Effect of Na$_2$O on alumina leaching property and phase transformation of MgO-containing calcium aluminate slags

WANG Bo, SUN Hui-lan, GUO Dong, ZHANG Xue-zheng
School of Materials Science and Technology, Hebei University of Science and Technology, Shijiazhuang 050018, China
Received 13 December 2010; accepted 23 May 2011

Abstract: In order to remove or reduce the negative effect of MgO in calcium aluminate slags, the method of adding Na$_2$O 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 Na$_2$O content increasing from 0 to 4% when MgO content is 3%. The XRD results show that the quaternary compound C$_{20}$A$_{13}$M$_3$S$_1$ disappears when Na$_2$O content increases to 4%. The addition of Na$_2$O cannot remove the negative effect of MgO on leachability completely. XRD and EDS results indicate that Na$_2$O can come into the lattice of 12CaO·7Al$_2$O$_3$ and promote the formation of 12CaO·7Al$_2$O$_3$

Key words: calcium aluminate slag; Na$_2$O; 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·7Al$_2$O$_3$ and γ-2CaO·SiO$_2$ [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·4Al$_2$O$_3$·MgO·SiO$_2$ 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·7Al$_2$O$_3$ and form limited C$_{20}$A$_{13}$M$_3$S$_1$ when the MgO content is less than 1.0%. But if it is above this level, a large amount of C$_{20}$A$_{13}$M$_3$S$_1$ 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 C$_{20}$A$_{13}$M$_3$S$_1$ was carried out in high-alumina cement [8–9]. At first, the composition of Q phase was thought as 6CaO·4Al$_2$O$_3$·MgO·SiO$_2$ [10]. The later research indicated that the steady chemical formula of Q phase was 20CaO·13Al$_2$O$_3$·3MgO·3SiO$_2$ [11]. And its general formula was given as 20CaO·(16−$\nu$)Al$_2$O$_3$·$\nu$MgO·$\nu$SiO$_2$ ($\nu$=2.5–3.5). The reaction equation of the formation of C$_{20}$A$_{13}$M$_3$S$_1$ was as follows [12]:

$$\text{C}_2\text{AS}+\text{CA(12A)}_7^+\text{MgO(Free)}\rightarrow\text{C}_{20}\text{A}_{13}\text{M}_3\text{S}_1 \quad (1)$$

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

Foundation item: Project (51104053) supported by the National Natural Science Foundation of China; Project (XL200921) supported by the Foundation Research funds for Hebei University of Science and Technology, China
Corresponding author: WANG Bo; Tel: +86-311-81668705; E-mail: wangbo@hebust.edu.cn
DOI: 10.1016/S1003-6326(11)61119-9
contains MgO, but no or little Al\textsubscript{2}O\textsubscript{3}. The other method is to stabilize the compound 12CaO·7Al\textsubscript{2}O\textsubscript{3} and to inhibit the formation of C\textsubscript{2}A\textsubscript{13}M\textsubscript{3}S\textsubscript{3}.

Previous study \[13\] demonstrates that Na\textsubscript{2}O addition could improve the alumina leaching properties of the slags. Therefore, Na\textsubscript{2}O 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\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, Na\textsubscript{2}CO\textsubscript{3}, MgO and CaCO\textsubscript{3}. The mass ratio of Al\textsubscript{2}O\textsubscript{3} to SiO\textsubscript{2} (A/S) in the slag was 1.3, and the molar ratio CaO to Al\textsubscript{2}O\textsubscript{3}, excluding the CaO of 2CaO·SiO\textsubscript{2} (C/A) of the slag was 1.7. The MgO contents in the samples were 1% and 3% and Na\textsubscript{2}O addition changed from 0 to 4% in this study.

2.2 Smelting of calcium aluminate slag

Samples with different Na\textsubscript{2}O and MgO contents were sintered in a graphite crucible in a MoSi\textsubscript{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\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} in slag and leaching residue were analyzed by XRF. Alumina leaching efficiency was calculated according to the following formula:

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

where $w(A)$ is Al\textsubscript{2}O\textsubscript{3} content of sample; $w(S)$ is SiO\textsubscript{2} content of sample.

2.4 Analysis methods

The contents of Al\textsubscript{2}O\textsubscript{3} and Na\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O contents](image)

The results of granularity showed that the self-disintegrating trends of calcium aluminate slag with different MgO contents are similar. When Na\textsubscript{2}O 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\textsubscript{2}O
had little effect on self-disintegrating property of the slag. But if Na$_2$O content was higher than 2.5%, the self-disintegrating ratio of the slag decreased obviously. When Na$_2$O 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 $\beta$-2CaO·SiO$_2$. The crystal transformation from $\beta$-2CaO·SiO$_2$ to $\gamma$-2CaO·SiO$_2$ (with volume expansion of 12%) caused the slag disintegrating [14–15]. When Na$_2$O 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 2CaO·SiO$_2$ inhibited the formation and growth of $\gamma$-2CaO·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 2CaO·SiO$_2$ and the defect reaction happens as $2\text{CaO}_\text{cr} \rightarrow 2\text{NaO}_\text{cr} + \text{V}''_{\text{Si}}$. In this case, a certain amount of CaO was released from 2CaO·SiO$_2$ because of the addition of Na$_2$O.

### 3.2 Effect of Na$_2$O 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$_2$O 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$_2$O contents](image)

Figure 2 shows that the alumina leaching efficiency of the slags increases with the increase of Na$_2$O content.

1) MgO content of 1%. When Na$_2$O content was 0.5%, the alumina leaching efficiency was only 71.90%. With the increase of Na$_2$O content, the leaching efficiency was increased linearly. When Na$_2$O content was 3%, the leaching efficiency was up to 81.03% and increased by about 10%. By further increasing the Na$_2$O 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$_2$O changed from 0.5% to 4%.

Therefore, the effect of Na$_2$O 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$_2$O 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$_2$O 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$_2$O 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$_2$O content was 4%. Therefore, the addition of Na$_2$O has little effect on the concentration of leaching solution.

### 3.3 Effect of Na$_2$O on slag phase transformation

The addition of Na$_2$O 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 C$_{20}$A$_{13}$M$_3$S$_7$ 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$_2$O contents was similar when MgO content was 1% and 3% respectively, which caused the similar leaching efficiency trend (Fig. 2). When Na$_2$O content was below 2%, the main phases in the slags were $\gamma$-2CaO·SiO$_2$, 12CaO·7Al$_2$O$_3$ and C$_{20}$A$_{13}$M$_3$S$_7$. But the intensity of characteristic peaks of 12CaO·7Al$_2$O$_3$ and C$_{20}$A$_{13}$M$_3$S$_7$
Fig. 3 XRD pattern of slags with 1% MgO and 1% Na$_2$O

Fig. 4 XRD pattern of slags with 1% MgO and 2% Na$_2$O

Fig. 5 XRD pattern of slags with 1% MgO and 4% Na$_2$O

Fig. 6 XRD pattern of slags with 3% MgO and 1% Na$_2$O

Fig. 7 XRD pattern of slags with 3% MgO and 2% Na$_2$O

Fig. 8 XRD pattern of slags with 3% MgO and 4% Na$_2$O

were changed with Na$_2$O content. The intensity of characteristic peaks of 12CaO-7Al$_2$O$_3$ was increased and that of C$_{20}$A$_{13}$M$_3$S$_7$ was reduced with the increase of Na$_2$O content. The results are shown in Table 1 and Table 2.

When the Na$_2$O content was increased to 4%, the quaternary compound C$_{20}$A$_{13}$M$_3$S$_7$ disappeared and was transformed to 12CaO-7Al$_2$O$_3$ completely in the slags. The phase transformation study revealed why the leaching efficiency was increased with the increase of
Table 1 Intensity of characteristic peak of 12CaO·7Al2O3 (d=0.269 nm)

<table>
<thead>
<tr>
<th>w(MgO)/%</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% Na2O</td>
<td>3 826</td>
</tr>
<tr>
<td>2% Na2O</td>
<td>3 947</td>
</tr>
<tr>
<td>3% Na2O</td>
<td>3 699</td>
</tr>
</tbody>
</table>

Table 2 Intensity of characteristic peak of C20A13M3S3 (d=0.288 nm)

<table>
<thead>
<tr>
<th>w(MgO)/%</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% Na2O</td>
<td>816</td>
</tr>
<tr>
<td>2% Na2O</td>
<td>793</td>
</tr>
</tbody>
</table>

Na2O content. Under this condition, periclase was found in the slag with 3% MgO (Fig. 8). However, periclase was not found in slag with 1% MgO because its content was too low (Fig. 5). Therefore, the following equation occurred with the addition of Na2O:

\[ C_{20}A_{13}M_3S_3 \xrightarrow{Na_2O} C_{12}A_7 + C_2S + MgO \] (3)

The intensity of characteristic peaks of 12CaO·7Al2O3 of the slags with MgO content of 3% was always lower than that of the slags with MgO content of 1%, which brought about the leaching efficiency of the former slags always lower than that of the latter slags.

XRD results also indicated that a great amount of \( \beta-2CaO\cdotSiO_2 \) was formed when Na2O content was 4%, which would obviously reduce the self-disintegrating property of the slags.

3.4 Effect mechanism of Na2O on slag properties

The existence of Na2O improved the alumina leaching property of MgO-containing slag obviously. The beneficial effect arose in the following two ways.

1) Na2O came into the lattice defects instead of CaO, resulting in the formation of \( \beta-2CaO\cdotSiO_2 \) (XRD results). This was equivalent to increase of the CaO ratio in calcium aluminate slag. The increase of CaO ratio had the effect of reducing or eliminating the compound C20A13M3S3 difficult to be leached [5]. In another word, the extra CaO could decompose the quaternary compound.

2) Na2O could promote the formation of 12CaO·7Al2O3, so the leaching efficiency of the slags was improved. XRD results showed that the crystal structure of 12CaO·7Al2O3 was changed with the increase of Na2O content. The interplanar spacing was shifted to the left. Table 3 shows the changes of the lattice constant (calculated by Celref Software) of 12CaO·7Al2O3 (cubic system, \( a=b=c \)) with different Na2O contents when MgO content was 3%.

Table 3 Lattice constants of 12CaO·7Al2O3 with 3%MgO and different Na2O contents

<table>
<thead>
<tr>
<th>C12A7 standard card/nm</th>
<th>Lattice constant/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% Na2O</td>
<td>1.19890</td>
</tr>
<tr>
<td>2% Na2O</td>
<td>1.19966</td>
</tr>
<tr>
<td>3% Na2O</td>
<td>1.19982</td>
</tr>
<tr>
<td>4% Na2O</td>
<td>1.20079</td>
</tr>
</tbody>
</table>

It can be seen from Table 3 that compared with 12CaO·7Al2O3 standard card its lattice constant was increased with the increase of Na2O content. Figures 9 and 10 show the SEM and EDS results of the slags with MgO content of 3% and Na2O content of 4%. Table 4 shows the elemental compositions of points 1–3 in Fig. 9.

Table 4 Elemental compositions at points 1, 2 and 3 in Fig. 9

<table>
<thead>
<tr>
<th>Point</th>
<th>Original data</th>
<th>Calculated data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>w(O)%</td>
<td>w(Na)%</td>
</tr>
<tr>
<td>1</td>
<td>47.450</td>
<td>3.227</td>
</tr>
<tr>
<td>2</td>
<td>38.463</td>
<td>2.719</td>
</tr>
<tr>
<td>3</td>
<td>39.033</td>
<td>3.056</td>
</tr>
</tbody>
</table>

Fig. 9 SEM image of slag with 3% MgO and 4% Na2O

Fig. 10 EDS spectra at points 1, 2 and 3 in Fig. 9
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 12CaO·7Al₂O₃. There was Na₂O in these particles with the content of about 4%. Therefore, combined with the XRD results, Na₂O came into the lattice of 12CaO·7Al₂O₃ in the form of solution. And this promotes the formation of 12CaO·7Al₂O₃.

4 Conclusions

1) The addition of Na₂O could improve the leaching property of MgO-containing calcium aluminate slags. And leaching efficiency will be increased with the increase of Na₂O content. But with increasing MgO content the beneficial effect will be reduced with the fixed addition of Na₂O.

2) The quaternary compound C₁₀A₃M₂S₂ will be transformed into 12CaO·7Al₂O₃ gradually with the increase of Na₂O content. And when Na₂O content reaches 4%, C₁₀A₃M₂S₂ will disappear in the slags.

3) The formation of β-2CaO·SiO₂ can release part of CaO and this extra CaO released can decompose C₁₀A₃M₂S₂. Na₂O can come into the lattice of 12CaO·7Al₂O₃ as a solution form and promote the formation of 12CaO·7Al₂O₃.

References


Na₂O 对含 MgO 铝酸钙熔体的相变规律和氧化铝浸出性能的影响

王 波, 孙会兰, 国 栋, 张学政

河北科技大学 材料科学与工程学院, 石家庄 050018

摘要: 采用向铝酸钙熔体体系中添加 Na₂O 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, Na₂O 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%Na₂O 的样品进行 XRD 分析, 发现四元化合物 C₁₀A₃M₂S₂ 已消失。添加 Na₂O 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, Na₂O 会进入 12CaO·7Al₂O₃ 的晶格并促进其形成。

关键词: 铝酸钙熔渣; Na₂O; MgO; 相变规律; 氧化铝浸出

(Edited by LI Xiang-qun)