# Influence of MgO and C/A and Cooling System on Alumina Leaching Properties of Calcium Aluminate Slag

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# Abstract

The influences of the content of MgO and C/A (molar ratio of CaO and Al<sub>2</sub>O<sub>3</sub>, excluding CaO in 2CaO • SiO<sub>2</sub>) and cooling system on alumina leaching properties of calcium aluminate slag were investigated by XRD, laser particle size analyzer and chemical analysis. The results showed that when the temperature of taking the sample out from furnace is 1200 °C, the alumina leaching rate is gradually decreased from 82.12% to 51.3% with the content of MgO increasing from 0% to 5%. The leaching rate is gradually increased from 51.3% to 74.74% with C/A increasing from 1.71 to 1.85. The leaching rate is gradually increased with the temperature decreasing under 4~5 °C/min of cooling rate. When the temperature is 500°C and C/A is 1.85, the main phases of slags are Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> and r-Ca<sub>2</sub>SiO<sub>4</sub>, the self-disintegrating rate is 94.45%, and the alumina leaching requirements.

#### Introduction

The comprehensive utilization of high iron-containing red mud in Pingguo alumina plant could be achieved through the following process: firstly recovery of iron by smelting reduction method, then recovery of alumina by leaching the calcium aluminate slag obtained in smelting reduction process, and finally recovery of the other elements enriched in the leached residue[1-3].

The ideal main phases of calcium aluminate slag are  $Ca_{12}Al_{14}O_{33}$ and  $\gamma$ - $Ca_2SiO_4$ . The phase of  $Ca_{12}Al_{14}O_{33}$  can be dissolved by sodium carbonate solution to produce sodium aluminate solution, and then alumina is extracted from the sodium aluminate solution. During the cooling process of slag from higher smelting temperature to normal atmosphere temperature, the phase of  $\beta$ - $Ca_2SiO_4$  in slag can change into  $\gamma$ - $Ca_2SiO_4$ , and the volume of slag can expand at 12% to make the slag powder. The selfdisintegrating process of slag can cancel the fragmentation process of raw materials and reduce costs[4-8].

The impurity in slag will affect the alumina leaching through forming other phase. MgO is the main impurity in calcium aluminate slag, which comes mainly from added lime during smelting reduction red mud in the blast furnace. Many correlation studies of the impacting of the impurity MgO on the calcium aluminate slag have been done by researchers in domestic and foreign.

Eremin [9] studied the effect of MgO on calcium aluminate slag and pointed out that the compound  $6\text{CaO} \cdot 4\text{Al}_2\text{O}_3 \cdot \text{MgO} \cdot \text{SiO}_2$ (C<sub>w</sub>A<sub>x</sub>M<sub>y</sub>S<sub>z</sub>) would be formed in the slag. Wang Bo[10-12] studied the mechanism of MgO effect and the effect of alteration of C/A on slags. The results showed that MgO will dissolve into the crystal lattice of  $Ca_{12}Al_{14}O_{33}$  and forms limited  $C_{20}A_{13}M_3S_3$  when the MgO content is less than 1.0%. 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.

The above research mainly focused on the effect of MgO on the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system. In fact, there are many other impurities in slag such as Na<sub>2</sub>O, TiO<sub>2</sub>, etc. The research report of the effect of MgO on slag under other impurity existence is few.

In this paper, the influences of the content of MgO and C/A (molar ratio of CaO and Al<sub>2</sub>O<sub>3</sub>, excluding CaO in 2CaO  $\cdot$  SiO<sub>2</sub>) and cooling system on alumina leaching properties of calcium aluminate slag containing Na<sub>2</sub>O and TiO<sub>2</sub> were investigated, and the measure of removing or reducing adverse effects of MgO on slag was proposed.

# **Experimental procedure**

The raw materials used in the experiment are CaO,  $Al_2O_3$ ,  $SiO_2$ ,  $Na_2CO_3$ ,  $TiO_2$  and MgO of analytical grade. The samples were prepared by grinding and mixing uniformly. The A/S ( $Al_2O_3/SiO_2$ , mass ratio) of the calcium aluminate slag was 0.8, the mass percent of Na<sub>2</sub>O and TiO<sub>2</sub> were 2.5% and 3.5%, respectively.

The samples placed in graphite crucible were smelted in high-temperature molybdenum disilicide resistance furnace. Melting temperature was 1500 °C, holding time was one hour, and then cool the slag to a certain temperature at the cooling rate of  $4\sim5^{\circ}C$  • min<sup>-1</sup> in the furnace, then put the slag out of furnace to cool in air.

Slag leaching: Prepare the adjustment fluid with NaOH, Na<sub>2</sub>CO<sub>3</sub> of AR and Al (OH)<sub>3</sub> of industrial grade. The concentrations of the adjustment fluid are: Na<sub>2</sub>O<sub>K</sub> 7g • L<sup>-1</sup>, Al<sub>2</sub>O<sub>3</sub> 7g • L<sup>-1</sup>, Na<sub>2</sub>O<sub>C</sub> 120g • L<sup>-1</sup>. Accurately measure 100ml adjusting liquid for the conical flask, and preheat it to 75 °C in constant temperature water bath box with the magnetic stirring, and then put 25g of slag into the adjusting liquid to leach with constant agitation rate. Leaching time was 120 minutes, then filter and analyze content of Al<sub>2</sub>O<sub>3</sub> in filter slag by chemical analysis method, and calculate the Al<sub>2</sub>O<sub>3</sub> leaching rate of slag.

The phase of slag was investigated using X-ray diffraction (Philips PW 3071 diffractometer with Cu K $\alpha$  radiation), the particle size distribution of slag using LS800 laser particle size analyzer. Use particle size distribution to analyze self-disintegrating properties (proportion of particles diameter less than 74 $\mu$ m).

## **Results and discussions**

# Effect of content of MgO on calcium aluminate slag

The phase compositions of slags with mass percent of MgO from 0% to 5% were analyzed, and the results are shown in figure 1. The results of particle size analyzed and alumina leaching experiment are shown in Figure 2.

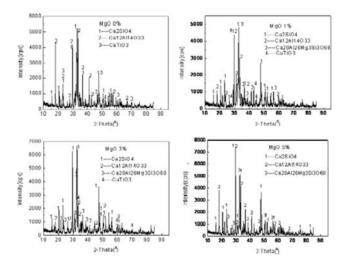


Fig.1 phase compositions of slags with different content of MgO(C/A=1.71, the temperature of taken slag out of furnace is  $1200^{\circ}$ C)

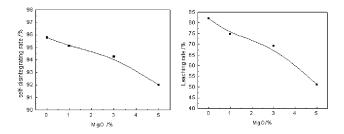


Fig.2 self-disintegrating rate and alumina leaching rate of slags with different content of MgO (C/A=1.71, the temperature of taking slag out of furnace is  $1200^{\circ}$ C)

It can be seen from Figure 2 that the self-disintegrating and alumina leaching rate of slag are decreased with the increase of mass percent of MgO. The self-disintegrating rate is gradually decreased from 95.7% to 91.9% with MgO from 0% to 5%. The alumina leaching rate is significant decreased from 82.1% to 51.3% with MgO from 0% to 5%.

Fig.1 shows that when the mass fraction of MgO is 0%, the main phases attained are  $Ca_{12}Al_{14}O_{33}$  and  $\gamma$ - $Ca_2SiO_4$ . With existence of MgO, the new phase of  $Ca_{20}Al_{26}Mg_3Si_3O_{68}$  is formed, and the content of  $C_{20}A_{26}M_3S_3O_{68}$  would increase with the increase of MgO content. The phase of  $Ca_{20}Al_{26}Mg_3Si_3O_{68}$  formed can consume a certain amount of SiO<sub>2</sub> and  $Al_2O_3$  to lead to decrease the content of  $Ca_2SiO_4$  and  $Ca_{12}Al_{14}O_{33}$  formed. The self-disintegrating rate of slag can be decreased with the content of

 $Ca_2SiO_4$  decreased. Because the alumina leachability of  $Ca_{20}Al_{26}Mg_3Si_3O_{68}$  is worse than that of  $Ca_{12}Al_{14}O_{33}$ , therefore, the alumina leaching rate decreased with the decrease of  $Ca_{12}Al_{14}O_{33}$  content and increase of  $Ca_{20}Al_{26}Mg_3Si_3O_{68}$  content.

# Effect of C/A on calcium aluminate slag containing MgO

The previous research[13] showed the adverse effect of MgO can be removed by increasing CaO content. So the method of changing the C/A (CaO/Al<sub>2</sub>O<sub>3</sub>, molar ratio, excluding CaO in 2CaO  $\cdot$  SiO<sub>2</sub>) of the calcium aluminate slag was studied.

The phase compositions of slags with the C/A from 1.71 to 1.9 were analyzed, and the results are shown in figure 3. The results of particle size analyzed and alumina leaching experiment are shown in Figure 4.

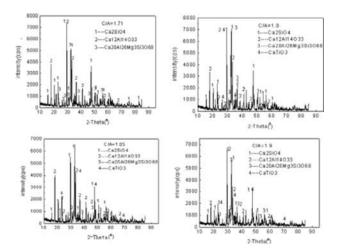


Fig.3 phase compositions of slags with different C/A (the content of MgO is 5%, the temperature of taking slag out of furnace is  $1200^{\circ}$ C)

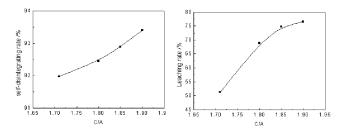


Fig.4 self-disintegrating rate and alumina leaching rate of slags with different C/A (the content of MgO is 5%, the temperature of taking slag out of furnace is  $1200^{\circ}$ C)

Fig.3 shows that there are not significant changes for the phases of slag with different C/A. The main phases of slag are Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>,  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub> and Ca<sub>20</sub>Al<sub>26</sub>Mg<sub>3</sub>Si<sub>3</sub>O<sub>68</sub>. It can be seen from Figure 4 that the self-disintegrating and alumina leaching rate of slag are increased with the increase of the C/A. The self-disintegrating rate is slightly increased from 91.9% to 93.4% with the C/A from 1.71 to 1.9. The alumina leaching rate is significant increased from 51.3% to 76.5% with the C/A from 1.71 to 1.9. When C/A is 1.85,

the alumina leaching rate is 74.7%. With C/A 1.9, the alumina leaching rate increase slightly. The reason of the alumina leaching rate increased is the extra-addition of CaO can probable decompose the quaternary compound  $Ca_{20}Al_{26}Mg_3Si_3O_{68}$  to make the content of  $Ca_{12}Al_{14}O_{33}$  increasing. The probable reaction between  $Ca_{20}Al_{26}Mg_3Si_3O_{68}$  and CaO is shown below:

$$7(20CaO \cdot 13Al_2O_3 \cdot 3MgO \cdot 3SiO_2)+58CaO \rightarrow$$
  
13(12CaO \cdot 7Al\_2O\_3)+21(2CaO \cdot SiO\_2)+21MgO

# Effect of the cooling system on calcium aluminate slag containing MgO

In spite of the alumina leaching rate increase to 74.7% when the C/A of slags is 1.85, but it is lower and not meet requirement of alumina leaching process. So the method of changing the cooling system of the calcium aluminate slag was studied.

The phase compositions of slags with the temperature of taking slag out of furnace from  $1200^{\circ}$ C to  $500^{\circ}$ C were analyzed, and the results are shown in figure 5. The results of particle size analyzed and alumina leaching experiment are shown in Figure 6.

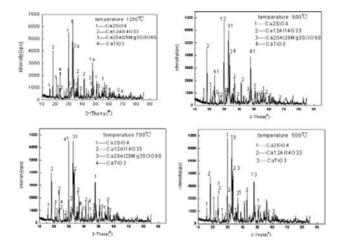


Fig.5 phase compositions of slags with different temperatures (the content of MgO is 5%, C/A=1.85)

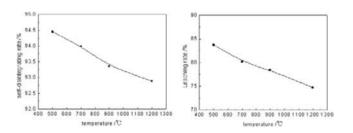


Fig.6 self-disintegrating rate and alumina leaching rate of slags with different temperatures (the content of MgO is 5%, C/A=1.85)

Fig.5 shows that the main phases of slag are  $Ca_{12}Al_{14}O_{33}$ ,  $\gamma$ - $Ca_2SiO_4$  and  $CaTiO_3$  when the temperature of taking gout of furnace is 500 °C. The phase of  $Ca_{20}Al_{26}Mg_3Si_3O_{68}$  is disappearance. The result indicated that decomposition reaction between  $Ca_{20}Al_{26}Mg_3Si_3O_{68}$  and CaO needs sufficient reaction

time on the condition of higher temperature.

Fig.6 shows that the self-disintegrating and alumina leaching rate of slag increase with the decrease of the temperature of taking slag out of furnace. The self-disintegrating rate is slightly increased from 92.9% to 94.4% with the temperature from  $1200^{\circ}$ C to 500°C. The alumina leaching rate is increased from 74.7% to 83.7% with the temperature from 1200°C to 500°C. The alumina leaching rate is only 74.7% when the temperature is 1200°C, the main reason is that the decomposition reaction time is too short to decompose completely the quaternary compound Ca<sub>20</sub>Al<sub>26</sub>Mg<sub>3</sub>Si<sub>3</sub>O<sub>68</sub>. Therefore, the decrease of the temperature of taking out of furnace can effectively improve or remove the adverse effect of MgO on calcium aluminate slag.

#### Conclusions

MgO can decrease the self-disintegrating and the alumina leaching properties of calcium aluminate slag due to the new phase of  $Ca_{20}Al_{26}Mg_3Si_3O_{68}$  formed. The increase of the C/A of calcium aluminate slag and the decrease of the temperature of taking out of furnace can improve or remove the adverse effect of MgO on calcium aluminate slag.

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#### References

- Li Chaoxiang. The success of semi-industrial test that recycling of iron from Pingguo red mud [J]. Mining and Metallurgical Engineering, 20(2000):58~61
- Jiang Yi-jiao, Ning Ping. Comprehensive Utilization of Red Mud in Alumina Plant [J].Environmental Science & Technology, 1(2003):15~17
- Zhang Jingdong, Li Yinta, Bi Shiwen. Comprehensive utilization of high-iron bauxite of Guigang in Guangxi province [J].Light Metal, 8(1992):16-18
- Bi Shiwen, Yang Yihong, Li Yitai. Extraction of aluminum from Calcium aluminate slag of the blast furnace [J].Light Metal, 6(1992):10~15
- Tong Zhifang.Study of Comprehensive utilization of high-iron bauxite of Guigang in Guangxi province [D].Northeastern University, 2005:3~6
- Grzymek J. Derdacka A. Konik Z. Method for obtaining aluminum oxide [P]. U.S. Patent: 4149898, 1978.
- Barr L K. Alumina production from andalusite by the Pedersen process [M].Stockholm: Almqlist & Wiksell International. 1977:64-70
- Nielsen K. The Pedersen processian old process in new light [J]. Erzmetall, 31(1978):523~525
- 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, 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.

- 11.WANG Bo, YU Hai-yan, MIAO Yu, SUN Hui-lan, BI Shiwen and TU Gan-feng, "Effect of MgO on leaching and selfdisintegrating property of calcium aluminate slag," Light Metals, (4)(2008), 11-13.
- WANG Bo, YU Hai-yan, SUN Hui-lan, BI Shi-wen, TU Ganfeng and GENG Hong-juan. "Effect of MgO on crystal and leaching property of 12CaO·7Al2O3," Minning and Metallurgical Engineering, 28(05)(2008), 68-71.
- 13 Grymek J. Influence of the structure of calcium aluminate on the process of manufacturing of metallurgical Al203 from nonbauxitic altaninosilicate raw materials[J]. Scientific Bulletins of Lodz Technical University, 19(1986): 48~57