Decomposition Property of γ-2CaO·SiO₂ during Leaching Process of Calcium Aluminate Slag

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Keywords: γ-CaO·SiO₂, decomposition property, alumina leaching, secondary reaction

Abstract

γ-2CaO·SiO₂ is one of the main phases of calcium aluminate slag, which is obtained under 1500°C. Although γ-2CaO·SiO₂ is more stable than β-2CaO·SiO₂, it will still be decomposed by sodium carbonate solution during alumina leaching process, and this will cause the occurrence of secondary reaction. The effect of liquid-solid ratio, caustic alkali, and temperature on decomposition property of γ-2CaO·SiO₂ are studied. The secondary reaction mechanism is discussed by XRD analysis. The results indicate that the amount of decomposed SiO₂ increase with the increase of caustic alkali concentration, which varies from $30g \cdot L^{-1}$ to $70g \cdot L^{-1}$. Leaching temperature affects the decomposition of γ-2CaO·SiO₂ and secondary reaction obviously. When temperature is above 75°C the influence degree of the latter is more serious than that of the former. XRD results indicate that the stable product of secondary reaction is hydrate garnet at lower temperature, but under higher temperature, hydrate garnet transforms into sodium hydrate alumina-silicate.

Introduction

With the great increase of alumina production the demand of bauxite increases every year in China[1]. The contradiction between the supply and the demand of the materials of bauxite in China is increasingly serious. Exploring and utilizing the low grade bauxite and non-bauxite with high alumina content is one of the methods to solve this problem. Grzymek[2, 3] put forward a method (lime sinter method) to extract alumina from iron-bearing bauxite. And this method could also treat other alumina-containing raw materials such as fly ash, alumina-contained slags and low grade bauxite [4-6]. The main phases of the sinter obtained by lime sinter process are 12CaO·7Al₂O₃ and γ-2CaO·SiO₂. The alumina of 12CaO·7Al₂O₃ is easy to be leached into sodium carbonate solution. This is different from lime-soda sinter process.

The main difference is the phase composition. 2CaO·SiO₂ of the lime-soda sinter process is in the form of γ type, but that of the lime sinter process is in the form of β type. β-2CaO·SiO₂ will be decomposed in sodium aluminate solution and causes the secondary reaction which will lead to the loss of alumina which has been leached out[7]. It has been reported that γ-2CaO·SiO₂ is inert in sodium aluminate solution, and it normally does not react with other phases[8, 9]. But in lime sinter process the leaching medium is sodium carbonate which has great effect on the decomposition of 2CaO·SiO₂. The stability of γ-2CaO·SiO₂ in sodium carbonate has not been reported. But our former research indicates that partial γ-2CaO·SiO₂ will be decomposed and cause secondary reaction in the solution with high sodium carbonate concentration[10, 11]. Therefore, in this paper, we studied the effects of liquid-solid ratio, caustic alkali, and leaching temperature on the decomposition of γ-2CaO·SiO₂ and discussed the secondary reaction mechanism.

1. Experimental

1.1 Materials

The adjusting fluid was prepared with the analytically pure sodium carbonate, sodium hydroxide, sodium aluminate and industrial aluminum hydroxide. Solid materials of γ-2CaO•SiO₂ and 12CaO•7Al₂O₃ were artificially synthesized and the X-ray diffraction spectra of them are shown in figure 1 and figure 2.
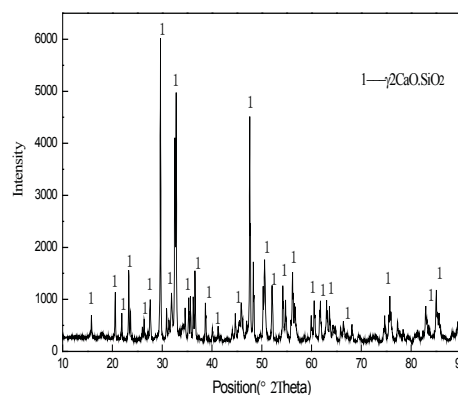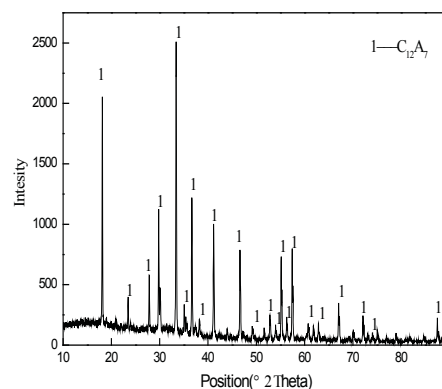

Figure 1. X-ray diffraction spectrum of γ-2CaO•SiO₂

Figure 2. X-ray diffraction spectrum of 12CaO•7Al₂O₃

1.2 Methods

The three-neck bottle was fixed in the constant temperature bath box. A condenser pipe was inserted into the one of three-neck; after adding the adjusting fluid and solid materials, another of three-neck was plugged with a rubber stopper; a mixing propeller

made from PTFE stirred the solution by the middle of three. And the experiment was carried out in the set conditions. Filtering the dissolution of slurry with funnel, the filter liquid was taken out. The decomposition amount of γ-2CaO•SiO$_2$ was the difference between silica concentration in the original adjusting liquid and silica concentration in the filter liquor, which was determined by silicon molybdenum blue colorimetric method.

2 Results and discussions

2.1 Effect of liquid-solid (L/S) on decomposition property of γ-2CaO•SiO$_2$

L/S (the ratio between the volume of solution and the mass of solid) is of importance in liquid-solid reaction. A certain concentration of alumina solution and a certain carbon alkali concentration of sodium aluminate solution are the decomposition fluid to decompose γ-2CaO•SiO$_2$ in the chapter. The composition of the dissolution liquid is close to the one obtained by digesting calcium aluminate slag from high iron bauxite. And the specific composition analysis is as follows: alumina concentration 50 g/L, carbon alkali concentrate 54.7g/L, caustic alkali concentrate 50g/L, molecular ratio 1.8, temperature 70°C and leaching time 1h. The results are shown in figure 3.
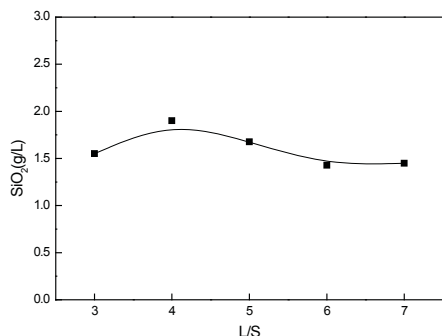

Figure 3. Effect of L/S on decomposition performance of γ-2CaO•SiO$_2$

When L/S range from 3 to 7, after decomposing the content of SiO$_2$ in solution first increases, then decreases, and finally stabilizes. This is because that the caustic alkali concentrate, the caustic alkali concentrate and caustic alkali concentrate are high and they all have an ability of decomposing γ-2CaO•SiO$_2$(Only the decomposition capacity differences between them). So SiO$_2$ is transferred from the solid phase into the liquid phase in the process of experiment. But because there is a certain concentration of alumina in the solution and when SiO$_2$ for dissolving to alumina is saturated, SiO$_2$ will react with alumina, which is called the secondary reaction. Sodium hydrate alumino-silicate or hdrogarnet is got and SiO$_2$ enters into the solid phase. Both of them are conducted in the process of decomposition. When the content of SiO$_2$ in solution is more than the one gained from the secondary reaction, the content of SiO$_2$ in solution will increase. Conversely the content of SiO$_2$ will decrease. However, when L/S is more than 5, the content of SiO$_2$ entering into the solution is less and SiO$_2$ don't reach to its solubility in the sodium aluminate solution. So most of the SiO$_2$ generated is dissolved in the sodium aluminate solution. But the content of it is slightly lower than the smaller liquid-solid.

2.2 Effect of caustic alkali concentration on decomposition performance of γ-2CaO•SiO$_2$

In the condition of liquid/solid 7, temperature 70°C, carbon alkali concentration 50g/L and molecular ratio 1.8, the effect of caustic alkali concentration on decomposition performance of γ-2CaO•SiO$_2$ is investigated. Every caustic alkali concentrations were experienced 60min in the decomposition process and the results are shown in figure 4. The figure 4 shows that when the concentration of caustic alkali changes between 30 ~ 70 g/L, the SiO$_2$ content of solution increases gradually. This suggests that NaOH has a certain decomposition capacity of γ-2CaO•SiO$_2$. And Reaction equation is that:

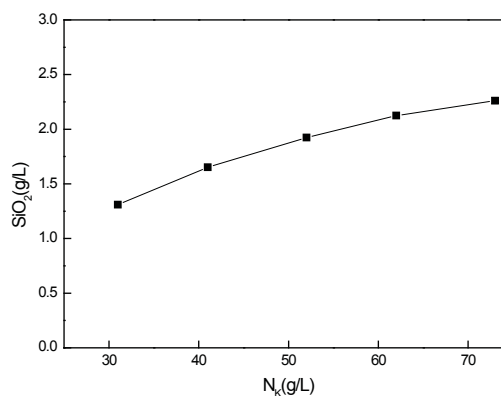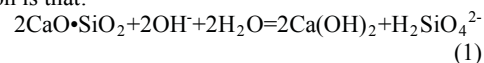$$2CaO•SiO_2+2OH^-+2H_2O=2Ca(OH)_2+H_2SiO_4^{2-} \quad (1)$$

Figure 4. Effect of caustic alkali concentration on the stability of γ-2CaO•SiO$_2$

2.3 Effect of leaching temperature on decomposition performance of γ-2CaO•SiO$_2$

According to the reports in the literature, temperature has a great effect on the secondary reaction in sintering clinker (2CaO•SiO$_2$ is β-type)[12]. β-2CaO•SiO$_2$ and γ-2CaO•SiO$_2$ are both silicate and the molecular formula of them are the same. But the crystal types of them are different. So the effect of temperature on γ-2CaO•SiO$_2$ cannot be ignored.

Decomposition rule of γ-2CaO•SiO$_2$ and the extent of secondary reaction at different temperatures are researched in detail in the section. The mixture of γ-2CaO•SiO$_2$ and 12CaO•7Al$_2$O$_3$ is leached as the solid material in the experiment. And the conditions of the experiment are: carbon alkali 120g•L^{-1}, caustic alkali 7g•L^{-1}, molecular ratio 1.6, leaching time 2h. The change of the SiO$_2$ content in the leaching liquid of mixed material and the leaching rate of alumina are shown in figure 5, when the leaching temperature range is 55~ 90°C.
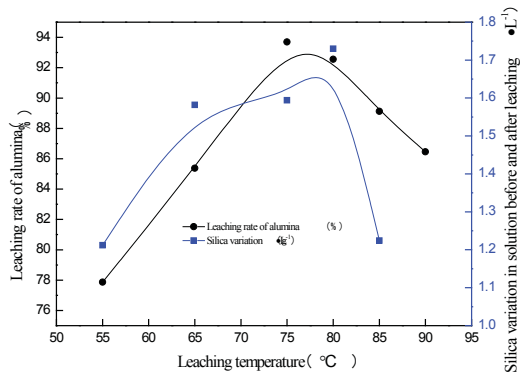
Figure 5. Effect of leaching temperature on the leaching rate of alumina and the stability of γ-2CaO•SiO₂

Figure 5 shows the following two points. Firstly, with the improvement of leaching temperature the content of silica in leaching liquid increases firstly and then decreases. And the temperature of inflection point is 80°C. It is reported that the increase of reaction temperature will increase the solubility of silica in the equilibrium solution. When the temperature is higher than 80°C, silica content drops. This illustrates that the silica in the solution transfers into the slag phase. Generally, silica in the slag phase exists in the form of hydrogarnet or sodium hydrate alumina-silicate. But both of the two phases will result in the loss of alumina.

Secondly, the leaching of alumina presents "V" rule with the increase of temperature. When the temperature is 75°C, the leaching rate of alumina reaches the extreme value (93.69%). When leaching temperature is higher than 75°C, the alumina leaching rate falls fast. And it can be explained by chemical reaction thermodynamics and secondary reaction: The reaction of leaching of $12CaO•7Al_2O_3$ is endothermic. Elevating temperature helps to the reaction. The higher of the temperature, molecular motion is more intense and the probability is greater contacting with each other. So the leaching of alumina is greater. The decomposition of γ-2CaO•SiO₂ and the synthesis of sodium hydrate alumina-silicate are the main reason of the appearance of inflection point. Therefore, alumina concentration and silica concentration will decrease with the improvement of temperature.

So suppose that the leaching rate of mixed material is the same to the leaching rate of $12CaO•7Al_2O_3$ at the temperature of 85°C and compare them at the temperature of 75°C. The difference of alumina concentration between 85°C and 75°C is calculated. The ratio of the difference of alumina concentration and the difference of silica concentration is also calculated and the value is 0.52. The molecular formula of sodium hydrate alumino-silicate is $Na_2O•Al_2O_3•2SiO_2•nH_2O$ and the mass ratio of alumina and silicon is 0.85, which is closed to 0.52. However, the molecular formula of hydrogarnet is $3CaO•Al_2O_3•nSiO_2•(6-2n)H_2O$, where n < 1, average of 0.1. And the mass ratio of alumina and silicon is more than 17. So the reason of the loss of alumina caused by mechanical mixing material in high temperature is the synthesis of sodium hydrate alumino-silicate. In order to prove it and further research the reaction mechanism of the secondary reaction in calcium aluminate slag, leaching slag is analyzed by XRD and the results are shown in section 2.4.

2.4 The mechanism of secondary reactions

2.4.1 The principle of secondary reactions

In the production of alumina with lime-soda sinter method, sintered clinker contains about 30% of the β-2CaO•SiO₂, it can be decomposition during the leaching of clinker and react with sodium aluminate, and resulting the loss of alumina, which the phenomenon is known as "secondary reaction losses"[13]. At present, there is no consistent conclusion on the dominant factor for causing the decomposition of calcium silicate in the academic community. The sodium aluminate solution mainly contains NaOH, Na_2CO_3 and $NaAl(OH)_4$, so several perspectives can be summarized sequentially as follows[12, 14].

(1) The decomposition of calcium silicate caused mainly by NaOH. Who hold this view argue that the decomposition reaction of dicalcium silicate is:

$$β-2CaO•SiO_2+2OH^-+2H_2O=2Ca(OH)_2+H_2SiO_4^{2-} \tag{2}$$
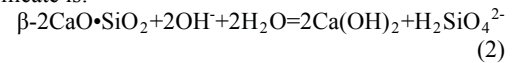
(2) The decomposition of calcium silicate caused mainly by Na_2CO_3. Who hold this view argue that the decomposition reaction of dicalcium silicate is:

$$β-2CaO•SiO_2+2CO_3^{2-}+2H_2O=2CaCO_3+H_2SiO_4^{2-}+2OH^- \tag{3}$$
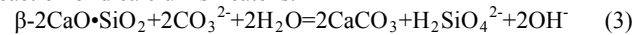
(3) The decomposition of calcium silicate mainly caused by $NaAl(OH)_4$. Who hold this view argue that the decomposition reaction of dicalcium silicate is:

$$3(2CaO•SiO_2)+4Al(OH)_4^-+2H_2O=$$
$$2(3CaO•Al_2O_3•4H_2O)+H_2SiO_4^{2-}+2OH^- \tag{4}$$
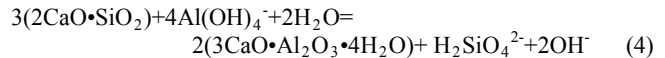
Thus, these three substances are likely to decompose calcium silicate under the proper conditions. Xiaobin Li et al[14], who studied the thermal of the reaction of calcium silicate decomposition in the three materials, thought that the order of its stability in the three materials was: NaOH >> NaAl (OH) ₄> Na_2CO_3, that is to say, on the decomposition of calcium silicate Na_2CO_3 is strongest. In addition, Bi et al[9], who believe that "separate Na_2CO_3 solution can decompose calcium silicate completely". Therefore this research is for extracting alumina from calcium aluminate slag and fly-ash sintered clinker, and these two process have two differences in extracting alumina from sintered, as follows: first, the former of the original calcium silicate is γ-type, with low activity, but the latter is β-type, with high activity; second, the former concentration of sodium carbonate is higher than the later, but the former concentration of caustic alkali and sodium aluminate is lower than the later. It can be seen that, the secondary reactions in process of extracting alumina from calcium aluminate slag is vary from the secondary reactions in process of extracting alumina from sintered clinker. For researching the mechanism of secondary reactions in leaching calcium aluminate slag process, we selected many leaching slag with different leaching time, different concentration of sodium carbonate and leaching temperature for XRD analysis.

2.4.2 The mechanism of secondary reactions of calcium aluminate slag

From 2.3 analysis we know that, the leaching temperature has a great influence on the decomposition of γ-2CaO•SiO₂, so we select the leaching residue of leaching temperature of 55°C and 80°C for phase analysis, the results is shown in Figure 6 and 7.
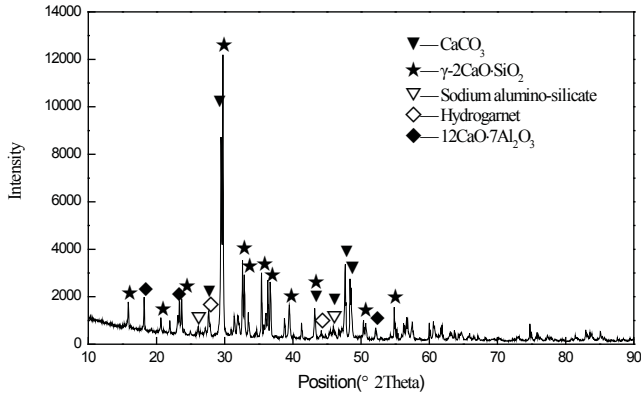
Figure 6. XRD pattern of slag with leaching temperature 55°C(Conditions: Na_2O_k 7g·L^{-1}, α_k= 1.6, t=120min, Na_2O_c 120 g·L^{-1}, and liquid-solid ratio 4.5ml/g)
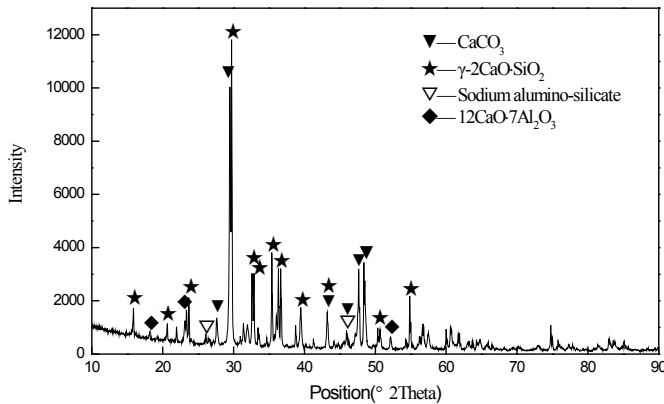
Figure 7. XRD pattern of slag with leaching temperature 80°C (Conditions: Na_2O_k 7g·L^{-1}, α_k= 1.6, t=120min, Na_2O_c 120 g·L^{-1}, and liquid-solid ratio 4.5ml/g)

As Figure 6 and Figure 7 present, there are large amounts of $CaCO_3$ and unreacted γ-2CaO•SiO_2 in leaching slag at different conditions. When the leaching temperature at 55°C, the leaching slag contains hydrogarnet and sodium hydrate alumina-silicate. When the reaction temperature is elevated, the hydrogarnet disappear, but sodium hydrate alumina-silicate remains. According to the reaction of decomposition of hydrogarnet equation:

$$3CaO•Al_2O_3•xSiO_2•(6-2x)H_2O+3Na_2CO_3+xH_2O=3CaCO_3$$
$$+x/2(Na_2O•Al_2O_3•2SiO_2•2H_2O)+(2-x)NaAl(OH)_4+4NaOH \quad (5)$$
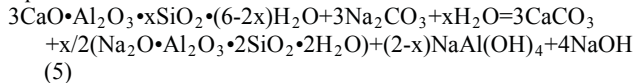
We know that, there exists sodium aluminate in the reaction product, and the lower of silicon saturation in hydrogarnet, the greater number of moles of sodium aluminate generated. Therefore, the re-introduced of sodium aluminate into the solution will increase the concentration of aluminium, the macroeconomic performance is the increase of alumina leaching ratio. While

Figure 5 shows that this is not the case: the alumina concentration is reduced at this temperature.

The reason for this phenomenon is that the secondary reaction is exacerbated by high temperature, and more hydrogarnet and sodium hydrate alumina-silicate will be generated. So even hydrogarnet decomposition, the amount of decomposition of aluminum is much less than the loss of the amount of aluminum in secondary reactions. Therefore, the alumina leaching ratio showed a decline.

In summary, the materials, which contains γ-2CaO•SiO_2, will decompose in the leaching process, and causing the secondary reactions. And when the leaching temperature is low, hydrogarnet and sodium hydrate alumina-silicate will be generated. While when the leaching temperature is high, the product is sodium hydrate alumina-silicate.

3 Conclusions

(1)The liquid-solid ratio has a certain influence on the decomposition performance of γ-2CaO•SiO_2. When 3<L/S<7, the content of SiO_2 will increases firstly and then decreases in solution after decomposition, and then leveled off. When the liquid-solid ratio is relatively low, the SiO_2, which decomposition into solution, will react with sodium aluminate, a secondary reaction, slagging again.

(2) When the concentration of caustic alkali is changed between 30 to 70 g·L^{-1}, the amount of decomposition of γ-2CaO • SiO_2 is gradually increased, which indicating that the concentration of caustic alkali is another major factor to affect the decomposition performance of γ-2CaO•SiO_2.

(3) Temperature has an important influence on the decomposition ofγ-2CaO•SiO_2 and the level of secondary reactions. The higher of the temperature is, the greater degree of decomposition of γ-2CaO•SiO_2. And when the temperature is higher than 75°C, the secondary reactions get intensified.

(4) In the case of the concentration of sodium carbonate is high, the leaching temperature is low, the secondary reactions product are hydrogarnet and sodium hydrate alumina-silicate, when the leaching temperature is high, the product is sodium hydrate alumina-silicate.

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