Improved hydration resistance of MgO–2CaO·SiO₂–3CaO·SiO₂ composite refractory using low-grade minerals

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Abstract
Three low-grade mineral raw materials, i.e., natural dolomite, high-silicon magnesite, and forsterite tailings were used to prepare a MgO–2CaO·SiO₂–3CaO·SiO₂ composite refractory, and its hydration resistance was essentially improved. Free CaO was converted into more stable calcium silicate which protected MgO from hydration, and low melting phases formed by impurities promoted densification. The composite refractory, predominantly composed of MgO, β-2CaO·SiO₂, and 3CaO·SiO₂ with a bulk density of 3.13 g cm⁻³ and apparent porosity of 4.6%, was obtained after being calcined at 1600 °C for 3 h. The prepared composite exhibited excellent hydration resistance with a weight increase of only 0.03% at 1600 °C. Microstructural analysis revealed that a dense matrix consisting of intergranular calcium–silicate phases, was dispersed by rounded MgO aggregates.

1. Introduction
Magnesia–doloma refractories play a very important role in metallurgy, the cement industry, and ceramics [1–3]. Magnesia–doloma refractories possessing superior chemical and mechanical properties are suitable for use in thermomechanical, wear-resistant, and other refractory applications [4, 5]. High-purity doloma refractories are increasingly used in the steel industry due to their thermodynamic stability as well as high refractoriness to metal and basic slags [6–8]. On account of their excellent coatability and tolerance to chemical attack, high temperature, and heat stress-induced damage, doloma and doloma–magnesia refractories are highly suitable for use in a cement rotary kiln’s burning zone [9–12]. The increasing demand of high-temperature industries has propelled the research and development as well as the applications of doloma-based refractories [1, 13, 14].

However, a disadvantage of doloma-based (CaO) refractories is their aptness to hydration when in contact with water or moisture; they powder and crumble and this hinders their practical applications [15–17]. Much research has been done to improve the hydration resistance of CaO-containing refractories by adding to them various additives [15, 18–26] and/or nanoparticles [2, 16, 27–29]. Adjusting the sintering temperature or coating CaO-containing refractories with tar or pitch and surface modifications involving mainly silicone oil, phosphoric acid, or phosphate have been applied to refractories to promote hydration resistance [30, 31]. Periclase-based (MgO) refractories also suffer from hydration. MgO hydrates to form magnesium hydroxide (Mg(OH)₂) in a humid environment, which causes the refractories to break due to volume expansion [2]. However, the hydration resistance of MgO is much better than that of CaO [29, 32]. Generally, increasing the relative content of MgO in magnesia–doloma refractories helps to improve hydration resistance [33]. Although much work has been carried out to develop highly water-resistant dolomite-based materials, the intrinsic property of vulnerability of CaO to hydration with water or water vapour is still the main barrier to production and utilisation of magnesia–doloma refractories. We have found that using CaO in a stabilised form, for example, calcium silicate or calcium ferrite, can promote hydration resistance remarkably [12].
Studies indicate that when iron oxide was added to doloma, resistance against hydration increased [15]. Moreover, this addition led to increased density of doloma [19]. F. Kashaninia et al [32] found that iron oxide addition led to the formation of iron-containing phases which increased the hydration resistance of samples both by encapsulating the CaO and MgO grains, and by promoting liquid-phase sintering. In terms of constituents, Fe$_2$O$_3$, SiO$_2$, and Al$_2$O$_3$ in forsterite and magnesite are common impurities in low-grade ores. However, consumers and researchers around the world focus on high-quality raw materials to improve the qualities of refractories [7, 34], but the neglected impact of impurities, which are similar to additives, leads to obstruction of sustainable development of refractories. Currently, there is no specific evaluation of the influence of impurities in low-grade ores on MgO–CaO refractories. The present work is focused on the preparation of a MgO–2CaO–SiO$_2$–3CaO–SiO$_2$ composite refractory using three low-grade minerals, and thereby essentially improving the hydration resistance of magnesia–doloma refractories.

### 2. Experiment

#### 2.1. Starting materials

Natural dolomite and forsterite tailings from Henan province in China were used as starting materials. High-silicon magnesite from Shandong province in China, a tailing ore containing higher amounts of especially SiO$_2$ content impurities, was also used. Chemical analysis and x-ray diffraction (XRD) patterns of these three raw materials were carried out and the results are shown in Table 1 and Figure 1, respectively. Dicalcium silicate (2CaO·SiO$_2$, C$_2$S) may exist in five polymorphs, among which the orthorhombic ($\beta$) to monoclinic ($\gamma$) transformation is irreversible; and the consequences of transformation can lead to the destruction of the material due to a 12% volume change [3, 7]. Therefore, in our research, 0.25 wt % boric acid (H$_3$BO$_3$, analytical purity, 99.5%) was chosen to stabilise C$_2$S existing in $\beta$-C$_2$S.

#### 2.2. Synthesis of composites

The composites were prepared by a process of two-step sintering. Natural magnesite and dolomite mine ores were jaw-crushed to a mean particle diameter of 3–5 cm and then pre-calcined at low temperatures (850 °C and 1000 °C, respectively for 2 h) for decarburisation. The preheated materials were then mixed with forsterite powders and H$_3$BO$_3$ based on the designed proportion. These compositions included 35 wt% CaO, and the

| Constituent  | MgO | CaO | SiO$_2$ | Fe$_2$O$_3$ | Al$_2$O$_3$ | Loss |
|-------------|-----|-----|---------|-------------|-------------|------|
| Dolomite    | 20.82 | 30.47 | 0.72    | 0.37        | 0.51        | 45.56|
| Magnesite   | 42.84 | 2.32 | 9.67    | 0.76        | 1.98        | 41.26|
| Forsterite  | 43.68 | 1.07 | 41.31   | 8.08        | 2.04        | 3.41 |

Figure 1. X-ray diffraction patterns of the starting materials.
CaO/SiO₂ molar ratio was fixed at 2.6, which is beneficial for the simultaneous generation of C₃S and C₂S. The compositions were investigated, with the formulations shown in table 2.

Homogeneous slurries of the mixture, obtained by thoroughly wet mixing for 4 h in a roller porcelain ball mill (GMS10–4B, China) with enough water, were dried in an electrical drying oven (403B, China) and then the mixtures were ground to a particle size of below 3 mm.

Cylindrical samples of 36 mm × 50 mm (diameter and height, respectively) were prepared using a uniaxial cold pressing machine (YT63T, China) under 120 MPa pressure. The samples were burnt in an air atmosphere MoS₂ electrical furnace (SX16–15–16, China) for 3 h at four different soaking temperatures: 1500, 1550, 1600 and 1650 °C, while the samples were heated at a slow rate of 3–5 K min⁻¹ to prevent deformation of the sample.

2.3. Characterisation

The apparent porosity and bulk density of composite refractories were characterised using Archimedes’ principle by the immersion method in water under a vacuum.

Cold crushing strength was calculated in a hydraulic compressive machine (NYL-2000A, China) at a crosshead speed 5 mm min⁻¹, and three samples were prepared for each test to ensure reliability and reproducibility.

A high-pressure boiling method was used to evaluate the hydration resistance of magnesia–doloma refractories. The calcined samples were ground into powders (3–6 mm) and dried to constant weight at 110 °C for hydration resistance tests. The powders, accurately weighed to about 50 g in a beaker (with a lid to prevent hydration from re-condensed liquid water), were subjected to hydration in an autoclave for 2 h. The autoclave chamber was maintained at 120 °C and 0.3 MPa. The percentage weight gained (Δm gained) after hydration was the measure of hydration resistance.

The crystallised phases were analysed by XRD (Philips X'Pert, Netherlands), in Bragg–Brentano geometry using Cu Kα (λ = 1.5418 Å) radiation. Diffraction patterns were identified in the 2θ range of 20–80° (step size of 0.04° and time per step of 1 s). Scanning electron microscopy (SEM, Carl ZEISS, EVO15, England) with Oxford INCA 2000 energy dispersive spectroscopy apparatus (EDS) was used for microstructure observations or elemental analysis on polished surfaces.

3. Results and discussion

3.1. Phase composition

The XRD patterns of samples after calcination at different temperatures ranging from 1500 to 1650 °C are shown in figure 2. The main phases presented in samples are periclase (MgO), β-C₂S, and tricalcium silicate (3CaO·SiO₂, C₃S), which indicate that β-C₂S and C₃S were generated 1500 °C. The minor phases are calcium ferrite–aluminate (4CaO·Al₂O₃·Fe₂O₃, C₄AF) and calcium ferrite (2CaO·Fe₂O₃, C₂F). The minor components of Fe₂O₃ and Al₂O₃ in the low-grade ores can react with CaO and generate C₄AF (Tₘ = 1415 °C) and C₂F (Tₘ = 1436 °C). These phases with low melting points are liquid at a sintering temperature of above 1500 °C and can promote the sintering process by liquid-phase mass transfer.

Phase equilibrium composition calculated from the starting materials is shown in figure 3. Phase composition was determined by the actual chemical composition and formulation of materials and phase equilibrium laws, and the relative phase contents were calculated on the basis of intensity of the XRD spectrum. The total relative amount of C₂F and C₄AF in the composites was about 8%, and the total relative content of β-C₂S and C₃S was about 45.8%, which is close to that of MgO (46.6%). In our analysis, there was little or no residual phase when the phases were equilibrated. It was interesting that free CaO did not appear, as shown in figure 3, but was completely consumed during the heating process. Additionally, the relative content of MgO is increased because the more reactive CaO was removed. So hydration resistance of the composites improved.

3.2. Microstructure observation

The microstructure of the samples sintered at different temperatures is presented in figure 4. Using SEM/EDS, the light grey areas were identified as C₂S and C₃S, round grain areas as C₃S, while columnar particles and fake hexagonal flake or plate areas represented C₂S. The dark grey and dark regions represent MgO (M) and pores (P), respectively.

| Table 2. The compositions of the mixture (wt%). |
|-----------------------------------------------|
| Pre-calcined dolomite | Pre-calcined magnesite | Forsterite | H₃BO₃ (additional) | C/S |
| 59.7 | 17.7 | 22.6 | 0.25 | 2.6 |
Figures 4(a)–(d) illustrate the microstructures of samples sintered from 1500 °C to 1650 °C. In figure 4(a), pores (30 ~ 50 μm) in the sample are observed. The number of pores in the structure decreased remarkably, and the large pores disappeared gradually when the sintering temperature increased from 1500 °C to 1650 °C (see figures 4(a)–(d)). Especially when the temperature rose to the range of 1600 °C to 1650 °C (figures 4(c), (d)), pores became almost invisible. After sintering at 1650 °C, areas of homogeneously distributed MgO grains in the calcium silicate matrix (figure 4(d)) can be seen in the SEM image. In figure 4(e), MgO grains (dark grains) can be seen as sub-rounded or rounded grains bordered by the C2S and C3S matrix. Therefore, MgO is protected from the moist environment. Moreover, the bright areas at grain boundaries and triple junctions represent C4AF or C2F filling the gaps in the ceramic composites’ matrix. The decrease in the number and size of pores can be attributed to the formation of low melting point phases (CA and C4AF), the transformation of mass transfer mode; and filling of pores, grain boundaries, and triple junctions. The decrease in the number and size of pores amplified the samples’ densification. Thus, the samples show a homogeneous microstructure at a high soaking temperature.

According to the analysis of SEM and EDS results, CaO was transformed into stabilised phases such as C2S and C3S. There is non-existent free CaO at 1500 °C–1650 °C, which is consistent with the analysis results of the phases’ composition.
Figure 4. Microstructural evolution of the samples as observed by backscattered SEM on polished surfaces after being sintered at different temperatures: (a) 1500 °C, (b) 1550 °C, (c) 1600 °C, (d, e) 1650 °C.

Figure 5. Bulk density (a) and apparent porosity (b) of samples after sintering at different temperatures.
3.3. Bulk density and apparent porosity

Bulk density and apparent porosity of samples sintered at different temperatures is presented in figures 5(a) and (b), respectively. As shown in figure 5(a), the values of bulk density of the samples increased from 2.31 to 3.07 g cm\(^{-3}\) as the sintering temperature rose from 1500 °C to 1600 °C. But the value of bulk density had a slight decrease to 3.05 g cm\(^{-3}\) as the temperature further increased to 1650 °C, which is ascribed to the thermal expansion of vapour in the closed pores caused by excessive burning. The maximum value of bulk density is 3.07 g cm\(^{-3}\) at 1600 °C. However, the values of apparent porosity show an opposite trend to that of the bulk density. In figure 5(b), apparent porosity started with a bigger value (13.2% at 1500 °C) then the value decreased to 4.9% as the sintering temperature increased from 1500 °C to 1600 °C. A slight increase (1.9%) in apparent porosity happened when the sintering temperature further increased to 1650 °C from 1600 °C. The densification process occurring with rising sintering temperature may be due to the improvement of microstructure.

3.4. Hydration resistance

It is known that refractories containing CaO or MgO easily hydrolyse in a wet environment. But MgO has a higher hydration resistance than CaO which has a more fragile Ca–O bond in a moist environment. The hydration of refractories containing CaO or MgO usually leads to destruction of material structure and frequent weakening of functions, which took a lot of research effort to solve in past decades. However, few researchers pay attention to the hydration resistance of magnesia-doloma refractories prepared from low-grade raw materials.

The samples’ percentage weight gained after hydration is shown in figure 6. Our study found that the samples’ weight gained decreased from a maximum of 0.30% to 0.03% with an increase of sintering temperatures from 1500 °C to 1600 °C, implying that there exists an effective limitation reaction between the composites and water or moisture. The preferable hydration resistance may due to the following reasons:

(i) Free CaO was transferred into more stable calcium silicates (C\(_2\)S and C\(_3\)S), which is the main reason for the improved hydration resistance. At about 1000 °C–1200 °C, CaO reacted with MgO·SiO\(_2\) in a solid state reaction, according to the equation:

\[
2\text{MgO} \cdot \text{SiO}_2(s) + 2\text{CaO}(s) \rightarrow 2\text{CaO} \cdot \text{SiO}_2(s) + 2\text{MgO}(s)
\]  

(1)

The residual free CaO reacted with 2CaO·SiO\(_2\) further in accordance with the equation:

\[
2\text{CaO}(s) + 2\text{CaO} \cdot \text{SiO}_2(s) \rightarrow 3\text{CaO} \cdot \text{SiO}_2(s)
\]  

(2)

The amount of C\(_3\)S increased with the reduction of C\(_2\)S until free CaO was completely consumed. Therefore, free CaO did not occur, but transferred into more stable calcium silicates (C\(_2\)S and C\(_3\)S). Hydration resistance of CaO-containing refractories is improved from this intrinsic property.

(ii) MgO was isolated by calcium silicates that are resistant to hydration.
(ii) Low melting point phases occurred, resulting in the decreased amounts and size of pores, and a more compact structure with a smaller active specific surface area, thus the possibility of contact between refractories and wet environment decreased.

4. Conclusions

Three low-grade minerals improve the hydration resistance of magnesia–doloma refractories by forming a MgO–2CaO·SiO₂–3CaO·SiO₂ composite, and the influence of sintering temperature on this composite developed from low-grade ores was evaluated. The results show that:

- Impurities (Fe₂O₃ and Al₂O₃) in the low-grade ores are helpful in improving hydration resistance of MgO–2CaO·SiO₂–3CaO·SiO₂ composites by forming low melting phases (C₃AF and C₃F) which enhance the calcination process and the composites’ densification.
- The hydration resistance improves with rising sintering temperature; the lowest weight gained is only 0.03%. The preferable hydration resistance mainly suggests free CaO did not occur, but was converted into more stable calcium silicate (C₂S and C₃S). Furthermore, the relative content of MgO content increased, and stable calcium silicates protected MgO from the moist environment.
- The densification process occurring with rise in sintering temperature may be due to the improvement of microstructure. The densification of composites is optimum after sintering at 1600 °C with a bulk density of 3.13 g cm⁻³ and an apparent porosity of 4.6%. Densification promotes improving hydration resistance.

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