Mineral Transition and Chemical Reactivity Evolution of a Low-Lime Calcium Aluminate Clinker with MgO and Na2SO4 Codopants

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ABSTRACT: The mineral formation—transition mechanism, microstructure evolution, crystal structure, pulverization property, and chemical reactivity of the CaO−Al2O3−SiO2 clinker with MgO and Na2SO4 dopants during the sintering process at 1300 °C for 2.0 h were systematically studied using CaO, Al2O3, SiO2, MgO, and Na2SO4 as raw materials when the molar ratio of CaO to Al2O3 is 1.4, the mass ratio of Al2O3 to SiO2 is 3.0, and the mass percentage of MgO and Na2SO4 is 2%. The MgO dopant could result in 12CaO·7Al2O3 and γ-2CaO·SiO2 transform into 20CaO·13Al2O3·3MgO·3SiO2, restrain the crystal transformation of 2CaO·SiO2 from β to γ, and then deteriorate the pulverization and alumina leaching property corresponding to parts of Al, Si, and Mg atoms occupying the same lattice positions of the crystal structure. MgO and Na2SO4 codeposited could promote transformation of 20CaO·13Al2O3·3MgO·3SiO2 into 3CaO·3Al2O3·CaSO4 as well as some 2CaO·Al2O3·SiO2, while 3CaO·3Al2O3·CaSO4 has good alumina leaching property in the Na2CO3−NaOH solution. The ultrasonic assistant mainly could promote the diffusion of reactive samples, enhance the separation of agglomeration, and then accelerate the chemical reaction of the sintered clinker with Na2CO3−NaOH.

1. INTRODUCTION

Calcium aluminate-based materials have become popular composites for scientific technological progress, which have wide applications in concrete (low density and hardness),1,2 biomaterials (physical, mechanical, bioactive, and biocompatible),3 functional ceramic, and refractory (high-temperature stability). Meanwhile, they also play an important role in the metallurgical industry recovering alumina from low-grade aluminum-containing resources with the lime sinter process,4,5 such as high-iron bauxite, Bayer red mud, kaolinite, and high-alumina fly ash. Obviously, they show incomparable advantages of dry sintering, self-pulverization, and being environmentally friendly and free from secondary pollution as compared with the soda sinter process, acid process, and acid-soda combined process.

CaO·2Al2O3, CaO·Al2O3, and 12CaO·7Al2O3 have good chemical reactivity in the Na2CO3−NaOH leaching process,6−7 while the β → γ crystal transformation of 2CaO·SiO2 is responsible for the pulverization process. Based on the crystal structure, CaO·Al2O3 contains double sheets of edge-sharing AlO6 octahedra or two crystallography-independent AlO6 octahedra forming edge-sharing double chains.8,9 12CaO·7Al2O3 contains vertex-shared AlO4 tetrahedra with some of the corners linked by bridging Ca atoms, in which O atoms are trapped in the Ca−Al−O cage.10−12 In the mineral transition and physical−chemical property, previous literature shows that the MgO dopant would deteriorate the chemical reactivity and pulverization property of the CaO−Al2O3 clinker sharply,13 but the effect mechanism has not been reported distinctly and systematically, especially on the mineral formation—transition process and crystal structure evolution. Actually, the negative effect of MgO is difficult to eliminate completely. Because the raw materials such as alumina-containing resources and lime usually contain trace amounts of MgO; it also could reduce the solubility of sulfur-containing compounds in calcium silicate, therefore compensating for the negative effects of SO3.14 MgO seems to favor exsolution of the sulfate to form 2CaO·SiO2, and the inhibition of conversion from 2CaO·SiO2 to 3CaO·SiO2 is more readily overcome.15 SO3 could promote the formation of 2CaO·SiO2 rims, while MgO could enhance 3CaO·SiO2 in the SO3-bearing clinker.16 Furthermore, the diffusion of the elements Na, Mg, Si, S, V, and Fe into the calcium aluminate and silicate compounds also has been observed, which mainly leads to the formation of spinels, vanadate sulfates, and silicates.17 Moreover, calcium sulfalo aluminate phases can partially accommodate metals (Cu, Cr, Cd, Pb, Zn, and Fe) in the crystal lattice, giving rise to chemical entrapment. It is also observed that calcium sulfalo aluminate (3CaO·3Al2O3·CaSO4) would decompose into CaO·Al2O3, CaO, and SO3 when the sintering temperature exceeds 1300 °C.18

The aim of this paper is to study the “structure−activity” relationship of the crystal structure characteristics and mineral formation—transition mechanism with the physicochemical...
property (self-pulverization property and chemical reactivity in the Na₂CO₃–NaOH solution) in the CaO–Al₂O₃–SiO₂ system with the MgO and Na₂SO₄ dopant. The influence mechanism of MgO on the mineral transition process and chemical reactivity will be studied comprehensively, while the eliminate mechanism of Na₂SO₄ on the MgO negative interaction will also be reported. Then, it would be a breakthrough application and development in the lime sinter process recovering alumina and other valuable elements from low-grade alumina-containing resources.

2. RESULTS AND DISCUSSION

2.1. Characterization of Sintered Clinker with MgO–Na₂SO₄ Dopant. The X-ray diffraction (XRD) patterns of the CaO–Al₂O₃–SiO₂ clinker with MgO and Na₂SO₄ dopants are shown in Figure 1. As shown in Figure 1, the main minerals of the CaO–Al₂O₃–SiO₂ clinker without MgO and Na₂SO₄ dopants are 12CaO·7Al₂O₃ [cubic system, Ia3d (220)] and γ-2CaO·SiO₂ [orthorhombic system, Pbam (62)] as well as some CaO-Al₂O₃ [monoclinic system, P2₁/n (14)]. The 12CaO·7Al₂O₃ and γ-2CaO·SiO₂ content of the sintered clinker with the MgO dopant decreases. So, MgO dopant could promote the process 12CaO·7Al₂O₃ and γ-2CaO·SiO₂ react with MgO transform into 20CaO·13Al₂O₃·3MgO·3SiO₂ (orthorhombic system, Pmmm (59), a = 27.15 Å b = 10.63 Å c = 5.09 Å), and it also could restrain the crystal transformation of 2CaO·SiO₂ from β to γ during the cooling process. The mineral compositions of the CaO–Al₂O₃–SiO₂ clinker with the MgO dopant are 12CaO·7Al₂O₃ γ-2CaO·SiO₂ β-2CaO·SiO₂ [monoclinic, P2₁/n (14)] and 20CaO·13Al₂O₃·3MgO·3SiO₂. Through the analysis, we can realize that the Na₂SO₄ dopant could restrain the formation of 20CaO·13Al₂O₃·3MgO·3SiO₂ and the main minerals are 12CaO·7Al₂O₃ and γ-2CaO·SiO₂ as well as some 2CaO·Al₂O₃·SiO₂ [tetragonal system, P421/m (113)] and 3CaO·3Al₂O₃·CaSO₄ (orthorhombic system, Pcc2 (27), a = 12.97 Å b = 13.03 Å c = 9.16 Å). The preferred indices of the crystal face are (1 2 3) in CaO-Al₂O₃, (4 0 0) in 12CaO·7Al₂O₃ (1 3 0) in γ-2CaO·SiO₂ (2 1 1) in 2CaO·Al₂O₃·SiO₂, (0 4 2) in 3CaO·3Al₂O₃·CaSO₄ and (8 2 0) in 20CaO·13Al₂O₃·3MgO·3SiO₂, which are calculated according to the XRD data.

The Visualizer module of Materials Studio is used to establish the three-dimensional models of 20CaO·13Al₂O₃·3MgO·3SiO₂ and 3CaO·3Al₂O₃·CaSO₄. The unit cell models data, corresponding to the space group, lattice parameters, and atom distribution position, are calculated according to the XRD results (Figure 1). 20CaO·13Al₂O₃·3MgO·3SiO₂ belongs to the orthorhombic crystal system, Pnmm (59) space group, and lattice parameters are as follows: a = 27.15 Å, b = 10.63 Å, c = 5.09 Å, and α = β = γ = 90°. 3CaO·3Al₂O₃·CaSO₄ belongs to the orthorhombic crystal system, Pcc2 (27) space group, and lattice parameters are as follows: a = 12.97 Å, b = 13.03 Å, c = 9.16 Å, and α = β = γ = 90°. The atom distribution position corresponds to the ICSD data, which is shown in Tables 1 and 2.

In addition, the unit cell models could provide the foundational models for the subsequent calculation and explanation, which are shown in Figure 2.

According to Figure 2a and Table 1, the unit cell of 20CaO·13Al₂O₃·3MgO·3SiO₂ has four lattice position Ca atoms (Ca₁, Ca₂, Ca₃, and Ca₄), six lattice position Al atoms (Al₁, Al₂, Al₃, Al₄, AI₅, and Al₆), two lattice position Mg (Mg₁ and Mg₂) and Si (Si₁ and Si₂) atoms, and 13 lattice position O atoms (O₁, n = 1, 2, 3...13). Further analysis show that O atoms distribute uniformly in the unit cell, while Ca, Mg, Al, and Si atoms distribute unevenly. It also shows that two forms of Al atoms and Mg atoms occupy the same lattice positions (x, y, z) in (0.9543, 0.8989, 0.1256) and (0.0161, 0.2500, 0.3719), while two forms of Al atoms and Si atoms also occupy the same lattice position in (0.2500, 0.8929, 0.8434) and (0.1943, 0.2500, 0.7376). The overlapping Al–Si atoms are in the corner of the tetrahedron by the composition of Al, Si, and O.
Table 2. Atom Lattice Position in the Unit Cell of 3CaO·3Al2O3·CaSO4

| atoms | X   | Y   | Z   | atoms | X   | Y   | Z   |
|-------|-----|-----|-----|-------|-----|-----|-----|
| Ca1   | 0.0580 | 0.2510 | 0.1490 | O1   | 0.7700 | 0.3360 | 0.3790 |
| Ca2   | 0.2370 | 0.9260 | 0.2860 | O4   | 0.6510 | 0.2010 | 0.4170 |
| Ca3   | 0.2570 | 0.5120 | 0.2540 | O2   | 0.4000 | 0.2460 | 0.4380 |
| Ca4   | 0.4830 | 0.2530 | 0.2280 | O5   | 0.5670 | 0.4090 | 0.1400 |
| Al1   | 0.5000 | 0.5000 | 0.2300 | O6   | 0.5550 | 0.1050 | 0.1550 |
| Al2   | 0.5000 | 0 | 0.2500 | O7   | 0.7550 | 0.5900 | 0.5040 |
| Al3   | 0 | 0 | 0.2050 | O8   | 0.5960 | 0.4430 | 0.8260 |
| Al4   | 0 | 0.5000 | 0.2000 | O9   | 0.9070 | 0.4460 | 0.8020 |
| Al5   | 0.6270 | 0.1210 | 0.0040 | O10  | 0.7570 | 0.9020 | 0.5360 |
| Al6   | 0.1220 | 0.6250 | 0.9490 | O12  | 0.9010 | 0.0340 | 0.8240 |
| Al7   | 0.3690 | 0.6290 | 0.9800 | O13  | 0.6080 | 0.0330 | 0.8540 |
| Al8   | 0.1220 | 0.8760 | 0.9600 | O14  | 0.1030 | 0.2470 | 0.3910 |
| S1    | 0.2536 | 0.2487 | 0.9821 | O15  | 0.9530 | 0.1150 | 0.1250 |
| O1    | 0.7290 | 0.3170 | 0.6120 | O16  | 0.9480 | 0.3890 | 0.1100 |
| O2    | 0.8380 | 0.1840 | 0.4600 |       |       |       |     |

atoms. The overlapping Al–Mg atoms are in the middle of the O–Mg (Al)–O bond. It mainly attributes to the atom substitution process in the formation of 20CaO·13Al2O3·3MgO·3SiO2. According to Figure 2b and Table 2, the unit cell of 3CaO·3Al2O3·CaSO4 has four lattice position Ca atoms (Ca1, Ca2, Ca3, and Ca4), eight lattice position Al atoms (Aln, n = 1, 2, 3...16), one lattice position Si atom, and 16 lattice position O atoms (On, n = 1, 2, 3...16). All atoms have no overlapping distribution. All O atoms distribute uniformly in the unit cell, while Ca, Al, and S atoms distribute unevenly. S atoms distribute in the center of the O tetrahedron.

The microstructure of the CaO–Al2O3–SiO2 clinker with MgO and Na2SO4 dopants are shown in Figure 3a–c. The selected characteristic regions are also confirmed by the energy-dispersive spectrometer (EDS) analysis, as also shown in Figure 3d.

As shown in Figure 3a, the CaO–Al2O3–SiO2 clinker without MgO and Na2SO4 dopants shows an irregular morphology with a wrinkled surface. According to the XRD results (Figure 1) and EDS analysis (Figure 3d), the selected region (A) in Figure 3a may correspond to the coexisting phases of 12CaO·7Al2O3 and γ-2CaO·SiO2. The CaO–Al2O3–SiO2 clinker with the MgO dopant (Figure 3b) shows a regular and porous morphology, and the magnified characteristic region (B) also shows a porous morphology, corresponding to the agglomeration of well-organized and cuboid molecules, which mainly attributes to 2CaO·13Al2O3·3MgO·3SiO2. Further, Figure 3c shows that the regular morphology (in Figure 3b) turns into a dense porous-layered morphology when Na2SO4 is added. The sintered clinker melts completely in the sintering process with amounts of pores, mainly because of Na2SO4 decomposition. It not only could decrease the melting point of the sintered materials but also could generate 3CaO·3Al2O3·CaSO4 with low melting point. The magnified characteristic region (C) in Figure 3c mainly corresponds to the coexisting phases of 12CaO·7Al2O3 and γ-2CaO·SiO2 as well as some 3CaO·3Al2O3·CaSO4 which is in accordance with the XRD results (Figure 1) and EDS analysis (Figure 3d).

Figure 4 shows the particle size distribution of the CaO–Al2O3–SiO2 clinker with MgO and Na2SO4 dopants, and its particle size parameters are also shown in Table 3. The CaO–Al2O3–SiO2 clinker without MgO and Na2SO4 dopants shows a bimodal distribution with the size ranging from 0.35 to 575.85 μm, and the two peaks are centered at 0.75 and 50.78 μm. The D50 and specific surface area are 33.26 μm2 and 0.86 μm2. According to the XRD results (Figure 1), scanning electron microscopy (SEM) analysis (Figure 3) and particle size distribution (Figure 4), the MgO dopant in the CaO–Al2O3–SiO2 clinker could not only consume part of 2CaO·SiO2, 12CaO·7Al2O3, and CaO·Al2O3 to form 20CaO·13Al2O3·3MgO·3SiO2 but also restrain the transformation process of 2CaO·SiO2 from β to γ. Because 2CaO·SiO2 is comprised of several polymorphs, such as α, α′, α″, γ, β, and γ′, the polycrystalline type transformation from β to γ is responsible for the pulverization process at 12 vol% expansion. Therefore, the decrease of the 2CaO·SiO2 content and the inhibition of the transformation process from β-2CaO·SiO2 to γ-2CaO·SiO2 are the main reasons that the MgO dopant could deteriorate the pulverization property obviously. The CaO–Al2O3–SiO2 clinker with the MgO dopant also shows a bimodal distribution with the size ranging from 0.85 to 768.55 μm. The two peaks are centered at 0.75 and 60.05 μm. The D50 increases, while the specific surface area decreases slightly, which are 5.84 μm2 and 0.68 μm2, respectively. It is in accordance with microstructural characteristics obtained by the SEM analysis (Figure 3) that the sintered clinker agglomerate easily with amounts of small particles in the surface of the major structure. MgO and Na2SO4 codopants could not only restrain the formation of 2CaO·13Al2O3·3MgO·3SiO2 but also result in the formation of 2CaO·Al2O3·SiO2 and 3CaO·3Al2O3·CaSO4. According to the XRD results (Figure 1) and SEM analysis (Figure 3), the low melting phase 2CaO·Al2O3·SiO2 and 3CaO·3Al2O3·CaSO4 formation is the major reason that the pulverization property of the CaO–Al2O3–SiO2 clinker with MgO and Na2SO4 codopants deteriorates significantly. The particle size of the CaO–Al2O3–SiO2 clinker with 2% MgO–2% Na2SO4 shows a trimodal distribution with the size ranging from 0.35 to 1000 μm, and the three peaks are centered on 0.71, 63.25, and 502.38 μm, respectively. The D50 and specific surface area are 56.71 μm and 0.50 μm2. The alumina leaching property of the CaO–Al2O3–SiO2 clinker with the MgO–Na2SO4 dopant, and the XRD patterns of leached residue from the sintered clinker are shown in Figures 5 and 6.

As shown in Figure 5, the alumina leaching property of the CaO–Al2O3–SiO2 clinker with the MgO–Na2SO4 dopant and the XRD patterns of leached residue from the sintered clinker are shown in Figures 5 and 6.
is 95.74%. The MgO dopant could deteriorate the alumina leaching property, which decreases circa 10%. Even then, the Na₂SO₄ dopant could increase the alumina leaching property circa 8%, but it also could not remove the negative effect absolutely of MgO in the CaO−Al₂O₃−SiO₂ clinker. As shown in Figure 6, the main minerals of the leached residue from the CaO−Al₂O₃−SiO₂ clinker are CaCO₃ and γ-2CaO·SiO₂ as well as some 2CaO·Al₂O₃·SiO₂. The mineral compositions of the leached residue from the CaO−Al₂O₃−SiO₂ clinker with the MgO dopant are CaCO₃, γ-2CaO·SiO₂, 2CaO·Al₂O₃·SiO₂, 20CaO·13Al₂O₃·3MgO·3SiO₂, and Na₆(AlSiO₄)₆·4H₂O [orthorhombic, Pbn2₁(33)]. The main minerals of the leached residue from the CaO−Al₂O₃−SiO₂ clinker with the MgO−Na₂SO₄ dopants are 12CaO·7Al₂O₃, CaO·Al₂O₃, γ-2CaO·SiO₂, and 2CaO·Al₂O₃·SiO₂. The mineral compositions of the CaO−Al₂O₃−SiO₂ clinker with the MgO dopant are 12CaO·7Al₂O₃, γ-2CaO·SiO₂, 2CaO·Al₂O₃·SiO₂, and 20CaO·13Al₂O₃·3MgO·3SiO₂. The mineral compositions of the CaO−Al₂O₃−SiO₂ clinker with the MgO−Na₂SO₄ dopant are 12CaO·7Al₂O₃ and γ-2CaO·SiO₂ as well as some 2CaO·Al₂O₃·SiO₂, 20CaO·13Al₂O₃·3MgO·3SiO₂, MgO, and 3CaO·3Al₂O₃·CaSO₄. According to Figures 1, 5, and 6, 12CaO·7Al₂O₃, CaO·Al₂O₃, and 3CaO·3Al₂O₃·CaSO₄ also have good chemical reactivity in the Na₂CO₃−NaOH solution, while γ-2CaO·SiO₂, 2CaO·Al₂O₃·SiO₂, and 20CaO·13Al₂O₃·3MgO·3SiO₂ have poor chemical reactivity that they maybe could not react with Na₂CO₃−NaOH.

Figure 2. Crystal structure and atom distribution: 20CaO·13Al₂O₃·3MgO·3SiO₂ (a) and 3CaO·3Al₂O₃·CaSO₄ (b).
are shown in eqs 1–3. Furthermore, additional sodium hydrate could restrain the hydrolytic process of NaAl(OH)₄, as also shown in eq 4.

\[ \begin{align*}
12\text{CaO} \cdot 7\text{Al}_2\text{O}_3 + 12\text{Na}_2\text{CO}_3 + 33\text{H}_2\text{O} & \rightarrow 12\text{CaCO}_3 \downarrow + 14\text{NaAl(OH)}_4 + 10\text{NaOH} \\
\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{Na}_2\text{CO}_3 + 4\text{H}_2\text{O} & \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaAl(OH)}_4 \\
3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 + 4\text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O} & \rightarrow 6\text{NaAl(OH)}_4 + 4\text{CaCO}_3 \downarrow + \text{Na}_2\text{SO}_4
\end{align*} \]

(1) (2) (3)

2.2. Chemical Activity Enhancement of Sintered Clinker with Ultrasonic Assistant. The alumina leaching property of the CaO–Al₂O₃–SiO₂ clinker with the MgO–Na₂SO₄ dopant varying with the leaching temperature, leaching duration, leaching solution system [Na₂O₃–NaOH] in the

| oxide dopant | D_{10}/μm | D_{50}/μm | D_{90}/μm | specific surface area/m²·g⁻¹ |
|--------------|-----------|-----------|-----------|-----------------------------|
| 0% MgO–0% Na₂SO₄ | 3.93 | 33.26 | 164.93 | 0.86 |
| 2% MgO–0% Na₂SO₄ | 5.84 | 45.05 | 211.72 | 0.68 |
| 2% MgO–2% Na₂SO₄ | 9.62 | 56.71 | 365.59 | 0.50 |

Figure 3. Microstructure and EDS analysis of the sintered clinker: CaO–Al₂O₃–SiO₂ clinker (a), CaO–Al₂O₃–SiO₂ with the 2% MgO clinker (b), CaO–Al₂O₃–SiO₂ with the 2% MgO–2% Na₂SO₄ clinker (c), and chemical composition of the sintered clinker in the magnified characteristic region (d).

Figure 4. Particle size distribution of the sintered clinker with the MgO–Na₂SO₄ dopant.

Figure 5. Alumina leaching property of the sintered clinker in the Na₂CO₃–NaOH solution.

Figure 6. XRD patterns of the leached residue from the sintered clinker.

\[ \text{NaAl(OH)}_4 \rightarrow \text{Al(OH)}_3 \downarrow + \text{NaOH} \]

(4)
form of NaOH) = 10 g·L⁻¹, Na₂O_C (in the form of Na₂CO₃) = 80–130 g·L⁻¹, and the ultrasonic assistant is shown in Figure 7a–c. The chemical compositions and XRD patterns of the leached residue (the leaching temperature is 80 °C, the leaching duration is 40 min, and the leaching solutions are Na₂O_C = 130 g·L⁻¹ and Na₂O_K = 10 g·L⁻¹) from the CaO–Al₂O₃–SiO₂ clinker with MgO and Na₂SO₄ dopants are shown in Figures 7d and 8.

As shown in Figure 7a–c, increasing leaching temperature from 50 to 70 °C could reinforce the chemical reactivity of the sintered clinker in the Na₂CO₃–NaOH solution significantly, and the alumina leaching property increases circa 12%. The process of the sintered clinker with Na₂CO₃–NaOH solution has a fast reaction rate. Improving the sodium carbonate concentration from 80 to 120 g·L⁻¹ also has an obvious effect on the alumina leaching property. The ultrasonic assistant could also improve the alumina leaching property, and the reinforcement decreases gradually with the increase of leaching temperature and sodium carbonate concentration. It has a remarkable reinforcement circa 6%, especially when the leaching temperature is lower than 70 °C or the sodium carbonate content is less than 110 g·L⁻¹. The reinforcement mechanism mainly attributes to the chemical effect and heat effect, and then the ultrasonic assistant could promote the diffusion process of the sintered clinker and accelerate the chemical reaction.

As shown in Figure 8, the mineral compositions of the leached residue without the ultrasonic assistant are CaCO₃ (calcite), γ-2CaO·SiO₂, 2CaO·Al₂O₃·SiO₂, 20CaO·13Al₂O₃·3MgO·3SiO₂, Na₆(AlSiO₄)₆·4H₂O, and MgO. The main minerals of the leached residue with the ultrasonic assistant have no obvious difference. A small amount of CaCO₃ (vaterite) generates and MgO disappears. The mineral compositions are CaCO₃ (calcite), CaCO₃ (vaterite), γ-2CaO·SiO₂, 2CaO·Al₂O₃·SiO₂, Na₆(AlSiO₄)₆·4H₂O, and 20CaO·13Al₂O₃·3MgO·3SiO₂.

Figure 9 shows the Raman spectra of leaching (Na₂CO₃–NaOH) and leached solution. According to the Raman spectra of leaching solution, it shows a sharp peak and a wide peak. The band situated at 1067 cm⁻¹ attributes to the C=O bond stretching vibration of CO₃²⁻ in Na₂CO₃, while the band situated at 3056–3444 cm⁻¹ attribute to the O–H bond stretching vibration in NaOH. In addition to the two existing peaks of C=O and O–H bonds in the leaching solution, two sharp peaks could be detected in the leached solution. The band situated at 620 cm⁻¹ attributes to the Al–OH stretching vibration of NaAl(OH)₄ which mainly corresponds to the chemical reaction of 12CaO·7Al₂O₃·CaO·Al₂O₃ with Na₂CO₃ (eqs 1 and 2). The band situated at 775 cm⁻¹ attributes to the stretching vibration of the Al–O–Si bond in Na₂O·Al₂O₃.
xSiO2·nH2O. Silicon-containing γ-2CaO·SiO2 and 20CaO-13Al2O3·3MgO·3SiO2 also have good chemical stability in the Na2CO3−NaOH solution, while β-2CaO·SiO2 have good chemical reactivity with Na2CO3. Therefore, the Na2O·Al2O3·xSiO2·nH2O (Na6[AlSiO4]6·4H2O) formation process mainly corresponds to the secondary reaction of NaAl(OH)4 with Na2SiO3, which is shown in eq 5. The Na2SiO3 formation mainly corresponds to the chemical reaction of β-2CaO·SiO2 with Na2CO3, and the reaction equation is shown in eq 6. The intensity of Al−O−Si stretching vibration decreases with the ultrasonic assistant when compared with the leached solution without it.

\[
xNa_2[HSiO_3] + 2NaAl(OH)_3 + aq \\
\rightarrow Na_2O·Al_2O_3·xSiO_2·nH_2O + 2xNaOH + aq \quad (5)
\]

\[
2CaO·SiO_2 + 2Na_2CO_3 \rightarrow 2CaCO_3 \downarrow + 2Na_2SiO_3 \quad (6)
\]

The morphology characteristics and particle size distribution of the CaO−Al2O3−SiO2 (2% MgO−2% Na2SO4) clinker (preball-milled) and the leached residue are shown in Figure 10, while the particle size parameters (D10, D50, D90, and specific surface area) are shown in Table 4.

According to Figure 10a,d and Table 4, the sintered clinker (ball-milled) shows a uniform particle size distribution with the size ranging from 0.26 to 179.74 μm. The bimodal peaks are centered at 0.76 and 40.15 μm, while the D50 and specific surface area are 36.38 μm and 0.17 m2·g−1. According to Figure 10b,d and Table 4, the leached residue from the CaO−Al2O3−SiO2 clinker without ultrasonic shows a complete irregular particle size distribution with the size ranging from 0.23 to 200.05 μm. Most parts of small particles agglomerate into larger particles, while it has a rough surface. The D50 and specific surface area are 39.14 μm and 0.16 m2·g−1, respectively. The leached residue with the ultrasonic assistant shows a relative regular particle size distribution when compared with the leached residue without ultrasonic. It also shifts toward much smaller particle size, and the D50 and specific surface area are 28.20 μm and 0.22 m2·g−1, respectively.

### Table 4. Particle Size Parameters of the Sintered Clinker and Leached Residue

| particle size categories | D10/μm | D50/μm | D90/μm | specific surface area/m2·g−1 |
|-------------------------|--------|--------|--------|-----------------------------|
| sintered clinker (ball-milled) | 14.28 | 36.38 | 83.23 | 0.17 |
| leached residue (without ultrasonic) | 15.60 | 39.14 | 97.10 | 0.16 |
| leached residue (ultrasonic assistant) | 12.36 | 28.20 | 59.35 | 0.22 |

### 3. CONCLUSIONS

The MgO dopant could result in 12CaO·7Al2O3 and γ-2CaO-SiO2, transform into 20CaO·13Al2O3·3MgO·3SiO2, restrain the crystal transformation of 2CaO·SiO2 from β to γ, and then deteriorate the pulverization and alumina leaching property. The overlapping Al−Si atoms are in the corner of the tetrahedron, and the Al−Mg atoms are in the middle of the O−Mg(Al)−O bond in the 20CaO·13Al2O3·3MgO·3SiO2 crystal structure, which attributes to the structure and physicochemical property evolution. MgO and Na2SO4 co-

![Figure 9. Raman spectra of Na2CO3−NaOH and leached solution.](image)

![Figure 10. Microstructure and particle size distribution: sintered clinker (ball-milled) (a), leached residue without ultrasonic (b), leached residue with the ultrasonic assistant (c), and particle size distribution of the sintered clinker and leached residue (d).](image)
doped could promote 20CaO·13Al2O3·3MgO·3SiO2, transform into 3CaO·3Al2O3·CaSO4 as well as some 2CaO·Al2O3·SiO2. 3CaO·3Al2O3·CaSO4 has good chemical reactivity in the Na2CO3–NaOH solution, and the Ca, Al, Si, and O have no overlapping distribution. The ultrasonic assistant mainly could promote the diffusion of reactive samples, enhance the separation of agglomeration, accelerate the chemical reaction, and then optimize the alumina leaching property.

4. EXPERIMENTAL SECTION

The raw materials used in this study are analytical reagent α-Al2O3, CaCO3 (calcite), SiO2, MgO, and Na2SO4, and the chemical analysis is shown in Table 5. The average particle size of Al2O3, CaCO3 (calcite), SiO2, MgO, and Na2SO4 are 0.31, 0.83, and 0.93 μm, respectively. The mass percentage of MgO ranging from 0 to 2%, and the mass percentage of Na2SO4 ranging from 0 to 2% (e.g., CaO–Al2O3–SiO2 (0% MgO–0% Na2SO4), CaO–Al2O3–SiO2 (2% MgO–0% Na2SO4), and CaO–Al2O3–SiO2 (2% MgO–2% Na2SO4)). After the milled process, the homogeneous material was subjected in cold-isostatic pressing (30 MPa) to produce a cylindrical sample with 10 mm in diameter and 30 mm in length using polyvinylidene fluoride as the binder. Then, the samples were sintered at 1300 °C for 2.0 h in the MoSi2 resistance furnace (KLS-1700x) followed by cooling in the furnace. The temperature system in the heating and cooling process is shown in Figure 11.

The sintered clinker varying with the oxide dopant is leached at 80 °C for 0.5 h in sodium carbonate with sodium hydrate (Na2CO3–NaOH) solution in a three-necked flask. The concentration of sodium carbonate (in the form of Na2CO3) and sodium hydrate (in the form of Na2O) in the solution is 80 and 10 g L−1. The liquid–solid ratio of leaching solution to the sintered clinker is 10. The alumina concentration (CAl2O3) in the filter liquor is analyzed by the volumetric method, and the alumina leaching property is calculated by eq 7.

\[
\eta_{Al2O3} = \frac{C_{Al2O3} \cdot V_{Al2O3}}{m \cdot w_{Al2O3}} \times 100\%
\]

where \(C_{Al2O3}\) is the alumina concentration in the leached solution, \(g\) L−1; \(V_{Al2O3}\) is the leached solution volume, \(L\); \(m\) is the reactive mass of the sintered clinker, \(g\); \(w_{Al2O3}\) is the alumina mass percentage of the sintered clinker.

The mineral compositions of the sintered clinker and the leached residue were determined by XRD (Rigaku D/MAX-2500). The microstructure was carried out by SEM (Bruker TESCAN Vega3) fitted with an energy-dispersive spectrometer (EDS, X-Flash 410M). The Raman absorption of leaching and leached solution was obtained by the MultiRAM FT-Raman equipment. The particle size distribution of the sintered clinker and leached residue was determined by Malvern Mastersizer instrument laser scattering equipment (Hydro 2000MU). The specific surface area of the sintered clinker and leached residue was determined by surface area and the pore porosimetry analyzer (V-Sorb 4800P).

Table 5. Chemical Compositions of Raw Materials

| Chemical Analysis/wt % | CaCO3 | Al2O3 | SiO2 | MgO | Na2SO4 |
|------------------------|-------|-------|------|-----|--------|
| CaO                    | 55.91 | 0.02  | 0.03 | 0.002 |
| Al2O3                  | 0.009 | 94.20 | 0.05 |
| SiO2                   | 0.007 | 96.46 |
| Fe2O3                  | 0.001 | 0.01  | 0.007 | 0.005 |
| SO2                    | 0.01  | 0.05  | 0.05  | 55.78 |
| MgO                    | 0.08  | 0.05  | 0.05  | 98.5  |
| Na2O                   | 0.10  | 0.1   | 0.2   | 43.22 |
| LOI                    | 43.88 | 5.0   | 3.0   | 4.5   | 0.2   |

Figure 11. Sintering temperature system in the heating–cooling process.
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