not react with alkali in leaching process and the other come from the reduction reaction of Si and MgO (equation 3) which has higher activity and easily decomposes by alkali. Both elemental Si and SiO_2 enter into leaching solution in the form of Na_2SiO_3 . Since the SiO_2 saturated concentration of sodium aluminate solution is low, the SiO_2 of leaching solution is supersaturated and unstable, and it would be precipitated spontaneously from leaching solution as sodium aluminosilicate hydrate (equation 3). The XRD of leaching residue is listed in Fig.2.



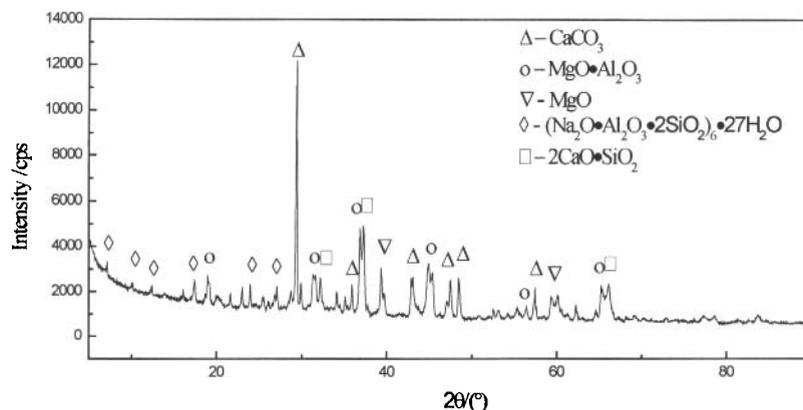


Fig.2 The XRD pattern of leaching residue

As shown in Fig.2, the main phase of the leaching residue is calcium carbonate, and there are some other phases such as magnesia-alumina spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$), sodium aluminosilicate hydrate ($(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2)_6 \cdot 27\text{H}_2\text{O}$) and calcium silicate ($2\text{CaO} \cdot \text{SiO}_2$). It is also found that the $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3$ are all decomposed and the alumina in the leaching residue exists in the forms of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and $(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2)_6 \cdot 27\text{H}_2\text{O}$ which are the two main cause of alumina lost. The main chemical composition of the leaching residue is listed in table 2.

Table2 The chemical composition of the leaching residue (%)

MgO	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃
10.93	32.18	9.29	15.82	0.78

There is a precipitation-solution equilibrium of SiO_2 in leaching process, and the SiO_2 concentration is directly related to the equilibrium. The precipitation-solution equilibrium of SiO_2 is related to leaching temperature, leaching time, content of Al_2O_3 , content of sodium carbonate and sodium hydroxide.

Effect of leaching temperature on the Al_2O_3 leaching rate and the content of SiO_2

Leaching temperature is an important factor of influence to Al_2O_3 leaching rate and content of SiO_2 , and its effect come from two respects, on the one hand the Al_2O_3 leaching rate increases with the rising of leaching temperature, but on the other hand, with leaching temperature increasing, the instability of SiO_2 increases and it is beneficial to desilication which makes a loss of Al_2O_3 and decreases the Al_2O_3 leaching rate. The results of effect of leaching temperature on the Al_2O_3 leaching rate and the content of SiO_2 is shown in Fig.3.

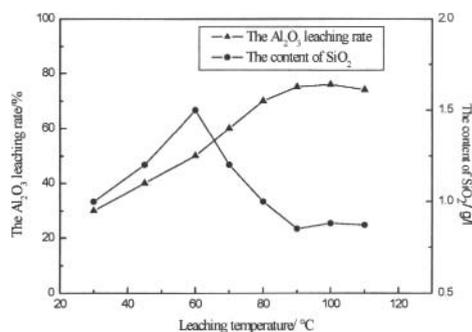


Fig.3 Effect of leaching temperature on the Al_2O_3 leaching rate and the content of SiO_2 (leaching L/S 5, leaching time 60 min, the content of sodium hydroxide 80g/L, and the content of sodium carbonate 120g/L)

As shown in Fig.3, leaching temperature has great effect on the Al_2O_3 leaching rate and the content of SiO_2 . The Al_2O_3 leaching rate and the content of SiO_2 increases at first, and then decreases, and there is a maximum at 90°C. Investigating its reason, the Al_2O_3 leaching rate increases with the rising of leaching temperature when the leaching temperature is lower than 90°C and little increases when the leaching temperature is over 90°C. Both the dissolved rate of SiO_2 and the formation rate of sodium aluminosilicate hydrate increases with the rising of leaching temperature. The dissolved of SiO_2 is faster when leaching temperature is lower than 80°C and the content of SiO_2 increases, but the formation of sodium aluminosilicate hydrate is faster when leaching temperature is over 80°C and the content of SiO_2 decreases. The formation of sodium aluminosilicate hydrate leads to some Al_2O_3 lost and reduces the Al_2O_3 leaching rate. The optimal temperature is 95°C.

Effect of leaching time on the Al_2O_3 leaching rate and the content of SiO_2

The effect of leaching time on the Al_2O_3 leaching rate and the content of SiO_2 also come from two respects, on the one hand, the Al_2O_3 leaching rate in reduction slag increases with the extension of leaching time, but on the other hand, the extension of leaching time is beneficial to the formation of sodium aluminosilicate hydrate and leads to some Al_2O_3 lost. The results of effect of leaching time on the Al_2O_3 leaching rate and the content of SiO_2 is shown in Fig.4.

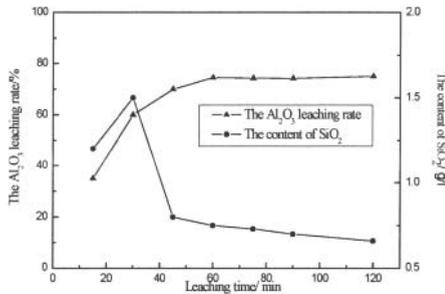


Fig.4 Effect of leaching time on the Al_2O_3 leaching rate and the content of SiO_2

(leaching L/S 5, leaching temperature $95^\circ C$, the content of sodium hydroxide $80g/L$, and the content of sodium carbonate $120g/L$)

As shown in Fig.4, the Al_2O_3 leaching rate in reduction slag increases with the extension of leaching time and levels off when the leaching time extends 60 min. The content of SiO_2 increases firstly and decreases when the leaching time extends 30 min. the optimal leaching time is 60 min.

Effect of the content of sodium carbonate on the Al_2O_3 leaching rate and the content of SiO_2

There are amount of $CaO \cdot Al_2O_3$ and $12CaO \cdot 7Al_2O_3$ in the reduction slag besides $CaO \cdot 2Al_2O_3$. $CaO \cdot Al_2O_3$ and $12CaO \cdot 7Al_2O_3$ only react with sodium carbonate when leaching by the mixture solution of sodium carbonate and sodium hydroxide. Increasing of the content of sodium carbonate is beneficial to the decomposing of $CaO \cdot Al_2O_3$ and $12CaO \cdot 7Al_2O_3$, and also $CaO \cdot 2Al_2O_3$, so the Al_2O_3 leaching rate would increase with the increasing of the content of sodium carbonate. It is generally acknowledged that the equilibrium concentration of SiO_2 decreases with the rising of the content of sodium carbonate, so the increasing of the content of sodium carbonate is beneficial to decrease the content of SiO_2 .

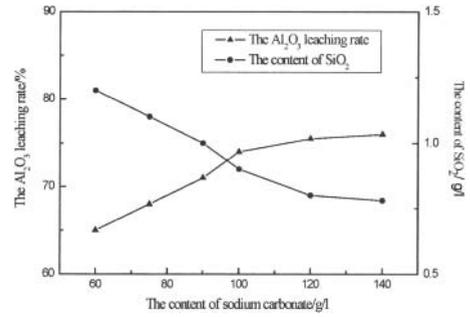


Fig.5 Effect of the content of sodium carbonate on the Al_2O_3 leaching rate and the content of SiO_2 (leaching L/S 5, leaching temperature $95^\circ C$, leaching time 60min, and the content of sodium hydroxide $80g/L$)

As shown in Fig.5, the Al_2O_3 leaching rate increases with the increasing of the content of sodium carbonate and levels off when the content of sodium carbonate is over 100 g/l. The content of SiO_2 decreases with the increasing of the content of sodium carbonate.

Effect of the content of sodium hydroxide on the Al_2O_3 leaching rate and the content of SiO_2

The results of effect of the content of sodium hydroxide on the Al_2O_3 leaching rate and the content of SiO_2 is shown in Fig.6.

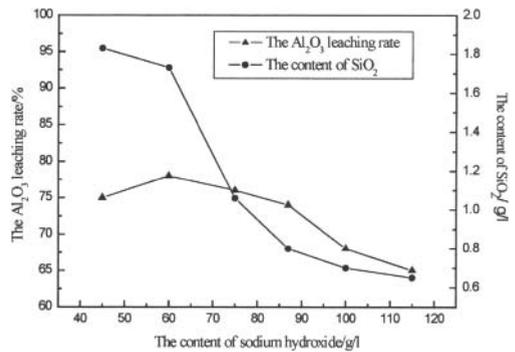


Fig.6 Effect of the content of sodium hydroxide on the Al_2O_3 leaching rate and the content of SiO_2

(leaching L/S 5, leaching temperature $95^\circ C$, leaching time 60 min, and the content of sodium carbonate $120g/L$)

As shown in Fig.5, the Al_2O_3 leaching rate and the content of SiO_2 decreases with the increasing of the content of sodium hydroxide and levels off when the content of sodium carbonate is over 100 g/l.

It could be concluded that the Al_2O_3 leaching rate of the reduction slag which using Al-Si alloy as reductant is about 75% when the reduction slag is leached in the optimal leaching conditions, and it is lower than the Al_2O_3 leaching rate of the reduction slag which using Aluminum powder as reductant by

10%. The alumina concentration is 80-100g/L, and SiO₂ concentration is 0.6-0.8 g/L, and the ratio of Al₂O₃ and SiO₂ is about 100 in the leaching solution.

Conclusions

The alumina leaching rate of the reduction slag from magnesium production by vacuum aluminothermic reduction using Al-Si alloy as reductant is about 75%. There are a lot of unreacted silicon and dicalcium silicate in the reduction slag. All of unreacted silicon and partial of dicalcium silicate dissolves into the leaching solution, and then most of silica in the leaching solution precipitates in form of (Na₂O·Al₂O₃·SiO₂)₆·27H₂O. The formation of (Na₂O·Al₂O₃·SiO₂)₆·27H₂O is one of main cause of loss of alumina.

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