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Development of cordierite-mullite refractory castables bonded with magnesium silicate hydrate cement

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Abstract

Cordierite-mullite refractory materials are widely used as kiln furniture in the ceramic industry due to their excellent thermal shock resistance and high mechanical strength at elevated temperatures. Cordierite-mullite ceramics possess excellent mechanical strength and thermal shock resistance, making them well-suited for kiln furniture. This research explores the development of cordierite-mullite refractory castables using a magnesium silicate hydrate (MSH) cement as a novel bonding system. Castables were prepared with varying molar ratios of MgO to SiO_2 (0.75 to 4) and characterized for their physical, mechanical, and thermal properties. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses revealed the formation of MSH cement phase at room temperature, which decomposed upon firing to form spinel and ultimately cordierite at high temperatures. The optimal MgO to SiO_2 molar ratio of 1 yielded the best physical properties, including a modulus of rupture (MOR) of 13.41 MPa after sintering at 1350 °C, bulk density of 2.01 g/cm^3, apparent porosity of 22.45%, and thermal expansion coefficient of 2.59×10^{-6} °C^{-1}. The microstructural evolution showed the transformation from loosely bound particles in the green state to a well-sintered cordierite matrix embedding mullite aggregates after firing. The developed castables exhibited properties comparable to commercial cordierite-mullite kiln furniture, demonstrating their potential as a viable option for high-temperature ceramic applications.

Keywords: Cordierite; Mullite; Magnesium silicate hydrate cement; Refractory castables

Introduction

Cordierite-mullite refractory materials are extensively used as kiln furniture in the ceramic industry due to their outstanding thermal shock resistance, and high mechanical strength up to 1300 °C [1-3]. These properties arise from the combination of cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) and mullite ($3Al_2O_3{\cdot}2SiO_2$) phases present in these materials. The low thermal expansion coefficient of cordierite enables the refractory materials to withstand the temperature changes during kiln firing without cracking or breaking. Additionally, the high mechanical strength of mullite allows the refractories to support the weight of ceramic products and maintain their shape during firing. The synergistic combination of these two phases makes cordierite-mullite refractories ideal for use as kiln furniture in various ceramic manufacturing processes.

Cordierite-mullite refractories typically comprise coarse aggregates and a fine matrix. Typical coarse aggregates are based on calcined clays or chamottes, andalusite, and recycled cordierite-mullite grains, in the size range of 1-10 mm. The fine matrix incorporates calcined alumina, silica, and magnesia, often as magnesium carbonate or magnesium hydroxide, which convert to cordierite upon firing at 1350 °C. The types and proportions of raw materials in the aggregate and matrix determine not only the relative amounts of cordierite and mullite phases produced during firing but also determine the final properties of the castable, such as thermal shock resistance, mechanical strength, and porosity.

Refractory castables offer a versatile and cost-effective solution for producing kiln furniture components with complex shapes and custom designs. Unlike traditional shaped kiln furniture, which is limited to standard shapes and sizes, castables can be easily molded into various forms, allowing manufacturers to create kiln furniture tailored to their specific needs. The design flexibility offered by refractory castables enables manufacturers to optimize the performance and functionality of their kiln furniture components, improving the overall efficiency of their ceramic production processes.

Previous studies developed cold-setting cordierite-mullite castables using the magnesium-phosphate chemical bond [1-3]. This type of bond is formed through an acid-base reaction between magnesium compounds and phosphates in aqueous solution. The sources of phosphate could be monoaluminum phosphate [1], ammonium dihydrogen phosphate [2], or phosphoric acid [3]. However, the phosphates can act as fluxes, lowering the melting point of the system, which can decrease refractoriness in high-temperature applications [2]. This negatively affects the performance of the castables, as phosphates promote liquid phase formation at lower temperatures, leading to softening, deformation, or failure of kiln furniture components. Consequently, the service life of the kiln furniture is reduced, and the ceramic products being fired may suffer from contamination or damage.

Magnesium silicate hydrate (MSH) cement presents a promising phosphate-free alternative for bonding in refractory castables. Its desirable properties, including high strength, excellent fire resistance, and superior mechanical characteristics, make it particularly suitable for high-temperature applications. The formation of MSH cement involves a complex chemical reaction between light-burned magnesia and a silica source, which is typically silica fume. This process can be described in two main steps that occur simultaneously. In the first step, light-burned magnesia reacts with water to form brucite ($Mg(OH)_2$), following the chemical equations [4]

$$MgO+H_2O \longrightarrow Mg(OH)_2 \qquad (1)$$

Concurrently, in the second step, reactive silica dissolves in water to form silicic acid (H_4SiO_4), which can be represented by the following equation:

$$SiO_2+2H_2O \longrightarrow H_4SiO_4 \qquad (2)$$

The formation of MSH cement can be explained by the interaction of anions and cations from brucite and silicic acid in the solution:

$$Mg(OH)_2 \longrightarrow Mg^{2+}+2OH^- \qquad (3)$$

$$H_4SiO_4 \longrightarrow SiO_4^{4-}+4H^+ \qquad (4)$$

$$3Mg^{2+}+6OH^-+2SiO_4^{4-}+8H^+ \longrightarrow Mg_3Si_4O_5(OH)_4+5H_2O \qquad (5)$$

$$3Mg^{2+}+6OH^-+4SiO_4^{4-}+16H^+ \longrightarrow Mg_3Si_4O_{10}(OH)_2+10H_2O \qquad (6)$$

The resulting product generally exhibits a structure similar to minerals in the talc group ($Mg_3(Si_4O_{10})(OH)_2$) or serpentine group ($Mg_3(Si_2O_5)(OH)_4$), which are minerals with low crystallinity that bind the aggregate particles together [5]. During firing, MSH cement undergoes thermal decomposition and reacts with Al_2O_3 and SiO_2 present in the mixture to form cordierite. This reaction ensures desired phase formation and contributes to overall strength and thermal properties of the refractory castables.

This study aims to prepare cordierite-mullite castables with a MSH cement bond. The phase composition, microstructure, physical properties, and thermal properties were analyzed to understand their potential as ceramic kiln furniture.

Materials and Methods

Cordierite-mullite castables were prepared with 60 wt% coarse fraction (aggregates) and 40 wt% fine fraction (matrix). The aggregates consisted of 0.04-0.6 mm calcined kaolin (Molochite, Imerys, UK). The matrix comprised calcined alumina (P122SB, Alteo, France), 325 mesh milled sand (Q325, Cerasil, Thailand), and light-burned magnesia obtained by calcining magnesium carbonate (Italian-Thai ceramic refractory, Thailand) at 800 °C for 2 hours. Silica fume (SiO_2, Elkem, Thailand) was used as the setting agent to form MSH cement. The raw materials were weighed in proper proportions to synthesize the theoretical cordierite composition.

The aggregate grains, matrix powder, and silica fume were mixed in a Hobart type mixer for 5 minutes at varying molar ratios of MgO to SiO_2 (0.75, 1, 2, 3, and 4). An appropriate amount of distilled water was added to obtain a suitable paste consistency: 17% for molar ratios of 0.75, 1, and 2; 18% for a molar ratio of 3; and 19% for a molar ratio of 4. For each molar ratio, five specimens were prepared by casting the resulting paste into 25 x 25 x 150 mm^3 acrylic molds and vibrated to remove air bubbles. After curing for 24 hours at room temperature, the samples were demolded, dried at 110 °C for 24 hours, and sintered at 1350 °C for 4 hours in an electric furnace under air atmosphere.

The phase composition was analyzed by X-ray diffraction (XRD) on powder samples using a Bruker AXS Model D8 Discover diffractometer with Cu-Kα radiation (λ = 0.15406 nm) at 40 kV and 25 mA. The modulus of rupture (MOR) was measured by 3-point bending tests using a Hungta HT-8116+9635S universal testing machine. Five samples from each batch were tested at room temperature with a load speed of 0.5 mm/min and a support span of 10 cm. Bulk density, water absorption, and apparent porosity were determined by the Archimedes method per ASTM C-20. The linear change and thermal expansion coefficient was measured using a NETZSCH DIL 402SE horizontal dilatometer at a heating rate of 5 °C/min on 5 x 5 x 50 mm^3 samples sintered at 1350 °C.

The microstructure of the samples was examined on the fracture surfaces of the samples using scanning electron microscopy (SEM, JSM-6480LV, JEOL) at various stages of processing: after curing, drying, and sintering. The samples were coated with gold for 180 seconds before being examined in the SEM at an accelerating voltage of 5 kV.

Results and Discussions

1. Physical properties

1.1 Modulus of rupture

The modulus of rupture (MOR) of the MSH cement-bonded castables was evaluated at various processing stages using 3-point bending tests (Fig. 1). In the green castable samples, the initial MOR increased as the molar ratio of MgO to SiO_2 decreased from 4 to 1 (Fig. 1a). This trend is attributed to the formation of the MSH cement phase, which serves as a binding agent, strengthening the samples.

Decreasing the MgO to SiO_2 molar ratio effectively increases the amount of silica fume in the mixture, allowing more MSH cement to form. The maximum green MOR of 0.78 MPa was achieved at a molar ratio of 1. However, further reducing the molar ratio to 0.75 led to a decrease in MOR, likely due to excess unreacted silica fume. Despite the relatively low green strength, it was sufficient for demolding and handling the castables without damage.

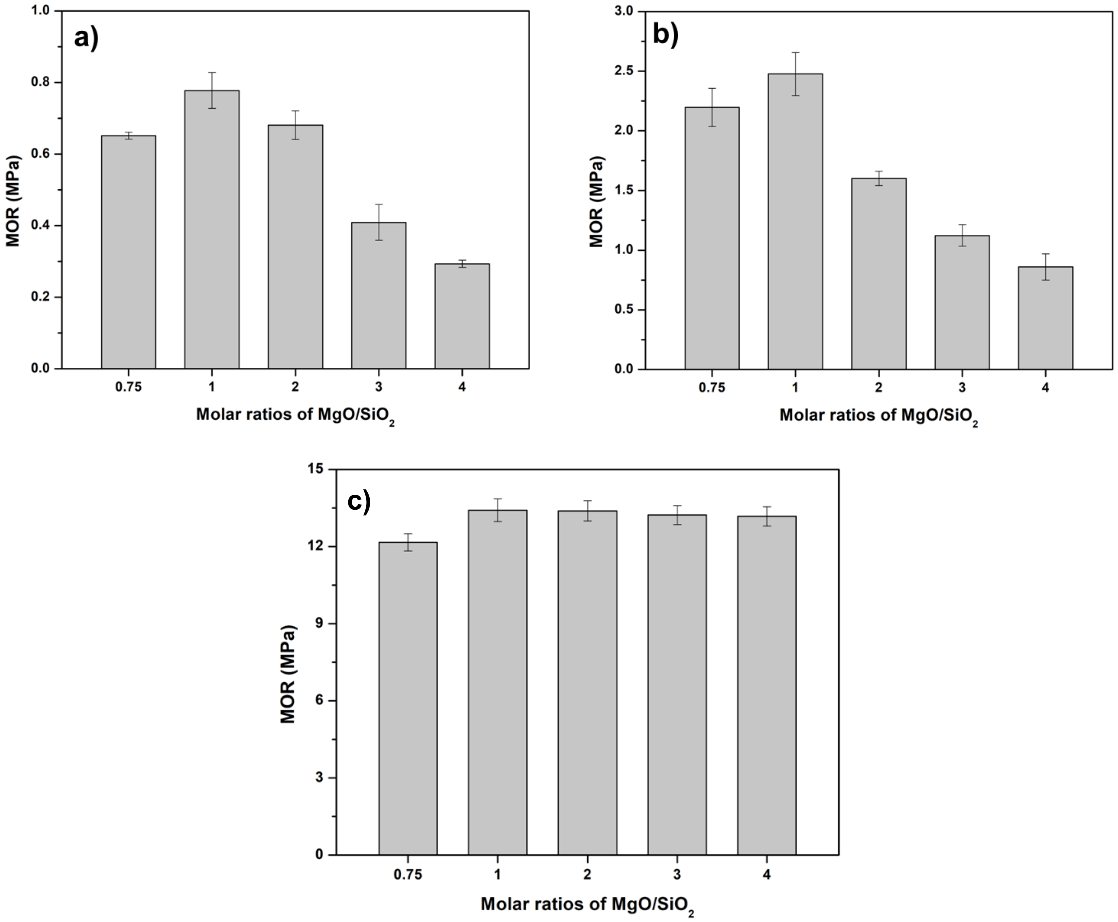

Fig. 1. Modulus of rupture of the MSH cement-bonded castable at varying molar ratios of MgO to SiO_2 (a) after curing at room temperature, (b) after drying at 110 °C, and (c) after sintering at 1350 °C.

After drying at 110 °C, the MOR values aligned with and exceeded those of the green samples (Fig. 1b). This significant increase can be attributed to water loss, which causes particle compaction and stronger interparticle bonding. Furthermore, water evaporation increases the concentration of anions and cations from brucite and silicic acid in the solution, promoting additional crystallization of the MSH cement phase. The newly formed MSH cement particles penetrate into pores between particles, creating a denser structure and binding aggregates together, which further enhances the strength. At a molar ratio of 1, the maximum MOR after drying reached 2.50 MPa.

After sintering the samples at 1350 °C, the flexural strength became similar across all MgO to SiO_2 molar ratios (Fig. 1c). The maximum MOR of 13.41 MPa was observed at a molar ratio of 1. The decrease in flexural strength at the 0.75 ratio suggests that an excess of silica may be detrimental to the high-temperature properties of the castable.

1.2 Bulk density, apparent porosity, and water absorption

Fig. 2 illustrates the bulk density, apparent porosity, and water absorption of the MSH cement-bonded castables at various MgO to SiO_2 molar ratios (0.75, 1, 2, 3, and 4) after sintering at 1350 °C. While these properties remained relatively consistent across the different molar ratios, a subtle trend was observed: as the MgO to SiO_2 molar ratio decreased, the bulk density tended to slightly increase, while the apparent porosity and water absorption marginally decreased.

The optimal properties were achieved at a molar ratio of 1, yielding the highest bulk density of 2.01 g/cm^3, corresponding to the lowest apparent porosity and water absorption of 22.45% and 11.19%, respectively. This improvement can be attributed to the fine particle size of silica fume, which effectively fills the gaps between coarser particles, resulting in a denser structure. Additionally, silica fume enhances the flowability of the mixture [6], reducing the water required for casting.

During the drying and firing processes, water evaporation creates pores. However, the reduced water content in the silica fume-rich mixtures leads to fewer pores, thereby decreasing apparent porosity and increasing bulk density. This structural enhancement contributes to the higher modulus of rupture observed after firing, as shown in Fig. 1.

Interestingly, when the molar ratio was further reduced to 0.75, a slight reversal in this trend was observed. The density decreased while apparent porosity and water absorption increased marginally. This phenomenon can be explained by the excess of fine particles creating additional voids, which compromises the overall compactness and density of the structure

Fig. 1 and 2 demonstrate that the MSH cement-bonded castable with a MgO to SiO_2 molar ratio of 1 exhibits superior physical properties compared to castables with other molar ratios. This optimal composition yields the highest flexural strength and bulk density, while achieving the lowest apparent porosity and water absorption. Based on these favorable characteristics, samples with a MgO to SiO_2 molar ratio of 1 were selected for more detailed characterization studies.

2. Phase composition

X-ray diffraction (XRD) analysis was employed to characterize the crystalline phases present in the MSH cement-bonded castable with a MgO to SiO_2 molar ratio of 1 at various temperatures (Fig. 3). In the green samples, XRD patterns revealed the presence of quartz (SiO_2), mullite ($3Al_2O_3{\cdot}2SiO_2$), and corundum (Al_2O_3) phases, originating from the raw materials used in the mixture. Additionally, a brucite phase ($Mg(OH)_2$) was detected, indicating an incomplete reaction between MgO and silica fume to form the MSH cement phase during the hydration process [7].

Notably, The MSH cement phase, which served as the binding agent, was not detected in the green samples. This absence can be attributed to two main factors. Firstly, the samples were cured at room temperature for only 24 hours, likely resulting in low crystallinity of the MSH cement phase. Secondly, the quantity of the MSH cement phase formed may be comparatively small relative to the other crystalline phases present in the mixture. These factors combined make it challenging to clearly identify the MSH cement phase using XRD analysis under these conditions.

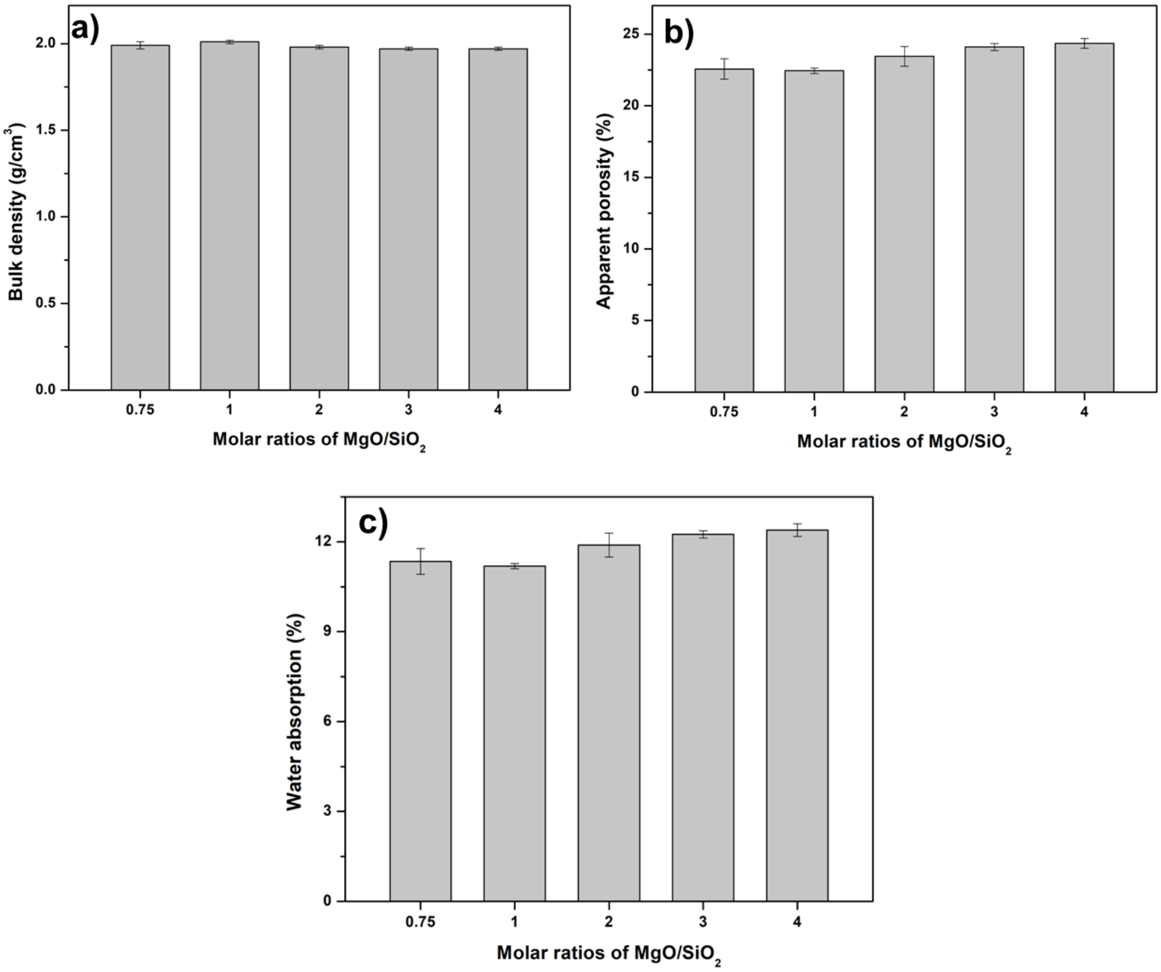

Fig. 2. (a) bulk density, (b) apparent porosity, and (c) water absorption of the MSH cement-bonded castable at varying molar ratios of MgO to SiO_2.

To observe the MSH cement phase more clearly, an additional experiment was conducted using the fine portion composed of MgO and silica fume with the MgO to SiO_2 molar ratio of 1. The mixture was cured for 28 days to allow sufficient time for the MSH cement phase to crystallize. The XRD pattern of this sample is shown in Fig. 4. This extended curing time revealed the presence of brucite, which forms when MgO reacts with water but does not undergo the hydration reaction with silica fume. More importantly, broad peaks were observed in three 2-theta ranges: 20 to 27 degrees, 32 to 37 degrees, and 58 to 62 degrees. These broad peaks, characteristic of low crystallinity [8, 9], indicated the presence of both silica fume and the MSH cement phase. Specifically, the broad peak in the 20 to 27 degree range is associated with silica fume, while those in the ranges of 32 to 37 degrees and 58 to 62 degrees are characteristic of the MSH cement phase ($Mg_8Si_8O_{20}(OH)_8 \cdot 12H_2O$), consistent with findings reported by Zhang, T., et al. [10]. These results confirm that extended curing time allows the MSH cement phase to crystallize sufficiently to become more detectable.

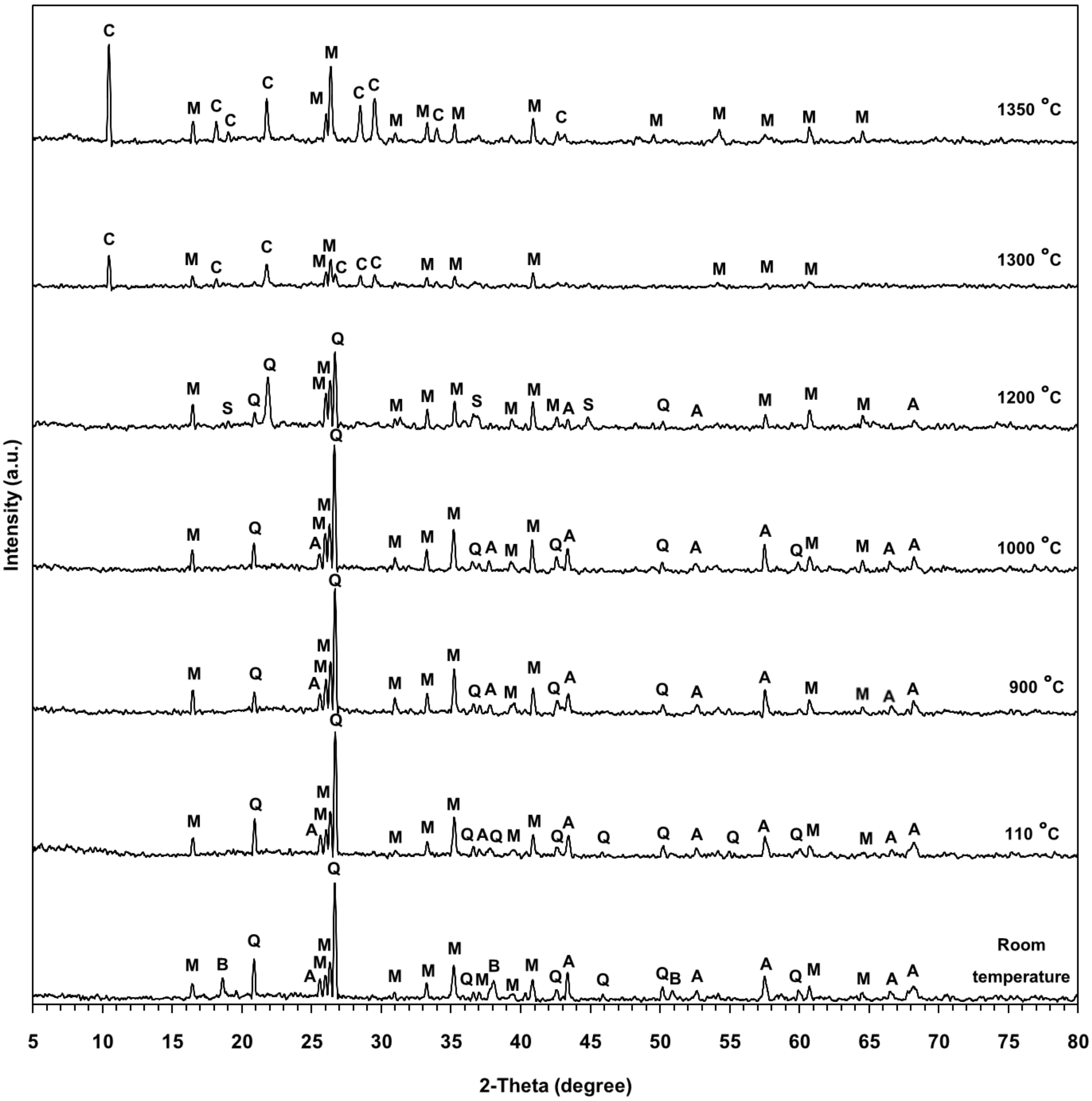

Fig. 3. XRD pattern of the MSH cement-bonded castable at MgO to SiO_2 molar ratio of 1 at different temperatures. C=cordierite, M=mullite, A=alumina, B=brucite, Q=quartz, S=spinel.

After drying at 110 °C, the brucite phase disappeared while quartz, mullite, and corundum phases remained. This suggests that brucite further reacted with silica fume to form the MSH cement phase. Water evaporation likely increased the relative concentration of Mg^{2+},OH^{-}, and SiO_4^{4-} ions, promoting further crystallization of MSH cement

At 1000 °C, the sample composition remained largely unchanged, with quartz, mullite, and corundum phases still present. However, at 1200 °C, magnesium aluminate spinel ($MgAl_2O_4$) appeared, formed by the reaction between magnesium and alumina, coexisting with the previously observed phases.

A significant transformation occurred in samples sintered at 1300 °C, with the appearance of peaks corresponding to crystalline cordierite alongside mullite. The cordierite phase likely formed through a high-temperature reaction involving quartz, alumina, and spinel phases. Further sintering at 1350 °C resulted in more intense peaks for both cordierite and mullite phases, indicating increased crystallization or grain growth.

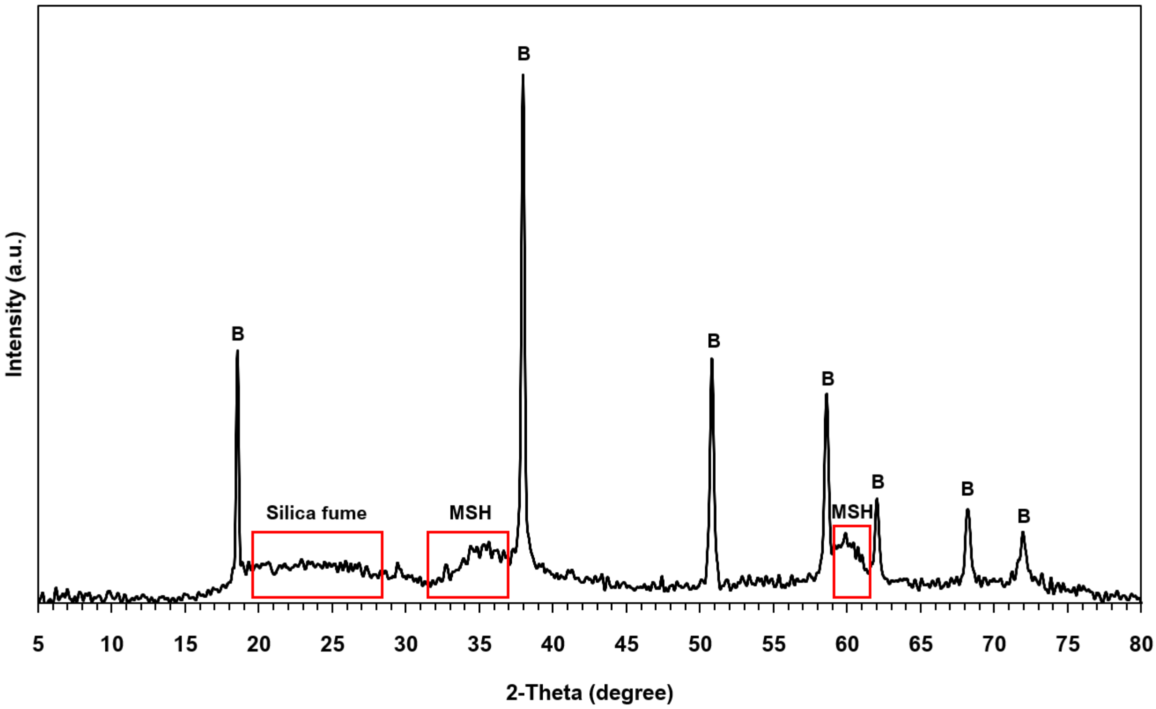

Fig. 4. XRD pattern of the MSH cement after curing 28 days
B=brucite, MSH=Magnesium silicate hydrate cement phase.

3. Microstructure

The microstructure of the MSH cement-bonded castable with a MgO to SiO_2 molar ratio of 1 at various stages of processing was examined using scanning electron microscopy (SEM) imaging (Fig. 5). In the green castable (Fig. 5a), the microstructure consists of large angular particles of raw materials surrounded by numerous small spherical silica fume particles. This initial arrangement provides insight into the distribution of components before any thermal processing.

Upon drying at 110 °C (Fig. 5b), a notable change in the microstructure was observed. Spherical MSH cement particles almost entirely covered the surface of the larger particles, with some penetrating into the pores, resulting in a more compact structure. This structural change correlated with the improved MOR observed at this stage, as shown in Fig. 1.

The characteristic spherical morphology of these MSH cement particles is attributed to the specific hydration process between silica fume and MgO in water. Silica fume, an amorphous compound with high reactivity, quickly interacts with MgO primarily on the surface of the silica fume particles. This surface reaction leads to the formation of MSH gel around these particles, resulting in their spherical shape [11].

After sintering at 1350 °C (Fig. 5c), the microstructure underwent a significant transformation. The mullite aggregates became embedded in the sintered cordierite matrix, which effectively bound the particles together [12]. This high-temperature transformation, coupled with the formation of high-temperature phases confirmed by XRD analysis (Fig. 3), led to a robust microstructure. The strengthened structure is reflected in the substantially increased MOR of 13.41 MPa.

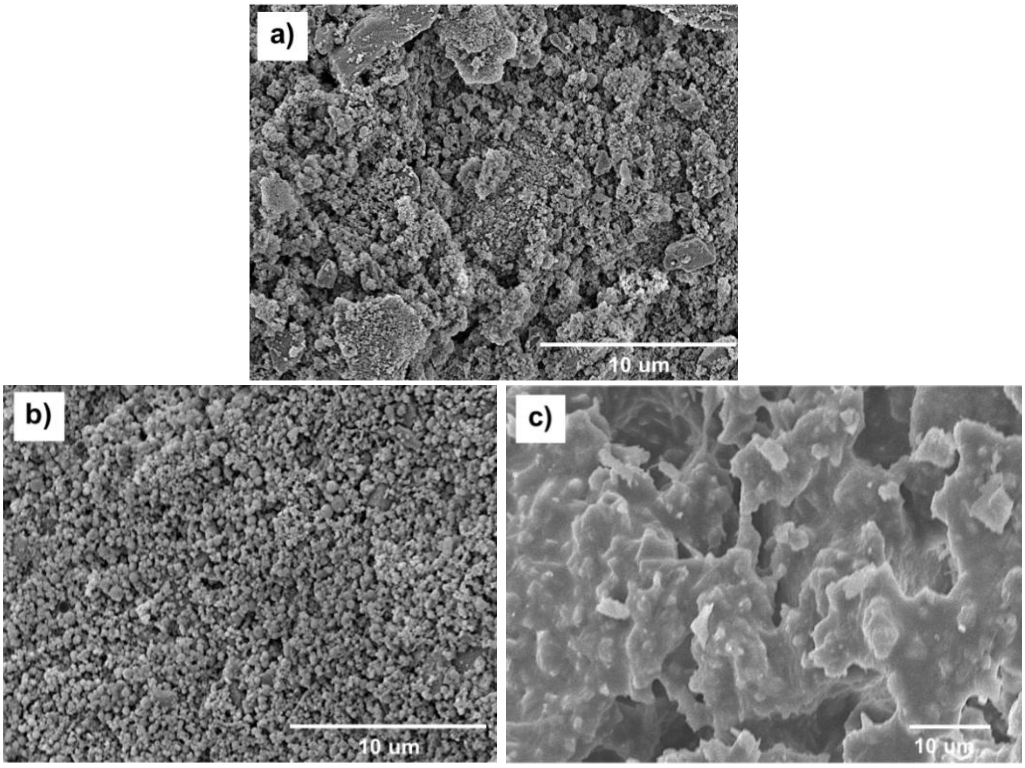

Fig. 5. SEM images of the fracture surface of the MSH cement-bonded castable at MgO to SiO_2 molar ratio of 1 (a) after curing at room temperature, (b) after drying at 110 ˚C, and (c) after sintering at 1350 ˚C.

4. Thermal Expansion

The thermal expansion behavior of the MSH cement-bonded castable with the MgO to SiO_2 molar ratio of 1 after sintering at 1350 °C was analyzed using a dilatometer (Fig. 6). The sample exhibited progressive expansion as the temperature increased from 100 to 1000 °C. Notably, at 1000 °C, the sample maintained its structural integrity without any signs of deformation due to melting. This thermal stability at high temperatures is a crucial characteristic for its intended application as kiln furniture. The thermal expansion coefficient, calculated over the temperature range of 100 to 1000 °C, was found to be 2.59×10^{-6} $°C^{-1}$. This relatively low expansion coefficient contributes to the thermal shock resistance of the material, further enhancing its suitability for high-temperature applications in ceramic manufacturing processes.

5. Comparison of the physical properties of the MSH cement-bonded cordierite-mullite castable developed in this study and commercial cordierite-mullite kiln furniture.

The physical properties of the newly developed MSH cement-bonded cordierite-mullite castable with the MgO to SiO_2 molar ratio of 1 were evaluated against those of commercial cordierite-mullite kiln furniture. The comparative data, presented in Table 1, indicate that the properties of the developed castable are similar to those of commercial cordierite-mullite kiln furniture. This close alignment in physical characteristics suggests that the MSH cement-bonded castable shows considerable promise as an alternative material for kiln furniture in ceramic firing applications.

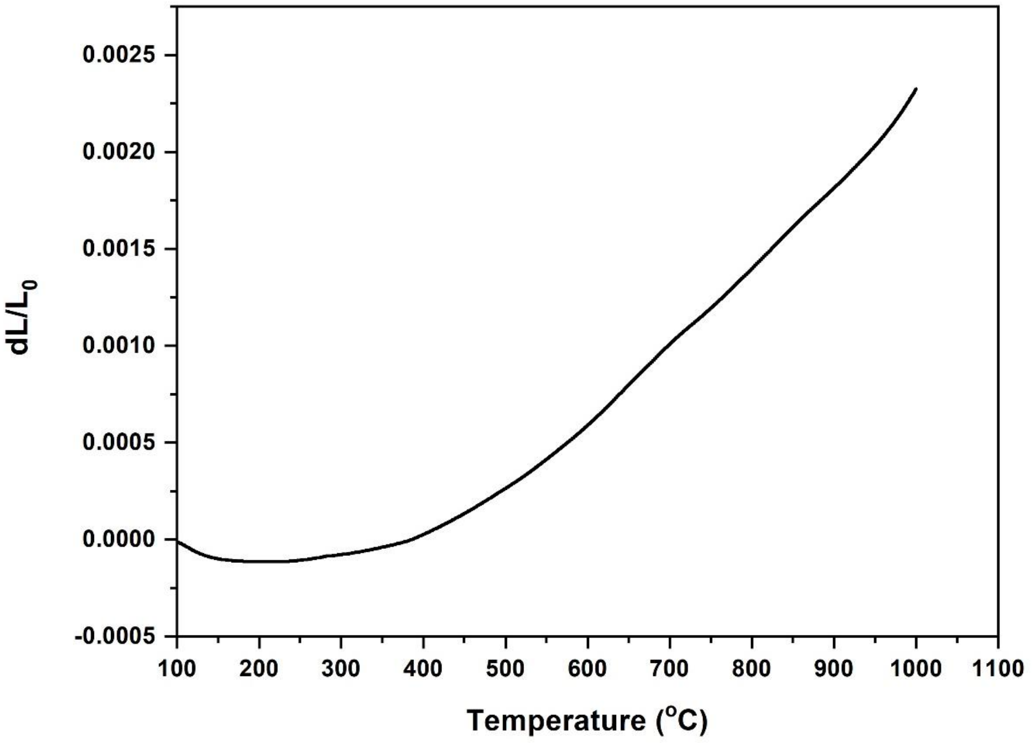

Fig. 6. Thermal expansion of the MSH cement-bonded castable at MgO to SiO_2 with a molar ratio of 1.

Table 1 Comparison of the physical properties of the MSH cement-bonded cordierite-mullite castable developed in this study and commercial cordierite-mullite kiln furniture.

Properties	**This Study**	**Commercial Product**
MOR after curing at room temperature (MPa)	0.78	-
MOR after drying at 110 °C (MPa)	2.50	-
MOR after sintering at 1350 °C (MPa)	13.41	12.21
Bulk density (g/cm^3)	2.01	1.85
Apparent porosity (%)	22.45	26.52
Water absorption (%)	11.19	13.64
Thermal expansion coefficient at 100-1000 °C ($x10^{-6}$ $°C^{-1}$)	2.59	2.72

Note: Commercial products supplied by Italian-Thai Ceramic Refractory Co.,Ltd

Conclusion

This research demonstrated that magnesium silicate hydrate (MSH) cement can effectively serve as a phosphate-free bonding system for cordierite-mullite refractory castables, showing promise for use as kiln furniture in the ceramic industry. The molar ratios of MgO to SiO_2 in the MSH cement played a crucial role in influencing the properties of castables. Silica fume reacted with brucite to form the MSH cement phase, which acted as a binder, providing strength to the green samples. Upon firing, a notable phase evolution was observed: at 1200 °C, the MgO that decomposed from the MSH cement reacted with alumina to form spinel, which further reacted with additional alumina and silica to form cordierite at 1300 °C. This phase transformation contributes to the high-temperature strength of the material. Microstructural analysis using SEM showed that MSH cement particles filled the gaps between coarse particles, increasing the density of castables. As the MgO to SiO_2 molar ratio decreased, the physical properties of the castables improved, with the optimal ratio found to be 1. It achieved the highest modulus of rupture after casting, drying, and sintering of 0.78, 2.50, and 13.41 MPa, respectively. Additionally, it demonstrated suitable bulk density, apparent porosity, and thermal expansion characteristics for high-temperature refractory applications.

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