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INFLUENCE OF TITANIA ON PHASE COMPOSITION AND SELF-POWDER AND ALUMINA LEACHING PROPERTIES OF CALCIUM ALUMINATE SLAG

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Abstract

The influence of TiO_2 on the phase composition, self-powder and alumina leaching properties of calcium aluminate slag was investigated by XRD, laser particle size analyzer and chemistry analysis methods, and the measure of eliminating the adverse impacts of TiO_2 on calcium aluminate slag was proposed. The results show that when the mass percent of TiO_2 is 2% or less than 2%, the main phases of slag are $Ca_{12}Al_{14}O_{33}$ and γ-Ca_2SiO_4, the self-powder rate of slag is above 95%, the alumina leaching rate is above 85%. The alumina leaching rate is gradually decreased when the TiO_2 content is above 2%, the leaching rate is 80.1% with 3% of TiO_2, and the leaching rate is only 73.4% with 5% of TiO_2. To add CaO into containing 5% TiO_2 of slag, the alumina leaching rate is 84.1% when the mole ratio of CaO added to TiO_2 is 1.25, the adverse effects of TiO_2 on the slag is basically eliminated, the calcium aluminate slag meets alumina leaching requirements.

Introduction

The main phases of calcium aluminate slag are γ-Ca_2SiO_4 and $Ca_{12}Al_{14}O_{33}$. Because the volume of slag can expand at 12% to make the slag powder when β-Ca_2SiO_4 changes into γ-Ca_2SiO_4 during the cooling process, so it is called self-powder slag. The $Ca_{12}Al_{14}O_{33}$ and $CaAl_2O_4$ in calcium aluminate slag can dissolve in sodium carbonate solution to produce sodium aluminate solution and calcium carbonate, and then alumina is extracted from the sodium aluminate solution. Simultaneously, because of slag self-powder, it has advantages that it can cancel the fragmentation process of raw materials and reduce costs. So since the 1970s, many scholars have studied to deal with the low-grade or refractory bauxite and secondary resources of containing aluminum by sintering or smelting reduction methods to obtain the calcium aluminate slag, and the alumina is extracted from the slag[1~5].

The phase composition can effect the self-powder and alumina leaching properties of slag, while the material ratio of calcium aluminate slag is also an important factor of impacting on the phase composition. Many correlation studies of the impacting of the material ratio on the calcium aluminate slag have been done by researchers in domestic and foreign[6~12]. Barr researched the andalusite ore and believed that the best mole ratio of CaO to Al_2O_3(for short C/A) was from 1.3 to 1.66. Nielsen thought that the mass ratio of Al_2O_3 to SiO_2(for short A/S) of raw materials should not be less than 5.5, otherwise it would reduce the leaching rate of Al_2O_3. Jingdong Zhang et al pointed out that the A/S of raw material had little impact on the leaching rate of Al_2O_3. Zhifang Tong synthesized the calcium aluminate slag with mixing CaO, SiO_2 and Al_2O_3 at the different ratios, and the results showed that the slag had better self-powder and leaching properties when C/A was range from 1.6 to 1.8, and A/S was range from 0.5 to 1.5. Although the above research on calcium aluminate slag were more, but the studies mainly focused on the CaO-Al_2O_3-SiO_2 system. The research report of the effect of the other components on calcium aluminate slag is few. There are many other element in actual slag, so each other effect of other composition will impact the phase composition of calcium aluminate slag.

The comprehensive utilization of high iron-containing red mud in Pingguo plant could be realized 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 leaching residue.

Pingguo red mud contains a certain proportion of TiO_2[13~14], which can enter into slag in smelting reduction process, and effects on phase composition, self-powder and alumina leaching properties of calcium aluminate slag, at present, the research reports about this field is lack. In this paper, the influence of TiO_2 on phase composition, self-powder and alumina leaching performances of calcium aluminate slag was investigated, and the measure of eliminating adverse effects of TiO_2 on slag was proposed, and to provide the corresponding theoretical basis for comprehensive utilization of high iron-containing red mud.

Experimental procedure

The raw materials are CaO, Al_2O_3, SiO_2 and TiO_2 of analytical grade. The experimental slags were prepared by grinding and mixing uniformly according to a certain condition that the mole ratio of CaO to SiO_2(for short $n(CaO)_1/n(SiO_2)$) is 2, A/S is 0.8, thr mole ratio of CaO to Al_2O_3(for short $n(CaO)_2/n(Al_2O_3)$) is 1.71, the mass fraction of TiO_2 is 1%、2%、3%、4%、5%、6%, respectively. The slag was placed in graphite crucible, and placed in high-temperature molybdenum disilicide resistance furnace to melt. Melting temperature is 1500℃, holding time is one hour, and then cool the slag to 1200℃ at the cooling rate of 4~5℃• min^{-1} in the furnace, then put the slag out of furnace to cool in air, and to test the slag.

Slag leaching: Prepare the adjustment fluid with NaOH, Na_2CO_3 of AR and $Al(OH)_3$ of industrial grade, in which the concentration of Na_2O_K is 7g • L^{-1}, Al_2O_3 is 7g • L^{-1}, Na_2O_C is 110g • L^{-1}. Accurately measure 150 ml adjusting liquid for the conical flask, and preheat it to 75℃ in constant temperature water bath box with the magnetic stirring, and then put the 10g of slag into the conical flask to leach with constant agitation rate. Leaching time is 100 minutes, then to filter and analyze content of

Al_2O_3 in filter slag by chemical analysis method, and calculate the Al_2O_3 leaching rate of slag.

The phase of slag was investigated using X-ray diffraction (Philips PW 3071 diffractometer with Cu Kα radiation), the particle size distribution of slag using LS800 laser particle size analyzer. Through particle size distribution to analyze self-powder property (proportion of particles diameter less than 74μm)

Results and discussions

Effect of TiO_2 on phase in CaO-Al_2O_3-SiO_2 system slag

The phase composition of slag with the mass percent of TiO_2 from 1% to 6% was analyzed by an X-ray diffraction, and the results are shown in figure 1.

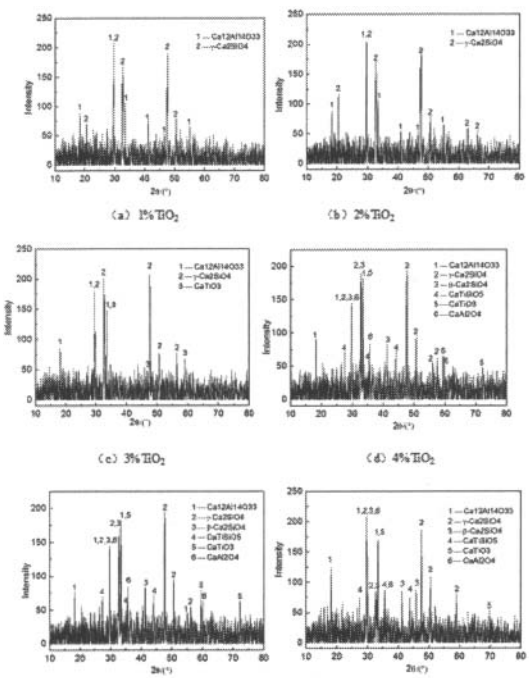
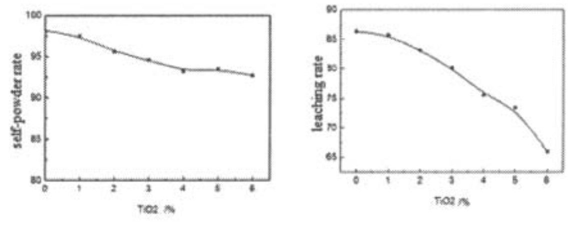


Fig.1 Effect of TiO_2 on phase composition of CaO-Al_2O_3-SiO_2 system

The figure 1 shows that when the mass fraction of TiO_2 is 1% and 2%, the main phases attained are $Ca_{12}Al_{14}O_{33}$ and γ-Ca_2SiO_4, and the phase containing titanium is not found. When TiO_2 increase to 3%, the main phases formed are $Ca_{12}Al_{14}O_{33}$, γ-Ca_2SiO_4 and a small amount of $CaTiO_3$. When TiO_2 is 4%, the phases are $Ca_{12}Al_{14}O_{33}$, γ-Ca_2SiO_4, β-Ca_2SiO_4, $CaTiO_3$, $CaTiSiO_5$ and $CaAl_2O_4$. Increase TiO_2 to 5% and 6%, the phase composition have not changed.

Effect of TiO_2 on self-powder and alumina leaching properties of CaO-Al_2O_3-SiO_2 system slag

The particle size distribution of synthetic slag with the mass perent of TiO_2 from 0% to 6% were analyzed, then through particle size distribution to analyze slag self-powder rate, and through alumina leaching experiment to study effect of TiO_2 on alumina leaching property of slag, the results are shown in Figure 2.



(a) self-powder rate (b) alumina leaching rate

Fig.2 Effect of TiO_2 on self-powder rate and alumina leaching rate of slag

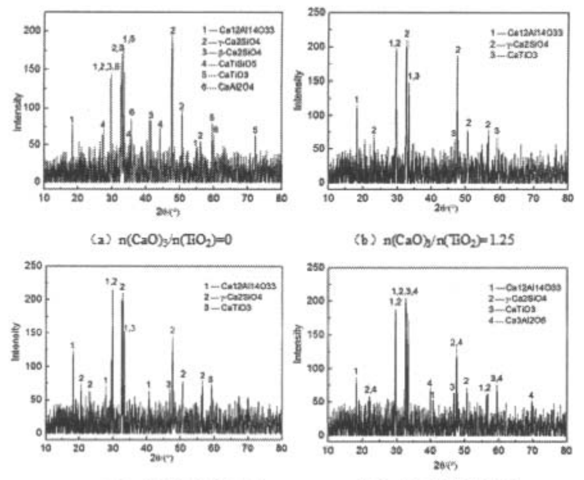
It can be seen from Figure 2 that the self-powder and alumina leaching rate of slag are gradually lowered with the mass percent of TiO_2 increase. The self-powder rate is gradually lowered from 98.1% to 92.7% with TiO_2 from 0% to 6%. When TiO_2 is 1% and less than 1%, the leaching rate is more than 85%. When TiO_2 is greater than 2%, the leaching rate is significant decreased with TiO_2 increasing, the leaching rate was 80.1% when TiO_2 is 3%, the leaching rate was only 66% when TiO_2 is 6%.

Combine figure 2 with the phase analysis in Figure 1 to discuss the change rules of the self-power and leaching rate of slag. When the content of TiO_2 is above 4%, TiO_2 could enter into β-Ca_2SiO_4 lattice and form a certain amount of solid solution phase of $CaTiSiO_5$ in slag cooling process, which could prevent change of part of the β-Ca_2SiO_4 to γ-Ca_2SiO_4, and lead to slag self-powder rate decreased. When TiO_2 is less than 2%, the influence of TiO_2 on phase formation of slag is not significantly, the main phases formed are γ-Ca_2SiO_4 and $Ca_{12}Al_{14}O_{33}$ which is easily for alumina leaching, so the alumina leaching rate of slag is more higher. When TiO_2 is above 4%, because TiO_2 combine with CaO, and form $CaTiO_3$, and consume a certain amount of CaO, and lead to cause the content of CaO deficiency which can not be satisfied demand of combined with Al_2O_3 to form $Ca_{12}Al_{14}O_{33}$, so there is a certain amount of $CaAl_2O_4$ formed in slag. Because $Ca_{12}Al_{14}O_{33}$ is more easily to extract alumina than $CaAl_2O_4$, so alumina leaching rate of slag is decreased gradually with the increase of the TiO_2 content.

Effect of adding CaO for TiO_2 on CaO-Al_2O_3-SiO_2-TiO_2 system

Because TiO_2 can combine with CaO to form $CaTiO_3$, so that the prime ratio of $n(CaO)_2/n(Al_2O_3)$ changes and decreases, and lead to CaO deficiency and form a certain amount of $CaAl_2O_4$, and to decrease the alumina leaching rate. Therefore, through adding CaO for TiO_2 in slag, in order to change phase composition of slag, and to improve each property of slag.

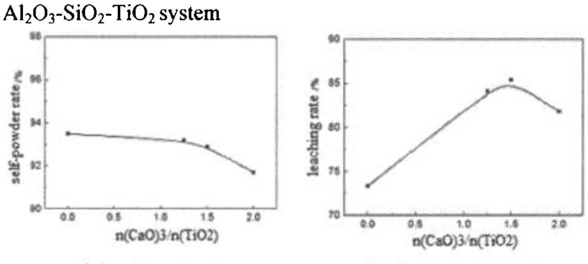
Under the conditions that $n(CaO)_1/n(SiO_2)$ is 2, $m(Al_2O_3)/m(SiO_2)$ is 0.8, $n(CaO)_2/n(Al_2O_3)$ is 1.71, the mass fraction of TiO_2 is 5%, add CaO for TiO_2 and make the mole ratio of CaO added to TiO_2 (for short $n(CaO)_3/n(TiO_2)$) be 0、1.25、1.5、2.0, respectively. Investigate the influence rules of different $n(CaO)_3/n(TiO_2)$ on phase composition, self-powder rate, alumina leaching rate of slag, the results of phase analysis are shown in figure 3, the results of self-powder and alumina leaching rate are shown in figure 4.



(a) $n(CaO)_3/n(TiO_2)=0$ (b) $n(CaO)_3/n(TiO_2)=1.25$

(c) $n(CaO)_3/n(TiO_2)=1.5$ (d) $n(CaO)_3/n(TiO_2)=2.0$

Fig.3 Effect of $n(CaO)_3/n(TiO_2)$ on phase composition of $CaO-Al_2O_3-SiO_2-TiO_2$ system



(a) self-powder rate (b) alumina leaching rate

Fig.4 Effect of $n(CaO)_3/n(TiO_2)$ on self-powder rate and alumina leaching rate of slag

As shown in Figure 3, With $n(CaO)_3/n(TiO_2)$ increasing, the phase of $CaAl_2O_4$ disappears. When $n(CaO)_3/n(TiO_2)$ is 1.25 and 1.5, respective, the main phase formed are $Ca_{12}Al_{14}O_{33}$ and γ-Ca_2SiO_4, in addition to a small amount of $CaTiO_3$. When $n(CaO)_3/n(TiO_2)$ increases to 2, there is a new phase of $Ca_3Al_2O_6$ formed.

Figure 4 shows that the self-powder rate of slag decrease with the increases of $n(CaO)_3/n(TiO_2)$. When $n(CaO)_3/n(TiO_2)$ is 2, the self-powder rate is lowest and 91.7%. Along with the $n(CaO)_3/n(TiO_2)$ increases, the leaching rate increase firstly and then decrease. The leaching rate is 84.1% when $n(CaO)_3/n(TiO_2)$ is 1.25, the leaching rate increase slightly and is 85.4% when $n(CaO)_3/n(TiO_2)$ is 1.5, continue to increase $n(CaO)_3/n(TiO_2)$ to 2, the leaching rate decrease to 81.8%.

Combine figure 4 with the phase analysis in Figure 3, it can be seen that with the content of CaO added increasing, the phase of $CaAl_2O_4$ disappear gradually, and the alumina leaching rate improve significantly from 73.4% of no adding CaO to 84.1% of 1.25 of $n(CaO)_3/n(TiO_2)$. It is reason that CaO added can make $n(CaO)_2/n(Al_2O_3)$ increase to promote phase of $Ca_{12}Al_{14}O_{33}$ formation, which has the better leaching properties, and significantly reduce the adverse effects of TiO_2 on slag. When $n(CaO)_3/n(TiO_2)$ is 2, the amounts of CaO added is excessive, the worst leaching performance of phase of $Ca_3Al_2O_6$ is formed, and lead to the leaching rate decline. Therefore, when $n(CaO)_3/n(TiO_2)$ is 1.25, the calcium aluminate slag basically meets alumina leaching requirement.

Conclusions

The influence of TiO_2 on phase composition, the self-powder and alumina leaching properties of calcium aluminate slag was ascertained. The measure to eliminate the adverse effects TiO_2 on slag was proposed.

In $CaO-Al_2O_3-SiO_2-TiO_2$ system, when the mass percent of TiO_2 is less than 2%, the main phase formed are $Ca_{12}Al_{14}O_{33}$ and γ-Ca_2SiO_4, the self-powder rate of slag is above 95%, the alumina leaching rate is greater than 85%. When the mass fraction of TiO_2 is greater than 2%, the leaching rate decreased obviously with the increase of TiO_2, the leaching rate is only 73.4% when the content of TiO_2 is 5%. For 5% of TiO_2 of slag, through adding CaO for TiO_2, the alumina leaching rate of slag is 84.1% when $n(CaO)_3/n(TiO_2)$ is 1.25, and the adverse effects of TiO_2 on slag are basically eliminated, and the calcium aluminate slag meets alumina leaching requirement.

Acknowledgements

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