Research Article

Characterization and Alumina Leachability of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ with Different Holding Times

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The effect of synthesis time on phase compositions, lattice constant, average grain size, preferred orientation, and surface morphology of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ synthesized at 1500°C was analyzed by XRD and SEM. The results indicate that the main phase of samples synthesized is $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ when holding time is over 30 min. The lattice constant increases and the preferred orientation decreases as synthesis time prolongs. The average grain size of samples is about 59 nm calculated by Scherrer formula, and it does not change with synthesis time. The synthesis time affects the micromorphology of samples greatly. There are more and bigger holes in samples synthesized for long time. The aspects mentioned above cause the alumina leaching ratio of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ to increase with the prolonging of synthesis time, but the rate of increase drops.

1. Introduction

Calcium aluminate slag is obtained from blast furnaces when smelting iron-bearing bauxite or red mud. $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ is one of the main components from which alumina can be leached out [1, 2]. $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ attracts wide attention because it has better alumina leaching property than other $\text{CaO}\cdot \text{Al}_2\text{O}_3$ compounds in sodium carbonate solution [3, 4]. This method realizes the comprehensive utilization of iron and alumina values in the ore, and the alumina leaching rate is about 85% [5, 6].

In order to improve the alumina leaching ratio, many studies have been carried out. Tong et al. studied the microwave-assisted alumina leaching and indicated that it could promote the leaching process [7]. Sun et al. studied the ultrasonic-assisted alumina leaching and pointed that ultrasonic can improve the alumina leaching ratio and decrease the leaching temperature and sodium carbonation concentration [8]. Two-stage leaching and adding Na_2O into slag to enhance leaching ratio were also used by Yu et al., and the results were also better [9].

The methods mentioned above improve the alumina leaching ratio of calcium aluminate slag to a certain extent.

And most of these methods are to change the leaching condition. The crystal structure of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ has been widely researched because of its unique nanoporous framework, but all of the works are in the fields of material and cement [10–13]. The relationship between crystal structure and alumina leaching ratio of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ has not been discussed from the literature.

Therefore, the synthesis of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ with raw materials of calcium oxide and alumina under the temperature of 1500°C during different holding time was carried out in this paper. The samples were leached under the same conditions. The microscopic characteristics of these samples were studied with the help of XRD and SEM.

2. Experimental

2.1. Materials. CaCO_3 , Na_2CO_3 , NaOH , and $\text{Al}(\text{OH})_3$ used in the experimental studies are analytically pure reagents. The C/A ($\text{CaO}/\text{Al}_2\text{O}_3$, mole ratio) of the $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ is 1.71.

2.2. Smelting of Calcium Aluminate. Samples were smelted in a MoSi_2 resistance furnace with different synthesis time (from

30 min to 150 min, and the interval was 30 min), and the container was a graphite crucible. The smelting temperature was 1500°C (if the temperature is below 1500, it is difficult to depart the slag from liquid iron). The sample was taken out at 400°C from the resistance furnace, and its cooling rate was 5°C·min⁻¹. Then, the sample was grinded into powders whose average particle sizes were within 74 μm.

2.3. Leaching of Calcium Aluminate. The sodium aluminate solution obtained from leaching calcium aluminate was treated using the carbonization precipitation process, and the circulating liquid was then used to leach calcium aluminate. The feasible conditions for alumina leaching obtained from literature [6, 14] and our previous study were as follows: leaching temperature 75°C, leaching time 30 min, L/S ratio 10, caustic alkali concentration 7 g/L, and sodium carbonate concentration 120 g/L. The leaching experiments were carried out in magnetically stirred constant temperature water bath. After leaching and filtrating, the filtrate was used to analyze the composition of the solution, and the filter residue was washed and dried for analysis.

2.4. Analysis. The contents of Al₂O₃ and CaO in samples were analyzed by X-ray fluorescence, and the contents of Al₂O₃ and Na₂O in filtrate were analyzed by chemical method. Phase components and crystal structure of the 12CaO·7Al₂O₃ were identified by X-ray diffraction (PANalytical PW3040/60). Scanning electron microscopy (SHIMADZU SSX-550) was used to observe the surface morphology of the 12CaO·7Al₂O₃.

3. Results and Discussion

3.1. Alumina Leachability of 12CaO·7Al₂O₃ with Different Holding Times. 12CaO·7Al₂O₃ can easily react with Na₂CO₃ solution and realize alumina recovery. The alumina leaching ratio is very important for the comprehensive utilization of iron-bearing bauxite and fly ash [15]. The reaction equation is shown as follows:

The standard leaching conditions are mentioned in Section 2.3, and the leaching results are shown in Figure 1.

12CaO·7Al₂O₃ has a good alumina leaching ratio (87.90%) when holding time is 30 min. When the holding time prolongs, the leaching ratio increases obviously. And it could reach 92.64% when holding time is 120 min. But it increases no longer when holding time is longer than 120 min. Compared to the previous research results [16], not only the sintering temperature but also the holding time has large influence on leaching ratio.

Although the sample is smelt and its reaction rate is much faster than solid reaction when the temperature is 1500°C, prolonged holding time is still a benefit to improve leaching ratio. The following analysis is carried out to study its effect mechanism.

FIGURE 1: Alumina leaching ratio of 12CaO·7Al₂O₃ with different holding times.

FIGURE 2: XRD pattern of samples synthesized at 1500°C with different holding times.

3.2. XRD Results of 12CaO·7Al₂O₃ with Different Holding Times. Phase components of sintered samples are the main factor which could affect the alumina leaching ability. The results are shown in Figure 2.

Figure 2 shows that the major phase of sample holding for 30 min is 12CaO·7Al₂O₃, and the minor phase is CaO·Al₂O₃. As to samples holding for more than 60 min, there is 12CaO·7Al₂O₃ only. According to the literature [4] alumina leaching property of 12CaO·7Al₂O₃ is better than that of CaO·Al₂O₃ (alumina leaching property of CaO·Al₂O₃ compounds: 12CaO·7Al₂O₃ > CaO·Al₂O₃ > 3CaO·Al₂O₃). This is one reason that alumina leaching ratio of sample holding for 30 min is lower than that of holding for more than 60 min. When holding time is above 60 min, it is difficult to study the effect mechanism of holding time on leaching ratio according to phase compositions. Therefore, further study is carried out.

TABLE 1: d values in X-ray diffraction of samples with different holding times.

Peak serial	(hkl)	30 min	60 min	90 min	120 min	150 min
1	(420)	2.67705	2.67824	2.67941	2.68201	2.68341
2	(211)	2.88512	4.88624	4.88508	4.89433	4.89955
3	(422)	2.44436	2.44539	2.44624	2.44887	2.44925
4	(521)	2.18660	2.18789	2.18803	2.18995	2.19073
5	(532)	1.94395	1.94407	1.94395	1.95581	1.96628
6	(400)	2.99582	2.99643	2.99735	2.99929	2.99938
7	(642)	1.60087	1.60160	1.60212	1.60296	1.60298
8	(640)	1.66104	1.66184	1.66249	1.66353	1.66376
9	(321)	3.19956	3.20032	3.20122	3.20449	3.20686
10	(750)	1.39310	1.39352	1.39376	1.39454	1.39464

The relative peak intensities decrease as the serial number increases.

FIGURE 3: Lattice constants of samples with different holding times.

3.3. Crystal Lattice of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ with Different Holding Times. XRD data of samples show that d value of Bragg diffraction changes regularly. Data of the first ten intensity peaks are shown in Table 1.

According to Table 1, the interplanar distance d of different (hkl) increases as the holding time prolongs. That is to say, the XRD pattern shifts to the left and the unit cell expands. The lattice constants of samples with different holding times are calculated by CELREF software, and the results are shown in Figure 3.

The trend of the increase of lattice constant is similar to that of alumina leaching ratio. The expansion of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ cell improves its leaching property. Grzymek [4] considered that the molecular structure of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ is as shown in Figure 4(a). There are six pyroaluminate groups [$\text{Ca}_2(\text{Al}_2\text{O}_5)$] for one part of Al_2O_3 in it. Ca^{2+} and O^{2-} of this structure are asymmetrically distributed. Hideo Hosono and other researchers [13, 17, 18] indicated that $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ is closely packed by subnanometer cages (Figure 4(b)), and its chemical formula is $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} + 2\text{O}^{2-}$. Ca^{2+} and O^{2-} are also asymmetrical in structure. Therefore, the asymmetrical distribution of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ molecular makes that polar

FIGURE 4: (a) Molecular structure of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$. (b) Framework of single cage.

water molecules permeate in $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ cell rapidly. The expansion of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ cell could intensify the asymmetrical distribution, so the alumina leaching ratio improves under this condition.

For covalent bounded crystal, the total interaction energy of each bond is as follows [19]:

$$u = u_0 + u_0(r) - u_{\text{bond}}, \quad (2)$$

where u_0 is the energy that needed to establish hybridization state, $u_0(r)$ is interaction energy between atoms, and it is

TABLE 2: Average crystallite size of samples synthesized for different times.

Holding time (min)	30	60	90	120	150
d_{ave} (nm)	59.48	59.67	59.06	59.35	59.57

TABLE 3: Relative intensity of X-ray diffractions and standard card.

hkl	Experimental Rel.Int. (%)				Standard Rel.Int. (%)
	60 min	90 min	120 min	150 min	
420	100	100	100	100	100
211	60.12	66.51	68.12	68.23	95
422	50.61	45.08	42.26	57.32	50
400	28.9	28.99	32.33	42.83	45
642	25.25	30.99	27.12	33.56	30
750	12.88	13.39	13.21	17.22	18

reciprocal proportion to r^2 , and u_{bond} is the lowest energy when cohesion of atoms takes place.

For one phase, u_0 and u_{bond} do not change. Therefore, the increase of unit-cell volume makes the bond energy of asymmetric structure weak and easy to break. Then, the reaction between $12CaO \cdot 7Al_2O_3$ and Na_2CO_3 solution will become more violent and the alumina leaching ratio increases.

3.4. Average Crystallite Size of $12CaO \cdot 7Al_2O_3$ with Different Holding Times. The average crystallite size of $12CaO \cdot 7Al_2O_3$ is another aspect which will affect the alumina leaching ratio. In this paper, we use classical Scherrer [20, 21] (3) for crystallite size according to the FWHM of characteristic peaks of $12CaO \cdot 7Al_2O_3$:

$$d = \frac{k\lambda}{B \cos \theta}, \quad (3)$$

$$B = (B_m^2 - B_s^2)^{1/2}, \quad (4)$$

where d is the crystallite size, λ is the X-ray wavelength (Cu target, $\lambda = 0.15406$ nm), θ is the Bragg angle, K is the Scherrer constant ($K = 0.89$, in this paper), and B_m and B_s are the FWHM of experimental sample and reference sample. The average crystallite size is obtained from the first ten strong peaks, and the results are shown in Table 2.

The average crystallite size of different samples is about 59 nm. That is to say, the holding time has little effect on the crystallite size of samples. Therefore, in this aspect, the holding time does not affect alumina leaching ratio.

3.5. Preferred Orientation of $12CaO \cdot 7Al_2O_3$ with Different Holding Times. Preferred orientation of $12CaO \cdot 7Al_2O_3$ crystal is another aspect which will affect the degree of leaching reaction. According to the XRD results, the relative intensity of characteristic peaks of $12CaO \cdot 7Al_2O_3$ changes with different holding times. The relative intensity data are shown in Table 3.

FIGURE 5: Effect of synthesis time on preferred oriented factor of crystal grains.

The crystal layer (420) is the first strongest characteristic peak of $12CaO \cdot 7Al_2O_3$, and its relative intensity does not change with different holding times. But the relative intensity of the crystal layer (211) decreases obviously compared with the standard card. Therefore, the preferred orientation of $12CaO \cdot 7Al_2O_3$ changes with different holding times. The preferred orientation factors are calculated from (5) [22, 23]. The calculated results are shown in Figure 5:

$$TC_{(hkl)j} = \frac{(I(hkl)_j / I(hkl)_{j,0})}{(1/n) \sum_{i=1}^n (I(hkl)_i / I(hkl)_{i,0})}, \quad (5)$$

where $I(hkl)_j$ is the experimental diffraction intensity value of a crystal layer, $I(hkl)_{j,0}$ is the diffraction intensity value of standard card, and n is the amount of peaks calculated.

Figure 5 shows that the first strongest orientation is (420) layer and the second is (211), and their preferred orientation factors decrease with the prolonging of holding time. When holding time changes from 60 min to 150 min, the orientation factor of (420) layer decreases from 1.191 to 0.918, and that of (211) layer decreases from 0.754 to 0.433. This is because the energy of the binary system tends to balance as holding time prolongs. The release of energy makes the enlargement of $12CaO \cdot 7Al_2O_3$ crystal lattice and disturbs its preferred orientation.

Besides, from Figure 6 (SEM results) it can be seen that, when holding time is shorter, the micromorphology of samples (30 min or 60 min) is present as a flake and smoothness structure. This is the result of the preferred orientation of crystal.

But the flake structure of samples (30 min or 60 min) are instead of gully and hole structure (120 min or 150 min) when holding time prolongs continuously. The images indicate that the preferred orientation of samples with long holding time is

FIGURE 6: SEM images of samples synthesized for different times: (a) 30 min, (b) 60 min, (c) 90 min, (d) 120 min, and (e) 150 min.

not obvious compared with that of samples with short holding time.

3.6. Microstructure of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ with Different Holding Times. The SEM results of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ with different holding times are shown in Figure 6. According to these results, the sample synthesized during 30 min (Figure 6(a)) has large gullies and with scalariform marking in it. The gullies become smaller when holding time is 60 min but the scalariform marking increases (Figure 6(b)). Besides, small holes can be observed occasionally. Scalariform markings disappear and holes increase when holding time is 90 min (Figure 6(c)). The combination of holes in adjacent takes place to form big gap when holding time is up to 120 min (Figures 6(d) and 6(e)). These gaps and the holes of different size distribute irregularly. The gaps become bigger and its amount become larger when holding time prolongs.

Another reason for the improvement of alumina leaching ability of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ with long holding time is the existence of these holes and gaps. The aqueous solution can get into the solid easily and enhance the reaction between

$12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ and Na_2CO_3 solution. From the reaction dynamics' point of view [24], the gaps and the holes of the unreacted core could promote the internal diffusion and the degree of liquid-solid reaction.

4. Conclusions

- (1) The main phase of samples synthesized for different time is $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$. But the crystal structure of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ is enlarged and the preferred oriented factor decreases with the increase of holding time.
- (2) The micromorphology of samples synthesized for different times changes greatly. There are more and bigger holes in samples synthesized for longer time than that of short time.
- (3) The comprehensive effects of phase compositions, lattice constant, preferred orientation, and surface morphology increase the alumina leaching ratio of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ synthesized for long holding time.

Conflict of Interests

The authors declare that they have no conflict of interests regarding the publication of this paper.

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