

Effect of Calcium/Aluminium ratio on MgO containing calcium aluminate slags

Wang Bo¹, Sun Hui-lan¹, Guo Dong¹, Bi Shi-wen²

¹Hebei University of Science and Technology; 70 Yuhua East Rd; Shijiazhuang, Hebei, 050018, China;

²Northeastern University; No.11, Lane 3, Wenhua Road; Shenyang, Liaoning, 110004, China

Keywords: calcium aluminate slag, CaO ratio, MgO, $C_{20}A_{13}M_3S_3$, alumina leaching

Abstract

MgO is the main impurity in calcium aluminate slags. The presence of MgO will change the nature of the alumina bearing phases and decrease the alumina leaching properties of the slag. In order to remove or reduce the negative effect of MgO, the method of changing the C/A (CaO/Al_2O_3 , molar ratio, excluding CaO in $2CaO\cdot SiO_2$) of the calcium aluminate slag was studied and the effect on leaching mechanism was also analyzed. The results showed that the formation of the quaternary compound $20CaO\cdot 13Al_2O_3\cdot 3MgO\cdot 3SiO_2$ ($C_{20}A_{13}M_3S_3$) is inhibited with increasing C/A in the calcium aluminate slag, and the MgO crystallized in the form of periclase under these conditions. There is an optimal C/A to improve the alumina leachability of the calcium aluminate slag. The increase of C/A could not remove the negative effect of MgO on leachability completely, and the optimal C/A of the slag increases with increasing MgO content.

Introduction

Calcium aluminate slag is obtained from blast furnaces when smelting iron-bearing bauxite. The ideal components of calcium aluminate slags are $12CaO\cdot 7Al_2O_3$ and $\gamma\text{-}2CaO\cdot SiO_2$ [1, 2]. The slag can react with a sodium carbonate solution and its alumina leaching rate can reach 85%. This method realizes the comprehensive utilization of iron and alumina values in the ore [3-5].

The existence of impurity MgO which comes from iron-bearing bauxite and lime, will affect the alumina leaching rate of calcium aluminate slag during the industrial process [6-8].

Eremin [9] studied the effect of MgO on calcium aluminate slag and pointed out that the compound $6CaO\cdot 4Al_2O_3\cdot MgO\cdot SiO_2$ ($C_wA_xM_yS_z$) would be formed in the slag when MgO was present. This compound does not react with the sodium carbonate solution. Wang Bo [10, 11] studied the mechanism of MgO effects on such slags systematically. The results showed that MgO will dissolve into the crystal lattice of $12CaO\cdot 7Al_2O_3$ and forms limited $C_{20}A_{13}M_3S_3$ when the MgO content is less than 1.0%. Above this level, a large amount of $C_{20}A_{13}M_3S_3$ was formed which decreased the alumina leaching rate. The results also showed that this quaternary compound could react with sodium carbonate solution but its alumina leaching rate was very low [12].

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

There are two methods to remove the negative effect of MgO from the phase components of the calcium aluminate slag. One is to make MgO form a more stable component which contained no, or little Al_2O_3 . The other method is to stabilize the compound

$12CaO\cdot 7Al_2O_3$ and to inhibit the formation of $C_{20}A_{13}M_3S_3$ [13-15].

Previous research demonstrates that the alteration of the CaO content could improve the alumina leaching properties of the slag. So the alteration of C/A (CaO/Al_2O_3 , molar ratio, excluding the CaO of $2CaO\cdot SiO_2$) of the calcium aluminate slag, to remove the negative effect of MgO, was studied and mechanism of this effect are discussed in this paper.

Experimental

2.1 Materials

$CaCO_3$, Na_2CO_3 , NaOH, SiO_2 and MgO used in the experimental studies were chemical pure reagents. $Al(OH)_3$ used in the experimental was an industrial pure reagent. The A/S (Al_2O_3/SiO_2 , mass ratio) of the calcium aluminate slag was 1.3.

2.2 Smelting of calcium aluminate slag

Samples with different C/A were smelted in a $MoSi_2$ resistance furnace, and the container was a graphite crucible. Another corundum crucible was used outside of the graphite crucible in order to prevent the break-out of the slag which could disintegrate and destroy the graphite crucible during cooling, thus contaminating the furnace. The smelting temperature was $1500^\circ C$ and the holding time was one hour. The sample was taken out at $400^\circ C$ from the resistance furnace, and its cooling rate was $5^\circ C/min$.

2.3 Leaching of calcium aluminate slag

The sodium aluminate solution obtained from leaching the slag was treating using the carbonization precipitation process, and the circulating mother liquid is then used to leach new calcium aluminate slag. The feasible conditions for alumina digestion are: leaching temperature $75^\circ C$, leaching time 2h, L/S ratio 4.5, caustic alkali concentration 7g/L and sodium carbonate concentration 120 g/L. The leaching experiments are carried out in magnetically stirred constant temperature water bath. After leaching and dry filtration, the filtrate is used to analyze the composition of the solution, and the filter residue is washed and dried for analysis.

2.4 Analysis

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 diffraction (PANalytical PW3040/60). A Malvern laser particle analyzer was used to analyze the particle size of the slag.

Results and discussion

3.1 Effect of C/A on self-disintegrating property of slag

The self-disintegration of calcium aluminate slag can reduce the energy consumption during leaching and alumina production, and this is a very important characteristic of calcium aluminate slags. The percent content of granularity which is lower than $74\mu\text{m}$ in samples is defined as the self-disintegrating rate. Slags with different MgO 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.

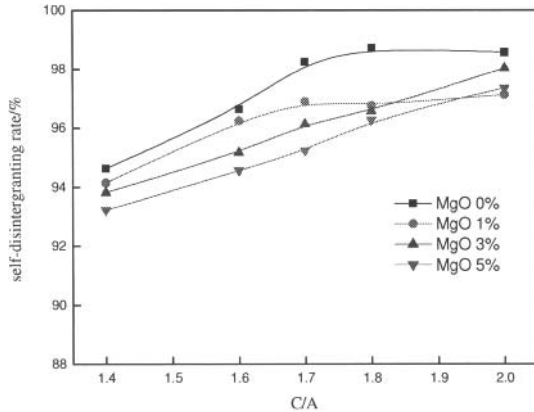


Fig. 1 Granularity of slag with different C/A and MgO content

The results of granularity showed that the self-disintegrating rate of calcium aluminate slag with different MgO content and C/A were good, and they were basically higher than 95%. The self-disintegrating rate was lower than 95% only when C/A was very low. It can be seen that when the C/A of slag was fixed the self-disintegrating rate decreased with the increase of MgO content, and also when the MgO content was fixed the self-disintegrating rate increased with the increase of C/A.

The self-disintegration of slag was caused by the crystal transformation from $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$ to $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$. With the increase of MgO content, self-disintegration of slag decreased because of the increase of $\text{C}_{20}\text{A}_{13}\text{M}_3\text{S}_3$ content. A certain amount of SiO_2 was consumed when the quaternary compound $\text{C}_{20}\text{A}_{13}\text{M}_3\text{S}_3$ was formed. Therefore, the content of $2\text{CaO}\cdot\text{SiO}_2$ decreased in the slag and the self-disintegrating rate of the slag decreased. The content of $\text{C}_{20}\text{A}_{13}\text{M}_3\text{S}_3$ decreased with the increase in C/A when the MgO content was fixed, so the self-disintegrating properties were improved. But the content of SiO_2 in $\text{C}_{20}\text{A}_{13}\text{M}_3\text{S}_3$ was low, so the decrease of $2\text{CaO}\cdot\text{SiO}_2$ was also low and had little effect on self-disintegration rate of the slag. Therefore, the self-disintegration rate of the slag was still sufficient to meet the demand of the alumina leaching process.

3.2 Effect of C/A on alumina leaching property of slag

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

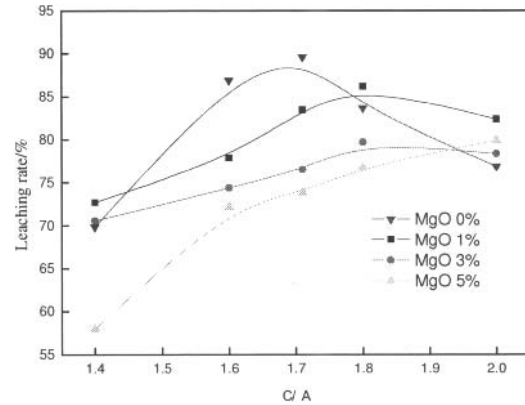


Fig. 2 Leaching rate of containing MgO slag with different C/A

Fig. 1 shows that the alumina leaching rate of slag increased at first and then decreased with increase of C/A. The highest alumina leaching rate of a slag which did not contain MgO appeared when C/A was 1.7. The highest alumina leaching rate of slag whose MgO content was 1% appeared when C/A was 1.8. The higher alumina leaching rate of slag whose MgO content was 3% appeared when C/A was between 1.8 and 2.0, and then the leaching rate decreased smoothly. The highest alumina leaching rate of slag with MgO content of 5% appeared when C/A was 2.0, and a maximum rate did not appear under these conditions.

Therefore, the alumina leaching rate of calcium aluminate slag decreased with increasing MgO content when C/A was 1.7. The increase of C/A could improve the leaching property of slag to some extent, and the optimal C/A of the slag also increased with increasing MgO content. In addition, the variation of C/A could not remove the negative effect completely, because the optimal alumina leaching rate decreased with the increase in MgO content.

3.3 Effect mechanism of C/A on MgO containing calcium aluminate slag

The increase of CaO can reduce the negative effect of MgO on leachability of calcium aluminate slags, so the mechanism of effect of C/A on MgO containing slags was analyzed by XRD. The existence of the quaternary compound $\text{C}_{20}\text{A}_{13}\text{M}_3\text{S}_3$ was also investigated. The XRD spectra are shown in Fig. 3~Fig. 5. Fig. 6 and Fig. 7 showed the relative intensity of independent characteristic peaks of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ and $\text{C}_{20}\text{A}_{13}\text{M}_3\text{S}_3$ as a function of MgO content and C/A.

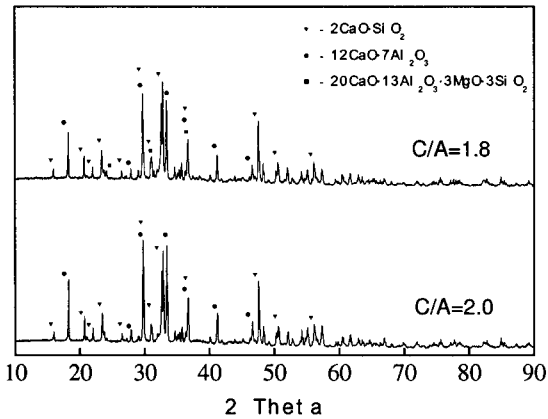


Fig.3 XRD spectra of slag with MgO=1%

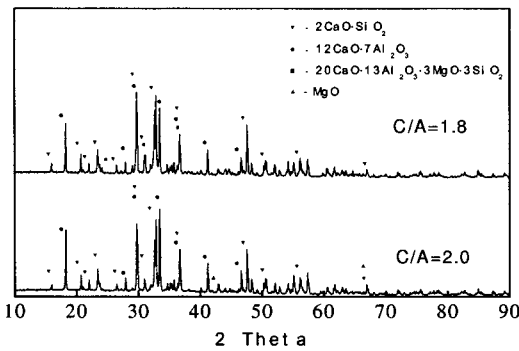


Fig.4 XRD spectra of slag with MgO=3%

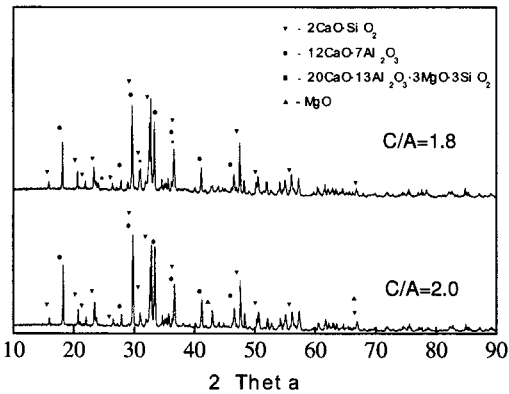


Fig.5 XRD spectra of slag with MgO=5%

The compound $C_{20}A_{13}M_3S_3$ which is difficult to leach was found in the slag whose C/A was 1.8, but it could not be found in the slag whose C/A was 2.0. The intensity of characteristic peaks of $12CaO \cdot 7Al_2O_3$ were clearly enhanced when the C/A of the slag increased. Thus some of the $C_{20}A_{13}M_3S_3$ transformed into $12CaO \cdot 7Al_2O_3$ which is easy to leach, with the increase of C/A of the slag. Some $3CaO \cdot Al_2O_3$ was also found in slag when the C/A was 2.0, and that was the reason why the alumina leaching rate of slag whose C/A was 2.0 was lower than that of a slag whose C/A

was 1.8. Crystalline MgO or its mineral forms, was not found in the slag under these conditions.

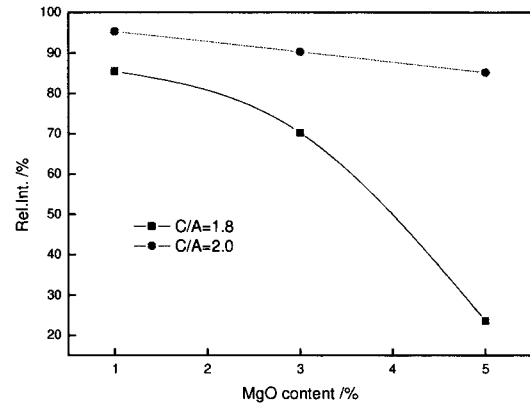


Fig.6 Relative intensity of characteristic peaks of $12CaO \cdot 7Al_2O_3$

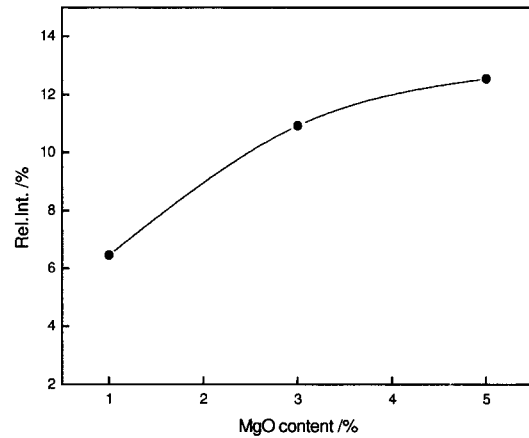
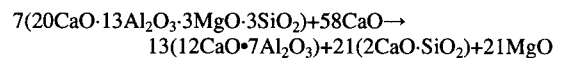


Fig.7 Relative intensity of characteristic peaks of $C_{20}A_{13}M_3S_3$ with $C/A=1.8$

Fig.6 and Fig.7 show the relative intensity of characteristic peaks of $12CaO \cdot 7Al_2O_3$ and $C_{20}A_{13}M_3S_3$. Relative intensity is defined as a peak intensity ratio between the strongest independent characteristic peaks of $12CaO \cdot 7Al_2O_3$ or $C_{20}A_{13}M_3S_3$ of slag and the strongest peak of slag.

The main phase in the calcium aluminate slag whose MgO content was 3% and C/A was 1.8, were γ - $2CaO \cdot SiO_2$, $12CaO \cdot 7Al_2O_3$, and $C_{20}A_{13}M_3S_3$. The intensity of the characteristic peaks of $C_{20}A_{13}M_3S_3$ is strong showing that a large amount of $C_{20}A_{13}M_3S_3$ was generated. A great deal of $12CaO \cdot 7Al_2O_3$ transformed into $C_{20}A_{13}M_3S_3$ under these conditions. This is why alumina leaching rate decreased. When the C/A of slag increased to 2.0, compound $C_{20}A_{13}M_3S_3$ disappeared and $3CaO \cdot Al_2O_3$ was not found either. Meanwhile periclase was found in the slag. So the extra-addition of CaO decomposed the quaternary compound $C_{20}A_{13}M_3S_3$ and that was the reason why the alumina leaching rate increased. The reaction between $C_{20}A_{13}M_3S_3$ and CaO is shown below:



The analysis of a slag whose C/A MgO content was 5% was similar to that of a slag whose MgO content was 3%. The only difference between them was the intensity of the characteristic peaks of periclase (MgO).

Therefore, the increase of C/A of calcium aluminate slag improved alumina leaching properties and decreased the negative effect of MgO on leachability of the slag, but it could not remove the negative effect of MgO completely. Thus the mechanism of this effect needs to be studied further.

Conclusions

1) MgO content and C/A of calcium aluminate slags had little effect on self-disintegration rate of the slag. The self-disintegrating rate of most samples was above 95%.

2) The increase of C/A could decrease the negative effect of MgO on leachability of the slag, but it could not remove the effect completely when the MgO content was less than 5%. The optimum C/A of the slag increased with the increase of MgO content.

3) The addition of CaO could decompose the quaternary compound $C_{20}A_{13}M_3S_3$, and MgO crystallized in the form of periclase.

Acknowledgements

The authors greatly acknowledge the financial support of the National Nature Science Foundation of China (Project No: 50674028), and the foundation of Hebei University of Science and Technology (Project No: XL200921). The authors express their profound gratitude to the editors and reviewers of TMS.

References

- [1] L.K.Barr, "Alumina Production from Andalusite by the Pedersen Process," (Stockholm: Almqvist & Wiksell international, 1977), 64-70.
- [2] J.Grzymek, A.Derdacka and Z.Konik, "Method for obtaining aluminum oxide," U.S Patent : 4149898 , 1978-2-21.
- [3] ZHANG Jing-dong, LI Yin-tai, BI Shi-wen and YANG Yi-hong, "Research on integrated utilization of high-ferrum bauxite in Guigang Guangxi," *Light Metals*, (8)(1992), 16-18.
- [4] BI Shi-wen, YANG Yi-hong, LI Yin-tai, ZHANG Jing-dong and DUAN Zhen-ying, "Study of alumina leaching from calcium aluminate slag," *Light Metals*, (6)(1992), 10-15.
- [5] J.Grzymek, "Complex Production of aluminium oxide and Iron from laterite raw materials applying the calcium aluminates polymorphism," TMS Annual Meeting and Exhibition, *Light Metals*, 1985, 87-99.
- [6] WANG Bo, YU Hai-yan, SUN Hui-lan and BI Shi-wen, "Effect of material ratio on leaching and self-disintegrating property of calcium aluminate slag," *Journal of Northeastern University: Natural Science*, 29(11)(2008), 1593-1596.
- [7] TONG Zhi-fang, BI Shi-wen, YU Hai-yan and WU Yu-sheng, "Leaching kinetics of non-constant temperature process of calcium aluminate slag under microwave radiation," *The Chinese Journal of Nonferrous Metals*, 16(2)(2006), 357-362.
- [8] D.J.Connor, *Aluminium extraction from non bauxitic materials*, (Sydney: Aluminium-Verlag GmbH, 1988), 230-250.
- [9] N.I.Eremin, "Investgations on the complex processing of bauxites," (Bauxite-Alumina-Aluminum, Symposium of ICSOBA . Budapest: Research Institute for Non-Ferrous Metals, 1971), 329-335.
- [10] WANG Bo, YU Hai-yan, MIAO Yu, SUN Hui-lan, BI Shi-wen and TU Gan-feng, "Effect of MgO on leaching and self-disintegrating property of calcium aluminate slag," *Light Metals*, (4)(2008), 11-13.
- [11] WANG Bo, YU Hai-yan, SUN Hui-lan, BI Shi-wen, TU Gan-feng and GENG Hong-juan. "Effect of MgO on crystal and leaching property of $12CaO \cdot 7Al_2O_3$," *Minning and Metallurgical Engineering*, 28(05)(2008), 68-71.
- [12] WANG Bo, YU Hai-yan, SUN Hui-lan, BI Shi-wen and TU Gan-feng, "Synthesis and Al_2O_3 leaching property of $20CaO \cdot 13Al_2O_3 \cdot 3MgO \cdot 3SiO_2$," *The Chinese Journal of Nonferrous Metals*, 19(2)(2009), 378-382.
- [13] I.Kapralik and F.Hanic, "Studies of the system $CaO-Al_2O_3-MgO-SiO_2$ in relation to the Quaternary phase Q," *Transation of British ceram society*, 1980, 128-133.
- [14] JIANG Feng-hua and XU De-long, "Influence of trace compositions on the formation of Q phase in high-alumina cement system," *Journal of the Chinese Ceramic Society*, 33(10)(2005), 1276-1279.
- [15] MENG Tao, YANG Li-qun and XU Xian-yu, "Studies of $CaO-Al_2O_3-MgO-SiO_2$ system in relation to the formation and hydration of phase Q," *Bulletin of the Chinese Ceramic Society*, (3)(1998), 21-34.