

The effect of cooling rate on the leachability of calcium aluminate slags

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Abstract

A calcium aluminate slag was synthesized by melting a CaCO₃, SiO₂ and Al₂O₃ mixture at 1500°C for 1h. The effect of cooling rate on alumina leaching and self-disintegration of the calcium aluminate slag were studied. The mechanism was examined using the methods XRD, SEM, and laser particle size analysis. The results indicated that the phase components, alumina leaching property and self-disintegrating property of the calcium aluminate slag were better when cooling rate was lower than 20°C·min⁻¹. The formation of 2CaO·Al₂O₃·SiO₂ and 3CaO·Al₂O₃ decreases alumina leaching rate and self-disintegrating rate when the cooling rate was higher than 20°C·min⁻¹. The conversion rate from β-2CaO·SiO₂ to γ-2CaO·SiO₂ was still high when cooling rate was between 20°C·min⁻¹ and 50°C·min⁻¹. Therefore, the main reason of the decrease in self-disintegrating rate was the formation of 2CaO·Al₂O₃·SiO₂.

Introduction

The cooling rate of calcium aluminate slags is one of the important parameters in the “sintering – blast furnace smelting – alumina leaching” process, which is used to utilize iron-bearing bauxite. During the process of blast furnace smelting, iron and a calcium aluminate slag are separated, and then the slag is subjected to a cooling and self-disintegrating procedure[1, 2].

Calcium aluminate slag is in a liquid state when the temperature is 1500°C. The slag completes the transformation from liquid phase to solid phase during the cooling process. There are many pathways as the melt of calcium aluminate slag cools down. The first is that the melt, which has no time to crystallize when the slag is quenched, exists in the form of a glass phase. The second is that the liquid has no time to react with the solid phase which is generated during cooling process, and then crystallizes independently. The third is equilibrium crystallization according to the phase diagram. Therefore, the cooling rate is the key to optimizing the alumina leaching properties and self-disintegration of the slag.

Calcium aluminate slag system is polysystem, so the components of solid, which is crystallized from the liquid phase, are different from that of liquid. If the cooling rate is very fast, it will affect the diffusion of liquid phase and then change the solid composition and crystallization path. And besides, it is important that there is a peritectic reaction between gehlenite and liquid phase, and this reaction is very slow. If the cooling rate is fast, the liquid has no time to react with gehlenite, it will form a new solid/liquid mixture and the effect will be different than if gehlenite had formed. That is, the new liquid system will deviate from the best operating region, and does not crystallize the phase which is optimal for leaching.

The cooling rate will not only affect the components and structure of the slag, but also affect the self-disintegration rate of the slag[3]. If the cooling rate is fast, the glass phase will be formed in the between the crystal grains. The glass phase first will prevent the crystal transformation of 2CaO·SiO₂ (from β to γ), and second will cover the surface of 2CaO·7Al₂O₃. Therefore, the alumina leaching rate of the slag decreases. Besides, a slag which does not self-disintegrate is hard to crush and grind, and this process will also consume a lot of energy.

With regard to the optimal cooling rate of calcium aluminate slags Eremin [4] considered that the proper value was 5°C·min⁻¹ ~ 6°C·min⁻¹. But Zhang Jing-dong suggested that if the cooling rate of slag was slower than 10°C·min⁻¹ when the initial temperature of the slag was between 1400°C and 1250°C, the alumina leaching rate would be higher.

Therefore, studies of the effect of cooling rate of calcium aluminate slags have been carried out by previous researchers, based on actual slags, and the results have been useful [5-7]. However, the optimal cooling system was not determined, and the effective mechanism was unclear according to these studies. Therefore, in order to confirm the phase transformation law and the effect of cooling rate on calcium aluminate slags, a study of cooling rate through XRD, SEM and particle size analysis has been carried out and is reported in this paper. In order to exclude the effect of impurities and other factors, the materials which were used to synthesis the slags were analytically pure.

Experimental

2.1. Materials and apparatus

Calcium aluminate slag was synthesized by mixing reagents Al₂O₃, SiO₂ and CaCO₃. The A/S (the weight ration of Al₂O₃ to SiO₂) of slag was 1.3, and the C/A (CaO/Al₂O₃, molar ratio, except CaO of 2CaO·SiO₂) of slag was 1.7. The components of materials were shown in Table 1.

Table1 Components of materials

Components	CaO	Al ₂ O ₃	SiO ₂
W%	57.25	24.16	18.59

2.2 Smelting of calcium aluminate slag

The samples with different cooling rates were smelted in a vacuum furnace, and the container was a graphite crucible. A Vacuum furnace was used in the experiments largely due to its thin insulating layer, and thus low thermal mass. It could thus realize rapid heating and cooling.

The smelting temperature was 1500°C and the holding time was one hour. The sample was taken out of the vacuum furnace at

400°C. Cooling rates of the calcium aluminate slag between $2^{\circ}\text{C}\cdot\text{min}^{-1}$ and $40^{\circ}\text{C}\cdot\text{min}^{-1}$ were studied in this paper.

2.3 Leaching of calcium aluminate slag

The sodium aluminate solution obtained from slag leaching should then be treated by a carbonization precipitation process, and the circulating mother liquor used to leach new calcium aluminate slag. Therefore, the feasible conditions for alumina digestion were: leaching temperature was 75°C , leaching time was 2h, L/S ratio was 4.5(by weight), caustic alkali concentration was 7g/L and sodium carbonate concentration was 120g/L . The leaching experiments were carried out in a magnetically stirred, constant temperature water bath. After leaching and dry filtration, the filtrate was used to analyze the composition of the solution, and the filter residue was washed and dried to preserve for analysis.

2.4 Analysis

The contents of Al_2O_3 and SiO_2 of samples and filtrate were analyzed by a chemical method. The Phase components of calcium aluminate slag were identified by X-ray diffraction analysis (PANalytical PW3040/60). A Malvern laser particle analyzer was used to analyze the particle size of the slag.

Results and discussion

3.1 Phase transformation law of slag with different cooling rate

In order to study the phase transformation law of calcium aluminate slags with different cooling rates, XRD analysis was used in the experiments. The results are shown in Fig. 1 to Fig. 4.

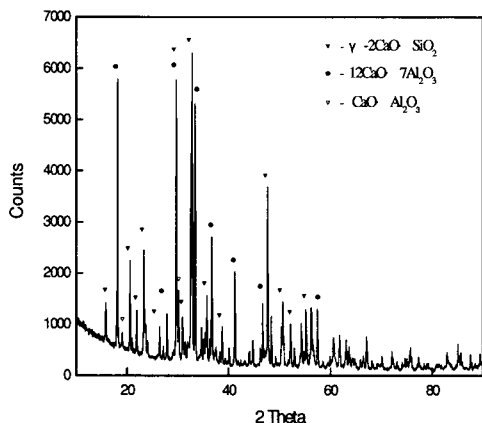


Fig.1 XRD spectra of slag with cooling rate= $2^{\circ}\text{C}\cdot\text{min}^{-1}$

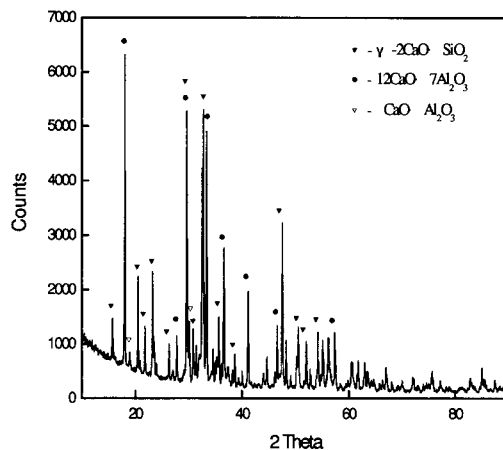


Fig. 2 XRD spectra of slag with cooling rate= $10^{\circ}\text{C}\cdot\text{min}^{-1}$

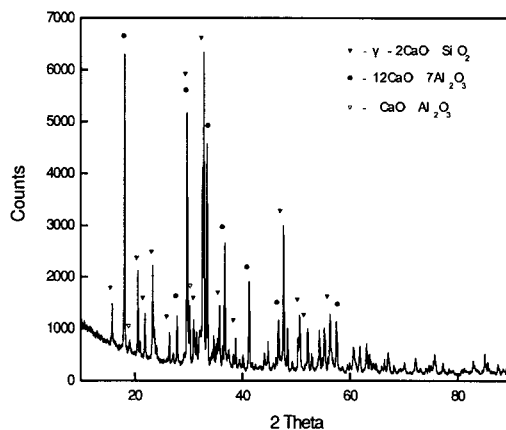


Fig. 3 XRD spectra of slag with cooling rate= $20^{\circ}\text{C}\cdot\text{min}^{-1}$

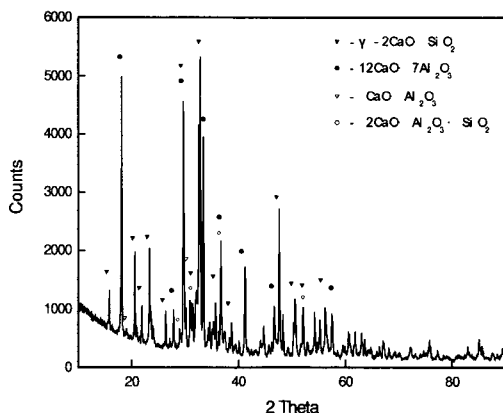


Fig. 4 XRD spectra of slag with cooling rate= $>40^{\circ}\text{C}\cdot\text{min}^{-1}$

Fig.1 shows that when the cooling rate was $2^{\circ}\text{C}\cdot\text{min}^{-1}$, the calcium aluminate slag had a proper phase component. The main phases were $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (alumina is easy to be leached out) and γ -

$2\text{CaO}\cdot\text{SiO}_2$ (slag could self-disintegrate because of its phase transformation). Little $\text{CaO}\cdot\text{Al}_2\text{O}_3$ (the alumina leachability is lower than $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$) was formed in the slag. When the cooling rate increased to $10^\circ\text{C}\cdot\text{min}^{-1}$ and $20^\circ\text{C}\cdot\text{min}^{-1}$ the phase components of slag were similar to the slag whose cooling rate was $2^\circ\text{C}\cdot\text{min}^{-1}$ (Fig.2 and Fig.3). $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ which was difficult to leach was not found under the three conditions. But $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ could be found in slag when cooling rate was above $40^\circ\text{C}\cdot\text{min}^{-1}$ (Fig.4). $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$ (2.78 , 2.61 , 2.19Å) was not found in slag either when cooling rate was not above $20^\circ\text{C}\cdot\text{min}^{-1}$. It could be found when cooling rate was above $40^\circ\text{C}\cdot\text{min}^{-1}$, but its amount was limited. Therefore, its characteristic peaks were very low and were not marked in Fig.4.

According to the former results when the cooling rate was under $20^\circ\text{C}\cdot\text{min}^{-1}$ the calcium aluminate slag would have an ideal phase composition. If the cooling rate was accelerated continuously, $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ would appear and effect the phase of slag. Trace quantities of $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$ was formed when cooling rate was over $40^\circ\text{C}\cdot\text{min}^{-1}$. And this indicated that $2\text{CaO}\cdot\text{SiO}_2$ had a rapid crystal transformation speed, so cooling rate had a little effect on crystal transformation of $2\text{CaO}\cdot\text{SiO}_2$ under the conditions studied in this paper. These results accorded with Zhang Xiong [8], who deemed that $2\text{CaO}\cdot\text{SiO}_2$ had a higher crystal transformation ratio when cooling rate was between $2^\circ\text{C}\cdot\text{min}^{-1}$ and $500^\circ\text{C}\cdot\text{min}^{-1}$. He further noted that the transformation rates of $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$ were 100%, 95% and 90% when the conditions were slow cooling (about $2^\circ\text{C}\cdot\text{min}^{-1}$), natural cooling (about $60^\circ\text{C}\cdot\text{min}^{-1}$) and wind cooling (about $500^\circ\text{C}\cdot\text{min}^{-1}$).

In addition, when the cooling rate of calcium aluminate slag was over $10^\circ\text{C}\cdot\text{min}^{-1}$ trace amount of particles (particle size bigger than 1mm) which didn't self-disintegrate completely appeared. XRD analysis was carried out on these grinded particles, and the result is shown in Fig.5.

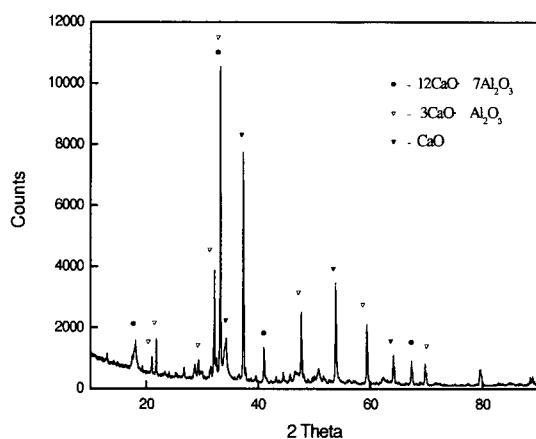


Fig.5 XRD spectra of particles without self-disintegrating

Fig.5 shows that the major phase of particles which didn't self-disintegrate was $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, and the minor phases were f-CaO and $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$.

Therefore, a certain amount of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ would appear when the cooling rate was very rapid. This would affect the alumina leaching property and self-disintegrating property of calcium aluminate slag.

3.2 Effect of cooling rate on self-disintegrating property of slag

The self-disintegration of calcium aluminate slag can reduce the energy consumption during production, and it 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.

The slag with different cooling rate was well-mixed in order to analyze the granularity of slag. The particle size results analyzed by Malvern 2000 are shown in Fig.6.

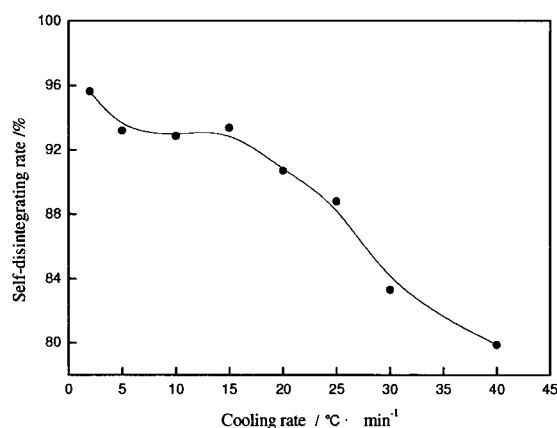


Fig.6 Self-disintegrating rate of slag with different cooling rate

Fig.6 indicates that the self-disintegrating rate of slag decreased with acceleration of cooling rate. However, the self-disintegrating rate of slag was still higher than 90% when cooling rate was not higher than $20^\circ\text{C}\cdot\text{min}^{-1}$, this suggested that under this condition the effect of cooling rate on pulverization was little. The results could be verified by XRD (Fig.1 to Fig.3). $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$ and $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ were not found in slag, so the crystal transformation of $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$ was complete and the particle size was relative stability.

If cooling rate increased continually, the self-disintegrating property of slag decreased obviously. When cooling rate was $40^\circ\text{C}\cdot\text{min}^{-1}$ the self-disintegrating rate was only about 80%. There were two points for the decrease according to XRD analysis. The first was the formation of $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ (Fig.4) which decreased the content of $2\text{CaO}\cdot\text{SiO}_2$ of slag, thus the self-disintegrating rate decreased. The second was the existence of the trace of $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$ which decreased the crystal transformation rate of $2\text{CaO}\cdot\text{SiO}_2$.

Further, according to report [8] the crystal transformation rate was still higher than 95% even under natural cooling condition (about $60^\circ\text{C}\cdot\text{min}^{-1}$). So the effect of the existence of $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$ on pulverization of slag was little.

Therefore, the major reason of the decrease of self-disintegrating rate was the formation of $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$; the minor reason was the existence of $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$.

4.3.4 Effect of cooling rate on alumina leaching property of slag

The alumina leaching experiment of slag was carried out in order to study the effect of cooling rate on the alumina leaching properties. The leaching conditions and process were as in section 2.3, and the results are shown in Fig.7.

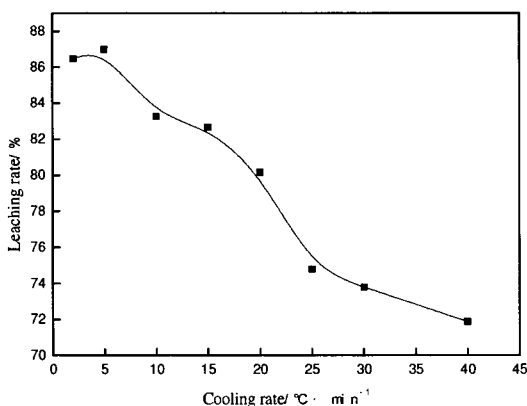


Fig.7 Leaching property of slag with different cooling rate

The alumina leaching rate of slag showed a decreasing tendency with the increase of cooling rate (Fig.7). When the cooling rate was in slow cooling stage ($\leq 5^\circ\text{C}\cdot\text{min}^{-1}$) the slag had a better phase components and particle size, so the alumina leaching rate was higher ($>85\%$).

When the cooling rate was in medium cooling stage ($5^\circ\text{C}\cdot\text{min}^{-1} \sim 20^\circ\text{C}\cdot\text{min}^{-1}$) the alumina leaching rate decreased but was still above 80%. That was because the main phases were still $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ and $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$. The decrease of leaching rate was because of the particles which didn't self-disintegrate. The formation of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and the existence of f-CaO which didn't react with Al_2O_3 or SiO_2 in these particles decreased the content of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$.

When cooling rate was in fast cooling stage ($20^\circ\text{C}\cdot\text{min}^{-1} \sim 50^\circ\text{C}\cdot\text{min}^{-1}$) the alumina leaching rate decreased obviously. The main reason was the formation of $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ and $3\text{CaO}\cdot\text{Al}_2\text{O}_3$; the minor reason was the decrease of the self-disintegrating rate. The two reasons interacted with each other, and decreased the alumina leaching property obviously under this condition.

Conclusions

(1) The phase component, self-disintegrating property and alumina leaching property of calcium aluminate slag was good when cooling rate was slower than $20^\circ\text{C}\cdot\text{min}^{-1}$. $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$

and $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ which were difficult to leach would be formed if the cooling rate increased continually. And because of that the self-disintegrating property and alumina leaching property of slag would decrease obviously.

(2) The crystal transformation rate was still high when cooling rate was between $20^\circ\text{C}\cdot\text{min}^{-1}$ and $50^\circ\text{C}\cdot\text{min}^{-1}$. Therefore, the main reason of the decrease of self-disintegrating rate was the formation of $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$.

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