

Effect of Na₂O on alumina leaching property and phase transformation of MgO-containing calcium aluminate slags

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Abstract: In order to remove or reduce the negative effect of MgO in calcium aluminate slags, the method of adding Na₂O into calcium aluminate slags was studied and its effect on leaching mechanism was also analyzed. The results show that the alumina leaching efficiency of the calcium aluminate slag increases from 68.73% to 80.86% with Na₂O content increasing from 0 to 4% when MgO content is 3%. The XRD results show that the quaternary compound C₂₀A₁₃M₃S₃ disappears when Na₂O content increases to 4%. The addition of Na₂O cannot remove the negative effect of MgO on leachability completely. XRD and EDS results indicate that Na₂O can come into the lattice of 12CaO·7Al₂O₃ and promote the formation of 12CaO·7Al₂O₃.

Key words: calcium aluminate slag; Na₂O; MgO; phase transformation; alumina leaching

1 Introduction

Calcium aluminate slag is obtained from blast furnaces when smelting iron-bearing bauxite. The ideal components of calcium aluminate slags are 12CaO·7Al₂O₃ and γ-2CaO·SiO₂ [1]. The slag can react with a sodium carbonate solution and its alumina leaching efficiency can reach 85%. The comprehensive utilization of iron and alumina values in the ore can be realized by this way [2–3].

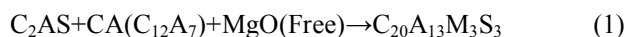
However, the existence of impurity MgO which comes from iron-bearing bauxite and lime, will affect the alumina leaching efficiency of calcium aluminate slag during the industrial process [4].

EREMIN [5] studied the effect of MgO on calcium aluminate slag composition and pointed out that the compound 6CaO·4Al₂O₃·MgO·SiO₂ would be formed in the slag when MgO was present. This compound is not able to react with the sodium carbonate solution. After that, the mechanism of MgO effects on the slags was studied systematically [6]. The results showed that MgO will enter into the crystal lattice of 12CaO·7Al₂O₃ and form limited C₂₀A₁₃M₃S₃ when the MgO content is less than 1.0%. But if it is above this level, a large amount of

C₂₀A₁₃M₃S₃ would be formed which decreased the alumina leaching efficiency. The results also showed that this quaternary compound could react with sodium carbonate solution and its alumina leaching efficiency would be very low [7].

Therefore, it is clear that MgO will affect the alumina leachability of the slags. The presence of MgO can not be avoided because it is the main impurity in the slag so that how to remove or reduce the negative effect of MgO becomes the focus of this research work.

The initial study on the compound C₂₀A₁₃M₃S₃ was carried out in high-alumina cement [8–9]. At first, the composition of *Q* phase was thought as 6CaO·4Al₂O₃·MgO·SiO₂ [10]. The later research indicated that the steady chemical formula of *Q* phase was 20CaO·13Al₂O₃·3MgO·3SiO₂ [11]. And its general formula was given as 20CaO·(16–ν)Al₂O₃·νMgO·νSiO₂ (ν=2.5–3.5). The reaction equation of the formation of C₂₀A₁₃M₃S₃ was as follows [12]:



According to the reaction equation mentioned above there are two methods to remove the negative effect of MgO on the phase components of the calcium aluminate slag. One is to make a more stable component which

contains MgO, but no or little Al_2O_3 . The other method is to stabilize the compound $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ and to inhibit the formation of $\text{C}_{20}\text{A}_{13}\text{M}_3\text{S}_3$.

Previous study [13] demonstrates that Na_2O addition could improve the alumina leaching properties of the slags. Therefore, Na_2O addition for removing the negative effect of MgO in calcium aluminate slag leaching was studied and its mechanism was discussed in this work.

2 Experimental

2.1 Materials

Calcium aluminate slag was synthesized from the chemical reagents Al_2O_3 , SiO_2 , Na_2CO_3 , MgO and CaCO_3 . The mass ratio of Al_2O_3 to SiO_2 (A/S) in the slag was 1.3, and the molar ratio CaO to Al_2O_3 , excluding the CaO of $2\text{CaO} \cdot \text{SiO}_2$ (C/A) of the slag was 1.7. The MgO contents in the samples were 1% and 3% and Na_2O addition changed from 0 to 4% in this study.

2.2 Smelting of calcium aluminate slag

Samples with different Na_2O and MgO contents were sintered in a graphite crucible in a MoSi_2 resistance furnace. Another corundum crucible was installed outside of the graphite crucible in order to prevent the graphite crucible from breaking-out during cooling of the slag, contaminating the furnace. The sintering was carried out at 1 500 °C for 1 h. The sample was cooled at 5 °C/min and taken out at 400 °C from the resistance furnace.

2.3 Leaching of calcium aluminate slag

The sodium aluminate solution obtained from leaching the slag was treated using the carbonization precipitation process, and the circulating mother liquid was then used to leach the new calcium aluminate slag. The feasible conditions for alumina digestion were as follows: leaching temperature 75 °C, leaching time 30 min, L/S ratio 4.5 (the ratio of volume to mass), caustic alkali concentration 7 g/L and sodium carbonate concentration 120 g/L.

The leaching experiments were carried out in a magnetically stirred and constant temperature water bath (stirring speed was about 500 r/min). After leaching and filtration, the filtrate was analyzed for its chemical composition, and the filter residue was washed and dried for analysis.

The contents of Al_2O_3 and SiO_2 in slag and leaching residue were analyzed by XRF. Alumina leaching efficiency was calculated according to the following formula:

$$\eta_{\text{AO}} = 1 - \frac{w(A)/w(S)_{\text{residue}}}{w(A)/w(S)_{\text{slag}}} \quad (2)$$

where $w(A)$ is Al_2O_3 content of sample; $w(S)$ is SiO_2 content of sample.

2.4 Analysis methods

The contents of Al_2O_3 and Na_2O in samples and filtrate were analyzed by a chemical method. Phase components of the calcium aluminate slag were identified by X-ray diffractometer (PANalytical PW3040/60). SEM (SHIMADZU SSX-550) and EDS (DX-4) were used for microstructure and components analysis.

A Malvern laser particle analyzer was used to analyze the particle size distribution of the slag. The content of granularity which was lower than 74 μm in samples was defined as the self-disintegrating ratio.

3 Results and discussion

3.1 Effect of Na_2O on self-disintegrating of slag

The self-disintegration of calcium aluminate slag can reduce the energy consumption during leaching and is a very important characteristic of calcium aluminate slags. Slags with different MgO and Na_2O contents were cooled slowly and then well-mixed in order to analyze the granularity of the slag. The particle size results analyzed by Malvern 2000 are shown in Fig. 1.

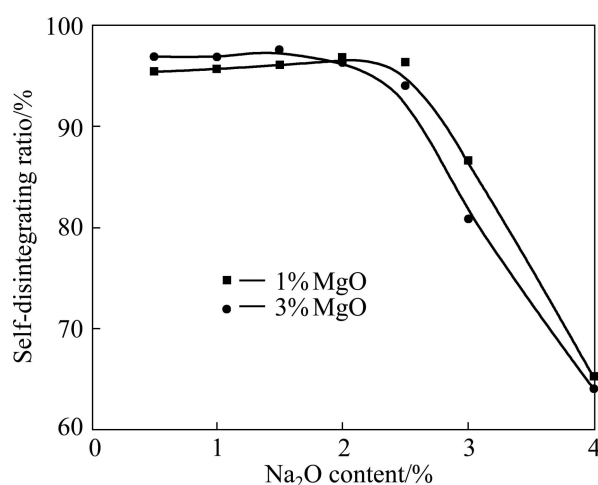


Fig. 1 Self-disintegrating ratio of MgO-containing slag with different Na_2O contents

The results of granularity showed that the self-disintegrating trends of calcium aluminate slag with different MgO contents are similar. When Na_2O content was below 2.5%, the self-disintegrating ratios of the slag with different MgO contents were good, and were basically higher than 90%. Under these conditions, Na_2O

had little effect on self-disintegrating property of the slag. But if Na_2O content was higher than 2.5%, the self-disintegrating ratio of the slag decreased obviously. When Na_2O content was 4%, only part of the slag was self-disintegrated and the ratio was only about 65% which is far less than 95%.

According to the XRD analysis, the variation of granularity was caused by the formation of $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$. The crystal transformation from $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$ to $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$ (with volume expansion of 12%) caused the slag disintegrating [14–15]. When Na_2O content was over 2.5%, this crystal transformation would be inhibited.

Plenty of work had been done on this inhibition. FENG and LONG [16] revealed that the stabilization ions enriched in the crystal boundaries and dislocations of $2\text{CaO}\cdot\text{SiO}_2$ inhibited the formation and growth of $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$ crystal nucleus. They used the polarization ability (C^2/R) to evaluate the stabilization effect of the ions, where C and R are the electrovalence and Pauling radius of the ions, respectively. The ions will have the stabilization effect if the C^2/R is over 39 or below 4. The electrovalence and Pauling radius of Na^+ are +1 and 0.95 Å, respectively. Therefore, it has a greater stabilization effect due to its C^2/R of 1.05. The effect mechanism is that Na^+ replaces Ca^{2+} in the crystal lattice of $2\text{CaO}\cdot\text{SiO}_2$ and the defect reaction happens as $2\text{Ca}_{\text{Ca}} \rightarrow 2\text{Na}_{\text{Ca}} + \text{V}''_{\text{Si}}$. In this case, a certain amount of CaO was released from $2\text{CaO}\cdot\text{SiO}_2$ because of the addition of Na_2O .

3.2 Effect of Na_2O on alumina leaching of slag

The alumina leaching experiment on the calcium aluminate slags was carried out in order to study the effect of Na_2O on the alumina leaching properties of MgO -containing slags. The leaching conditions are as in section 2.3, and the results are shown in Fig. 2.

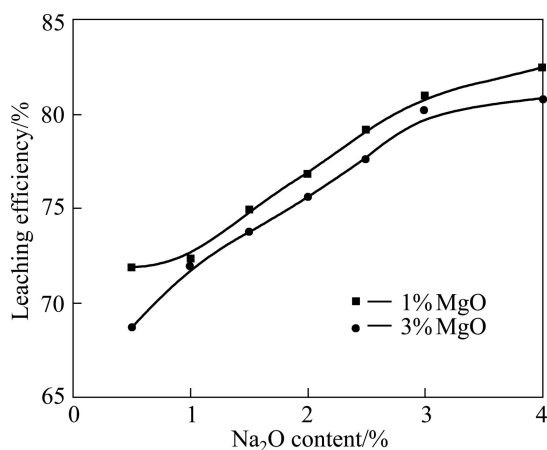


Fig. 2 Leaching efficiency of MgO -containing slags with different Na_2O contents

Figure 2 shows that the alumina leaching efficiency of the slags increases with the increase of Na_2O content.

1) MgO content of 1%. When Na_2O content was 0.5%, the alumina leaching efficiency was only 71.90%. With the increase of Na_2O content, the leaching efficiency was increased linearly. When Na_2O content was 3%, the leaching efficiency was up to 81.03% and increased by about 10%. By further increasing the Na_2O content, the leaching efficiency was only increased by 1%.

2) MgO content of 3%. The leaching efficiency change trend of the slags was similar to that of the slags with MgO content of 1%. The alumina leaching efficiency was increased from 68% to 81% with the addition of Na_2O changed from 0.5% to 4%.

Therefore, the effect of Na_2O on leaching efficiency of the slags was obviously great when its content was below 3%. The leaching efficiency would be changed only little for Na_2O content over 3%. But at the same time the self-disintegrating property was decreased obviously (Fig. 1).

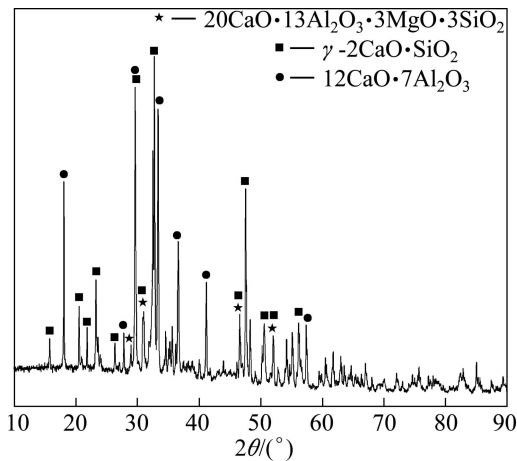
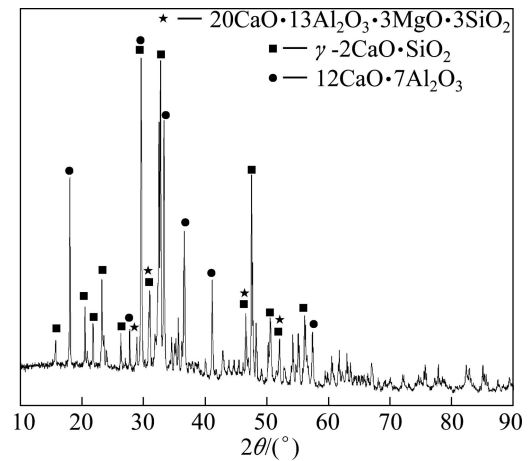
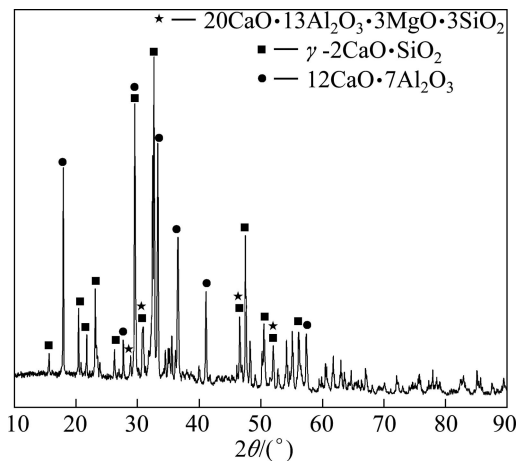
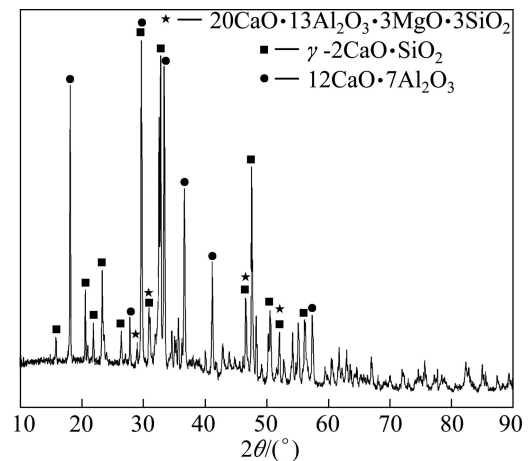
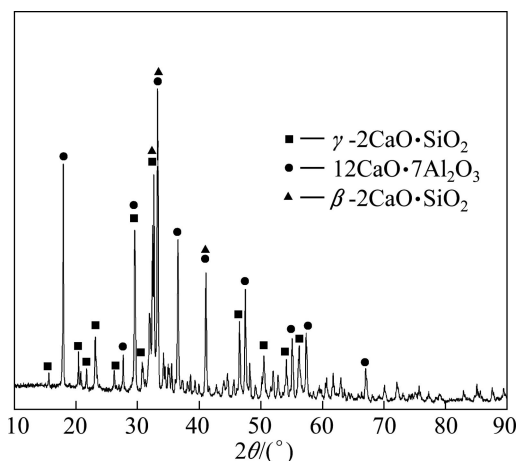
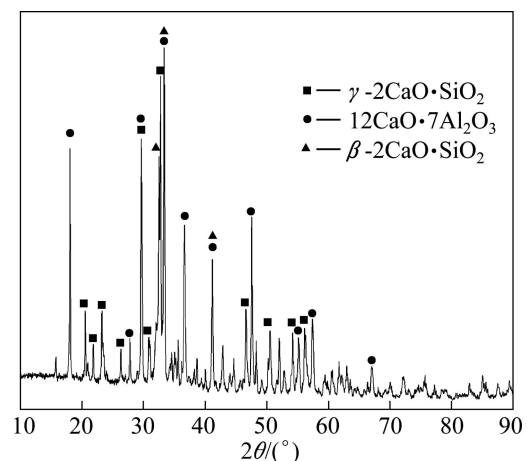
3) The leaching efficiency curve of the slags with 3% MgO was below that of slag with 1% MgO under all the conditions. That is, the increase of Na_2O content could reduce the negative effect of MgO on leachability of the slags, but it could not remove the effect completely. And the beneficial effect of Na_2O on alumina leaching efficiency would be reduced with the increase of MgO content.

The concentrations of total soda of leaching solutions were analyzed by acid-base titration. The results showed that the concentration of total soda changed little (from 127 to 130 g/L) after alumina leaching when Na_2O content was 4%. Therefore, the addition of Na_2O has little effect on the concentration of leaching solution.

3.3 Effect of Na_2O on slag phase transformation

The addition of Na_2O can reduce the negative effect of MgO on leachability of calcium aluminate slags. The mechanism of C/A effect on MgO -containing slags was studied by XRD. The quaternary compound $\text{C}_{20}\text{A}_{13}\text{M}_3\text{S}_3$ was also investigated. The XRD patterns of slags with 1% MgO and 3% MgO are shown in Figs. 3–8.

It can be seen from these figures that the phase transformation of the slags with different Na_2O contents was similar when MgO content was 1% and 3% respectively, which caused the similar leaching efficiency trend (Fig. 2). When Na_2O content was below 2%, the main phases in the slags were $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$, $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ and $\text{C}_{20}\text{A}_{13}\text{M}_3\text{S}_3$. But the intensity of characteristic peaks of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ and $\text{C}_{20}\text{A}_{13}\text{M}_3\text{S}_3$

Fig. 3 XRD pattern of slags with 1% MgO and 1% Na₂OFig. 6 XRD pattern of slags with 3% MgO and 1% Na₂OFig. 4 XRD pattern of slags with 1 %MgO and 2% Na₂OFig. 7 XRD pattern of slags with 3% MgO and 2% Na₂OFig. 5 XRD pattern of slags with 1% MgO and 4% Na₂OFig. 8 XRD pattern of slags with 3% MgO and 4% Na₂O

were changed with Na₂O content. The intensity of characteristic peaks of 12CaO·7Al₂O₃ was increased and that of C₂₀A₁₃M₃S₃ was reduced with the increase of Na₂O content. The results are shown in Table 1 and Table 2.

When the Na₂O content was increased to 4%, the quaternary compound C₂₀A₁₃M₃S₃ disappeared and was transformed to 12CaO·7Al₂O₃ completely in the slags. The phase transformation study revealed why the leaching efficiency was increased with the increase of

SEM results indicated that the appearance of the slag granules which were not grinded was irregular, and was composed of both large particles and small particles. It can be seen from Table 4 that the large particles were close to the composition of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$. There was Na_2O in these particles with the content of about 4%. Therefore, combined with the XRD results, Na_2O came into the lattice of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ in the form of solution. And this promotes the formation of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$.

4 Conclusions

1) The addition of Na_2O could improve the leaching property of MgO -containing calcium aluminate slags. And leaching efficiency will be increased with the increase of Na_2O content. But with increasing MgO content the beneficial effect will be reduced with the fixed addition of Na_2O .

2) The quaternary compound $\text{C}_{20}\text{A}_{13}\text{M}_3\text{S}_3$ will be transformed into $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ gradually with the increase of Na_2O content. And when Na_2O content reaches 4%, $\text{C}_{20}\text{A}_{13}\text{M}_3\text{S}_3$ will disappear in the slags.

3) The formation of $\beta\text{-}2\text{CaO}\cdot \text{SiO}_2$ can release part of CaO and this extra CaO released can decompose $\text{C}_{20}\text{A}_{13}\text{M}_3\text{S}_3$. Na_2O can come into the lattice of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ as a solution form and promote the formation of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$.

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Na_2O 对含 MgO 铝酸钙炉渣相变规律和 氧化铝浸出性能的影响

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摘 要: 采用向铝酸钙炉渣体系中添加 Na_2O 的方法, 降低或消除铝酸钙炉渣中 MgO 的负作用, 并分析其影响机理。结果表明: 当 MgO 含量为 3% 时, Na_2O 的添加量由 0 增加至 4% 后, 炉渣的氧化铝浸出率由 68.73% 提高到 80.86%。对含 4% Na_2O 的样品进行 XRD 分析, 发现四元化合物 $\text{C}_{20}\text{A}_{13}\text{M}_3\text{S}_3$ 已消失。添加 Na_2O 不能完全消除 MgO 对炉渣浸出性能的负作用。XRD 和 EDS 分析结果表明, Na_2O 会进入 $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ 的晶格并促进其形成。

关键词: 铝酸钙炉渣; Na_2O ; MgO ; 相变规律; 氧化铝浸出

(Edited by LI Xiang-qun)