

Review

Magnesium Oxychloride Cement: Development, Opportunities and Challenges

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Abstract: Magnesium oxychloride cement (MOC), an alternative to ordinary Portland cement (OPC), has attracted increasing research interest for its excellent mechanical properties and its green and sustainable attributes. The poor water resistance of MOC limited its usage mainly to indoor applications; nevertheless, recent advances in water-resistant MOC have expanded the material's potential applications from indoor to outdoor. This review aims to showcase recent advances in MOC, including water-resistant MOC and ductile fiber-reinforced MOC (FRMOC), exploring their potential applications including in sustainable construction for future generations. The mechanism under different curing procedures such as normal and CO₂ curing and the effect of different inorganic and organic additives on the water resistance of MOC composites are discussed. In particular, the review highlights the recent developments in achieving over 100% strength retention under water at 28 days as well as advancements in FRMOC, where tensile strength has surpassed 10 MPa with a remarkable strain capacity ranging from 4–8%. This paper also sheds light on the potential applications of MOC as a fire-resistant coating material, green-wood-MOC composite building material, and in reducing solid waste industrial byproduct accumulations. Finally, this study suggests future research directions to enhance the practical application of MOC.

Keywords: CO₂ curing; green cement; magnesium oxychloride cement (MOC); water resistance; fiber-reinforced MOC (FRMOC)



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1. Introduction

Magnesium oxychloride (MOC) was discovered for the first time by Stanislas Sorel in 1867, hence it is also referred to as Sorel cement [1]. It is an eco-friendly and nonhydraulic cement developed by blending magnesia (light burnt MgO) with a concentrated magnesium chloride (MgCl₂) solution. MOC has gained favorable attention due to its many characteristics that distinguish it from ordinary Portland cement (OPC). OPC production is an energy-intensive process and a leading source of CO₂ emissions, responsible for 5–10% of global greenhouse gas emissions. Studies have reported that approximately 0.85 tons of CO₂ are emitted for every ton of OPC produced [2,3]. This substantial release of CO₂ poses significant environmental risks, including ozone depletion and exacerbation of global warming, underscoring the urgent need for more sustainable cement and production methods. On the other hand, the manufacturing of MgO, the main raw material of MOC, requires lower temperatures (<1000 °C) making it an energy-efficient alternative [4]. Moreover, the resulting cement using MgO also has high mechanical strength [5], air hardening ability, light weight, low thermal conductivity [6], good abrasion resistance [7], and resistance to oils, greases, and paints [8]. In addition, MOC possesses high early-age strength and has good bonding potential with various fillers, including gravel, sand, wood particles, expanded clays, asbestos, and marble dust [6,9,10]. MgO could also capture the greenhouse gas CO₂ to generate a variety of carbonates and hydroxy carbonates, making MOC a green and “carbon-neutral” cement [11].

Over the past few decades, extensive research has been conducted to investigate the strength development, reaction mechanism, and microstructure of the MgO-MgCl₂-H₂O ternary system. MOC production typically creates four primary reaction crystal phases, i.e., phase 2 (2Mg(OH)₂·MgCl₂·4H₂O), phase 3 (3Mg(OH)₂·MgCl₂·8H₂O), phase 5 (5Mg(OH)₂·MgCl₂·8H₂O), and phase 9 (9Mg(OH)₂·MgCl₂·5H₂O) [12]. The crystallization of such primary reaction phases is influenced by several significant factors, including the reactivity of MgO [13], MgO/MgCl₂ molar ratio, curing conditions [14], and chemical admixtures [10,15]. Phases 2 and 9 stabilize when the curing temperature exceeds 100 °C, whereas phases 3 and 5 remain stable at temperatures below 100 °C. Phases 3 and 5 are described as scroll-tubular whiskers that resemble well-crystallized needles. The interlock and compact microstructure that occurs during the production of these phases make them the main reaction products that are responsible for the hardening and strength development of MOC. Phase 5 also undergoes rapid development, initiating approximately two hours after paste blending, and exhibits good void-filling characteristics, leading to a compact microstructure with minimal porosity. As a result, phase 5 is the preferred phase in the design of MOC.

Despite the unique characteristics and advantages of MOC, it faces significant challenges in its use as a structural material. Firstly, MOC has very poor water resistance capability. It significantly degrades in a moist environment as a result of the leaching of MgCl₂, causing a loss in strength. Existing research has revealed that the compressive strength drastically decreases when MOC is soaked in water, owing to the transition of phases 3 and 5 [16,17]. In consequence, the damaged matrix also considerably accelerates the process of water infiltration, increasing deterioration and creating a vicious circle of continuing damage [18]. In recent years, significant contributions have been made by researchers to enhance the water resistance of MOC [8,19,20]. Various additives such as silica fume [19,21], fly ash (FA) [22], sulphates [23,24], nanomaterials [25,26], silica glass [27], active silica, and soluble phosphates or phosphoric acid (PA) [28,29] have been incorporated in MOC to obtain a dense matrix and water-stable hydration products [8,19,30], with some breakthrough in the development of water-resistant MOC. Past studies found that these additives facilitate the development of gel-like phase 5 and may induce the transformation of the micromorphology of phase 5, which may be the possible reason for its improved water-resistant behavior [8,20]. Li et al. [30] extensively examined the effect of silica fume and FA on the water resistance of MOC, observing improved water resistance due to the formation of silicate 5.1.8 gel or alumina-silicate 5.1.8 gel in MOC modified with these additives. Guo et al. [19] incorporated silica fume and a hybrid of FA and silica fume into MOC, achieving high compressive strength retention of around 100% and 95% with 28-day and 56-day water immersion, respectively, for a mix containing 15% FA and 15% silica fume. They attributed the improved water resistance to the formation of Mg-Cl-Si-H gel and the filler effect of FA and silica fume, resulting in a densified MOC matrix. These studies show that the incorporation of SCMs has the potential to produce water-resistant MOC.

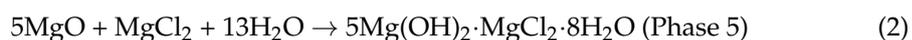
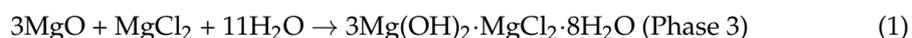
In addition to the issue related to water resistance, MOC is unsuitable for steel reinforcement. It is because of the chemical composition of the MOC which contains approximately 1.5–6% free chloride ions thus making MOC matrix more vulnerable to corrosion [31]. Chlorine ions are recognized to be a type of very potent depassivator. Its high concentration can break the passivating film of steel under low alkalinity conditions, which causes significant corrosion [12,32]. Moreover, the susceptibility of MOC to failure under tension and its poor durability are other main flaws. Significant dimensional instability, poor weathering resistance, and the discharge of corrosive solutions upon steel reinforcements have all hindered MOC from being widely used in civil engineering infrastructures [32,33]. Despite the above-mentioned challenges, MOC has been regarded as intrinsically fire-resistant [11,34] attracting practical implementation in fire-resisting infrastructural applications like cladding and façade. However, the research efforts in this area are minimal, and to date, the systematic research work conducted to evaluate the mechanical performance of MOC-based composites at elevated temperatures is very

scarce [35]. Nonetheless, some past studies have shown that MOC has the potential to be used as a fireproof coating material and can resist high temperatures without deteriorating the interior substrate [11,34,36].

Despite the extensive research and development, there remains a lack of studies which systematically summarize the findings focusing on the primary potential applications of MOC such as outdoor and fire-resistant applications. On account of the evident potential of MOC across various civil engineering applications, there is a need for a comprehensive review to aid ongoing researchers and engineering practitioners in understanding the developments, challenges, and future investigations. Therefore, this review attempts to bridge this gap by comprehensively summarizing the recent advancements in principal application domains of MOC. The paper is structured as follows. First, the strength development mechanism of MOC is introduced in Section 2. The curing method, including normal curing and CO₂ curing of MOC, and the effect of curing on the mechanical properties of MOC are explained in Section 3. Section 4 describes the effect of SCMs, including fly ash, ground granulated blast furnace slag (GGBFS), and metakaolin (MK) on the properties of MOC. The recent research and development of ductile FRMOC-based composites and water-resistant MOC are presented in Sections 5 and 6, respectively. The application of MOC as a fire-resistive material and in solid waste management are discussed in Sections 7 and 8, respectively. The application of MOC and wood as a composite building material is also covered before the conclusion, which also indicates the future research needed to further advance MOC application.

2. Strength Development Mechanism of MOC

MOC is a potential construction material with relatively high compressive strength, elastic modulus, and flexural strength [37–39]. The developed hydration products and microstructure of MOC have a significant impact on its strength development. The primary phases in MOC consist of MgO, Mg(OH)₂, and crystalline phases (phases 3 and 5). The phases are produced through the hydration process of MOC as represented in Equations (1)–(3) [40].



Particularly, the development of phase 5 crystals has generally been considered as the most desired reaction product, and it is largely recognized that the fast development of interlocked phase 5 crystals had a significant role in the mechanical characteristics of MOC [12,41]. Needle-shaped phase 5 crystals formed during hydration extend into gaps, growing in a staggered and interlocking manner, leading to a dense microstructure and significant strength increase [42]. Sglavo et al. [43] found that the hardening behavior and strength characteristics of MOC were primarily due to the development of needle-shaped phase 3 and phase 5 crystals within the matrix. Further, they mentioned that these crystals exhibit robust growth characteristics within the porous zones, resulting in a denser and more compact matrix.

Moreover, Matkovic et al. [44] suggested that the earlier hardening and commencement of stiffness were produced by the dense and compacted microstructure which was driven by needles (phase 5 crystals) produced in regions of porosity. The development of strength was due to the crystal phases' free growth into a denser structure. In addition to this, the fast chemical reaction of MgO with high reactivity may also result in an immediate increase in strength [44]. MgO is classified into three types based on the calcination temperature, resulting in different reactivity levels [45,46].

- (a) Dead-burned magnesia: High-temperature calcination (1500–2000 °C) reduces available surface area, resulting in unreactive MgO.

- (b) Hard-burned magnesia: Calcination temperatures ranging from 1000–1500 °C yield MgO with limited reactivity.
- (c) Light-burned magnesia: Produced at 600–1000 °C, also known as caustic calcined magnesia, this form exhibits a reactive nature.

Harper et al. [47] investigated the impact of MgO calcined at temperatures between 600–1000 °C on the compressive strength of MOC. They observed a rise in compressive strength with increasing calcination temperature from 600 to 800 °C. However, no significant difference in compressive strength was noted between temperatures ranging from 800 to 1000 °C. Avanish et al. [45] also investigated the effect of MgO reactivity by analyzing the compressive strength of MOC with MgO calcined at varying temperatures. They observed that the 1-day (d) compressive strength of MgO (calcined at 600 °C) modified MOC ranged from 5 to 7 MPa, significantly lower than the 1-day strength of 25–32 MPa for MgO (calcined at 900 °C) modified MOC. Furthermore, MgO calcined at 1500 °C (dead-burned magnesia) failed to set even after 24 h. Avanish et al. [45] further recommended MgO calcined at 900 °C as optimal for MOC manufacturing. In summary, the discussion indicates that MgO calcined within the range of 800–900 °C may be best suitable for MOC production.

3. Curing Mechanism of MOC

3.1. Normal Curing of MOC

MOC can be cured at ambient temperatures (22–26 °C) and with a relative humidity of $60 \pm 5\%$, in contrast to OPC, which is typically cured at a relative humidity of 90–95% at room temperature [12,13,22,41]. Since the primary MOC phases are temperature-sensitive, it is crucial to regulate the curing temperature of MOC as otherwise the performance can be significantly affected. Sglavo et al. [43] examined the development of MOC pastes at a range of curing temperatures from 5–40 °C to imitate standard industrial processing settings and identify the optimum parameters for the development of MOC with a high level of chemical and mechanical resistance. It was revealed that at low temperatures, phase 3 instead of phase 5 was produced, and some MgO remained unreacted, thereby resulting in reduced strength and more water solubility. Conversely, phase 5 presence was found at higher temperatures, and at 40 °C, phase 5 was predominantly observed, contributing significantly to the strength enhancement.

Furthermore, Xu et al. [14] observed that elevated-temperature (75 °C) curing might alter the typical crystal behaviors of phase 5 crystals, making them more susceptible to water and having a negative impact on their water resistance. Gue et al. [19,20,48] and Yu et al. [2], on the other hand, used the curing conditions of temperature 24 ± 1 °C and relative humidity $60 \pm 5\%$ in their study and reported that MOC with excellent water resistance performance was obtained. Overall, the controlled curing conditions such as temperature 24 ± 1 °C and relative humidity $60 \pm 5\%$ are found suitable for curing MOC composites.

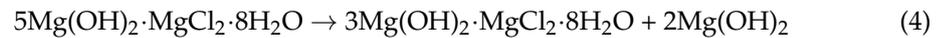
3.2. CO₂ Curing and Its Effect on MOC-Based Cementitious Composites

Cementitious composites are generally cured with CO₂ (accelerated curing) as opposed to natural carbonation since the carbonation reaction begins promptly and is utilized to quicken strength gains and lessen early drying shrinkage of cement products. Thus, the distinctive characteristics of rapid carbonation in hydration products, accelerated strength development, and reduced drying shrinkage in cementitious composites render CO₂ curing distinct from natural carbonation [49,50]. Moreover, the high pressure and purity of CO₂ gas provide a quick interaction between CO₂ and cementitious materials [51].

Compared to OPC (calcination temperature 1450 °C), the reactive magnesia (MgO) is produced at a calcining temperature of 700–1000 °C [46]. The reactive MgO produces interfacial bonding by reacting with H₂O and CO₂ to sequester CO₂ and acquire strength [52–54]. It has been suggested that CO₂ curing can lead to a variety of chemical modifications in the MgO cement system that result in the formation of hydrated magnesium carbonates like lansfordite (MgCO₃·5H₂O), nesquehonite (MgCO₃·3H₂O), artinite (MgCO₃·Mg(OH)₂·3H₂O), hydromagnesite (4MgCO₃·Mg(OH)₂·4H₂O), and dypingite

($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$) [55–57]. The strength and density of cement pastes can be increased by these hydrated magnesium carbonate compounds, which can also fill microscopic pores [58,59]. Also, CO_2 curing might produce a weak acid source, which could be advantageous for increasing the strength of MOC cement [60–62].

According to the reported studies, phase 5 would be converted into phase 3 hydration products during the natural carbonation of MOC. The following new phases would form after phase 3 experienced further carbonation (Equations (4) and (5)) [32,63]:



Furthermore, this carbonation process has the potential to enhance the water resistance of MOC, attributed to the formation of a new phase ($\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 2\text{MgCO}_3 \cdot 6\text{H}_2\text{O}$), which exhibits significantly lower solubility in water compared to phase 3 or phase 5. He et al. [64] studied the influence of pulverized fuel ash (PFA) and CO_2 curing (25 °C and relative humidity 55%) on the water resistance and volume stability of MOC and found that both CO_2 curing and PFA addition significantly improved the water resistance of MOC. It was further reported that the strength retention coefficient of MOC increased from 7.9% to 72.2% when 30% of PFA was incorporated in the MOC mix as a partial replacement of MgO powder. After exposure to CO_2 curing, the strength retention coefficient for the control mix increased from 7.9% to 40%, whereas for the mix with 30% PFA, it increased from 72.2% to 81.4%. The authors attributed the improved water resistance (increased strength retention coefficient) to the development of insoluble amorphous gel (i.e., magnesium-chloride-silicate-hydrate (M-Cl-S-H) gel and magnesium-chloride-hydrate (M-Cl-H) gel) and densification of microstructure (Figure 1). Hence, CO_2 curing can enhance the water resistance of MOC blended with PFA but could not play any role in declining the expansion of MOC samples caused by water immersion [64]. Moreover, Jankovsky et al. [65] highlighted the potential of MOC to sequester CO_2 from the atmosphere, indicating its sustainable nature. However, the detailed mechanism of the interaction between CO_2 and MOC remains unexplored and requires further investigation. Currently, limited studies exist on the carbonation of MOC, emphasizing the need for thorough research to uncover its in-depth mechanisms and insights.

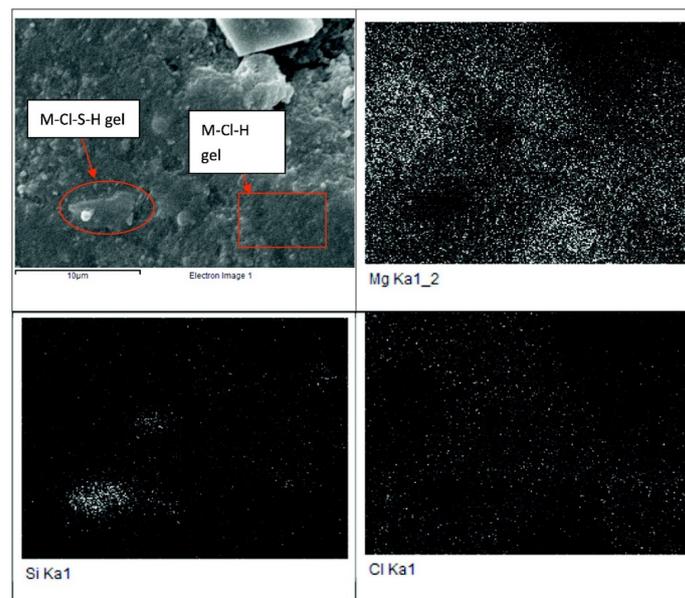


Figure 1. SEM-EDX analysis of PFA-modified MOC [64].

4. Influence of SCMs on the Properties of MOC

4.1. Effect of FA on MOC

FA is a byproduct of the coal industry, and it was discovered that using FA considerably increased the water resistance of MOC. Figure 2 depicts the water resistance coefficients of FA-modified MOC composites as reported in previous studies [66,67]. Previous research has shown that incorporating 30% FA into MOC mortar (14 d air-cured) resulted in 80% compressive strength retention with respect to the initial value after 28 d of immersion in water [22,68]. Furthermore, the inclusion of 30% FA increased the flowability of MOC mortar, and the initial and final setting periods were delayed by 4 to 8 h and 6 to 9 h, respectively [22]. It was also reported that the compressive strength decreased as the amount of FA increased and that a 35% reduction in compressive strength occurred with the addition of 30% FA by weight of MgO [22]. Guo et al. [20] discovered that mixing 30% FA with MOC mortar increased compressive strength retention after 28 d of water immersion. They also stated that the addition of 30% FA to MOC mortar reduced fluidity, delayed setting time, enhanced strength parameters such as compressive strength, elastic modulus, and flexural strength, and improved water resistance. Likewise, Guo et al. [19] further studied the effect of a hybrid combination of FA and silica fume and discovered that the water resistance of MOC was significantly improved. They reported that a MOC mix of 15% FA and 15% silica fume was effective in terms of water resistance, with strength retention coefficients of 1.0 and 0.95 after 28 d and 56 d of water immersion, respectively.

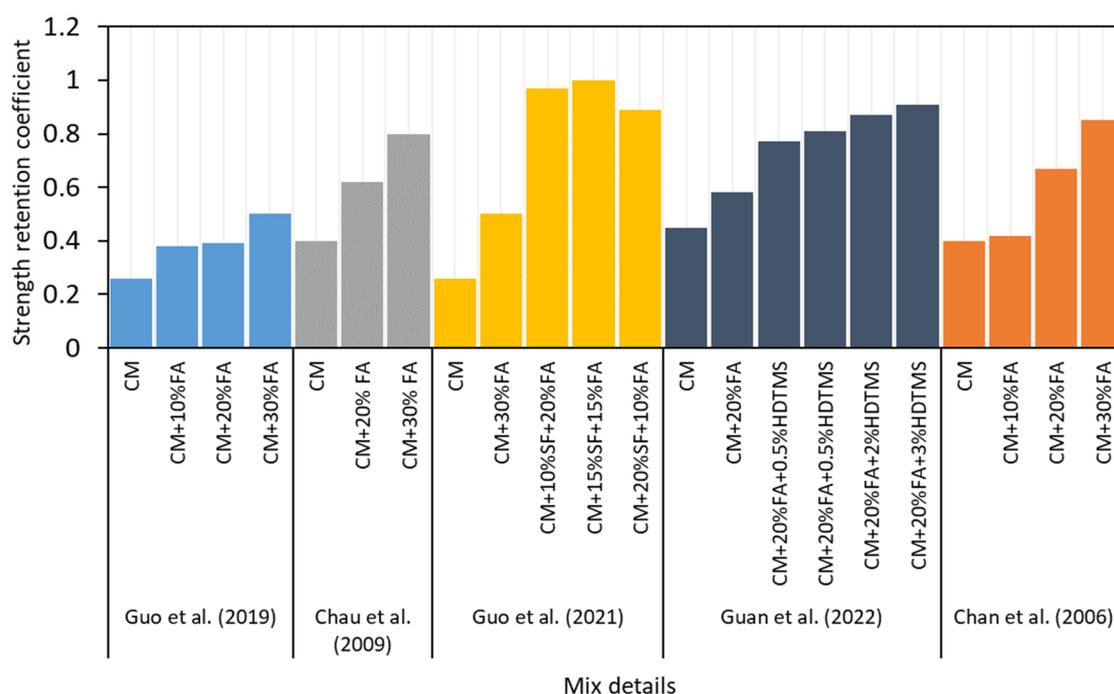


Figure 2. Strength retention coefficient of FA-modified MOC after water immersion. (Note—CM: control mix, HDTMS: hexadecyltrimethoxysilane, and SF: silica fume) [19,20,22,66,68].

4.2. Effect of GGBFS on MOC

GGBFS is an industrial byproduct generated from the iron and steel industries and is widely used as an OPC replacement in concrete. It is believed that approximately 530 million tons of GGBFS are produced worldwide, out of which only 65% are used by the building sector [69]. The use of GGBFS in cement mortar can enhance the strength, durability, and resistance to sulfate attack due to its pozzolanic activity [70–72]. In high-performance cementitious composites, it has been demonstrated that partial substitution of cement with GGBFS can increase workability; decrease hydration heat; improve sulfate attack resistance; decrease shrinkage, permeability, and chloride-ion diffusion into a com-

posite; reduce the risk of degradation due to alkali-silica reaction; and improve composite durability [73].

Considering the high potential of GGBFS, its influence on MOC cement has also been investigated. Jin et al. [74] investigated the influence of GGBFS on the strength and water resistance behavior of MOC and found positive results. They reported that by replacing MgO with GGBFS ranging from 5 to 30%, the compressive strength of MOC increased, whereas no significant change in flexural strength was reported. Further, it was found that the addition of GGBFS significantly improves the water repellency, and the softening coefficient of MOC was even higher than 0.82 with a maximum of 1.07. Aiken et al. [75] incorporated GGBFS as a partial substitute of MgO in MOC cement paste at various substitutional levels ranging from 10% to 30% and studied its impact on the fresh, mechanical, and water resistance properties of MOC cement. They found that the water resistance of MOC increased with the inclusion of GGBFS. The 28 d strength retention coefficient after water immersion of MOC paste without GGBFS was found to be 0.31, which increased to approximately 0.42 when 30% GGBFS was incorporated. Moreover, it was found that the addition of GGBFS increased the fluidity and setting time of the mix but decreased the compressive strength. The compressive strength of MOC cement pastes reduced from 126 MPa to approximately 101 MPa when 30% of GGBFS was incorporated.

Qiao et al. [76] substituted MgO with GGBFS to develop an MOC cement-based composite and revealed mostly promising findings regarding the development of compressive strength. The compressive strength increased progressively over time, reaching approximately 48 MPa at 1 d of curing, followed by 51 MPa and 57 MPa, respectively, at 14 d and 28 d curing age. Wang et al. [77] studied the behavior of GGBFS-incorporated MOC-solidified waste sludge and reported that the GGBFS–MOC mixture is effective in solidifying sludge. Further, they stated that the addition of GGBFS prevents the strength retraction of MOC-solidified sludge and develops C-S-H gels upon alkaline activation, thereby causing an enhancement in the long-term strength and durability. They stated that the combined action of GGBFS–MOC can be considered as an efficient and eco-friendly approach for disposing of urban sludge. In conclusion, the existing observations show that GGBFS seems compatible with MOC, and its addition has the potential to enhance the overall performance of MOC.

4.3. Effect of MK on MOC

MK is typically utilized as SCM in concrete owing to its reactive aluminosilicate constituent [78,79]. The influence of metakaolin on MOC was recently documented for the first time [75,80]. Gong et al. [80] incorporated MK in MOC cement paste and stated that it accelerates the setting time. Furthermore, it was reported that when the content of MK in MOC increased, the compressive strength, mass change, and compactness decreased. Aiken et al. [75] incorporated MK as a partial substitute of MgO in MOC paste at different substitution levels ranging from 10% to 30% and studied its fresh, mechanical, and water resistance properties. It was reported that the addition of MK slightly increased the setting time but reduced the fluidity. They also found that the water resistance increased with the incorporation of MK. The strength retention coefficient after 28 d of water immersion of MOC paste without MK was found to be 0.31, which increased to approximately 0.77 when 30% MK was incorporated, as illustrated in Figure 3. The 28 d compressive strength of MOC cement pastes containing 20% MK increased from 126 MPa to approximately 133 MPa. In summary, MK-modified MOC composites demonstrate outstanding mechanical and water resistance performance; however, further investigation is required to comprehensively explore its behavior.

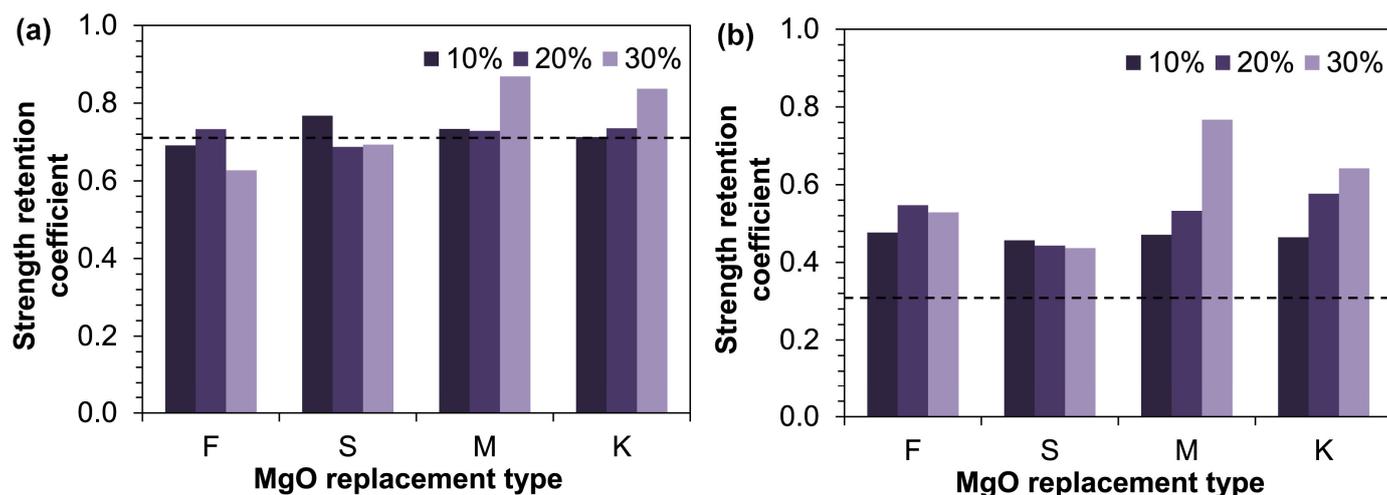


Figure 3. Strength retention coefficient of MOC cement pastes: (a) 7 d and (b) 28 d water immersion. Note: F: Fly ash; S: GGBFS; M: Metakaolin-A (alumina-rich kaolinitic clay); and K: Metakaolin-B (iron-rich kaolinitic clay) [75].

5. Recent Developments in FRMOC-Based Composites

MOC-based cementitious composites normally have high strength but are brittle in nature [81]. This can be overcome by the use of fibers which are found to impart excellent ductility in OPC-based cementitious composites. This is particularly relevant as it is common practice in the MOC industry to add multiple layers of fiber mesh or grid to increase the flexural strength of MOC boards and decrease the size of the member [2]. However, working efficiency inevitably suffers as a result of the addition of multiple layers of fiber mesh. Thus, FRMOC composite might have the capability of achieving high strength and ductility (high strain capacity), which will not only enhance structural performance and optimize MOC member dimensions, but also increase construction efficiency [2]. Previous studies showed that the MOC-based cementitious composite has an outstanding bonding ability with fibers [31,82]. However, research in this area is very scarce.

Wang et al. [81] examined the effect of PE fiber on the performance of MOC composites and found that PE fiber significantly enhanced the tensile behavior, strain hardening capacity, and multi-cracking behavior of MOC composites. Further, they reported that the FRMOC had a tensile strength of above 7 MPa and an improved tensile strain capability of up to 8% (Figure 4). They attributed this to the excellent chemical bonding between fiber and MOC composite matrix. Yu et al. [2] also examined the effect of PE fiber on the behavior of MOC composites and achieved high compressive strength and high tensile ductility. The FRMOC achieved an overall strain-hardening capability of up to 8% (Figure 5). They studied the mechanical properties of FRMOC under different curing periods ranging from 12 h to 28 d and reported that the compressive, tensile, and flexural strength of the FRMOC at 1 d reached 71.4 MPa, 8.28 MPa, and 25.2 MPa, respectively, which accounts for 56%, 75%, and 84% of the equivalent values at 28 d. The water resistance ratios for the compressive and flexural strength of the FRMOC were found to be substantially greater than the corresponding values for the plain MOC. They reported that the compressive and flexural strengths' water resistance ratios for FRMOC (28 d cured) were 0.68 and 0.58, respectively, after 28 d immersion in hot water (60 °C), whereas the values were 0.35 and 0.25, respectively, for plain MOC. Wei et al. [31] developed MOC-based engineered cementitious composites (MOC-ECC) containing PE fiber (2% by volume) to further extend the application of MOC in the construction industry. They found that the MOC-ECCs have a tensile strength of around 5 MPa and a tensile strain capacity of between 5% to 7%. Also, MOC-ECC demonstrated a saturated fracture pattern, close crack width control under tension, and superior ductility. They recommended that MOC-ECC with enhanced ductility has the potential to introduce construction material free from steel reinforcement and as a

viable solution for steel corrosion that has limited MOC applicability in civil engineering applications. In general, the literature regarding FRMOC containing 2% PE fiber showed a significant improvement in the ductility of the composites (as shown in Figure 4) without compromising the overall mechanical performance.

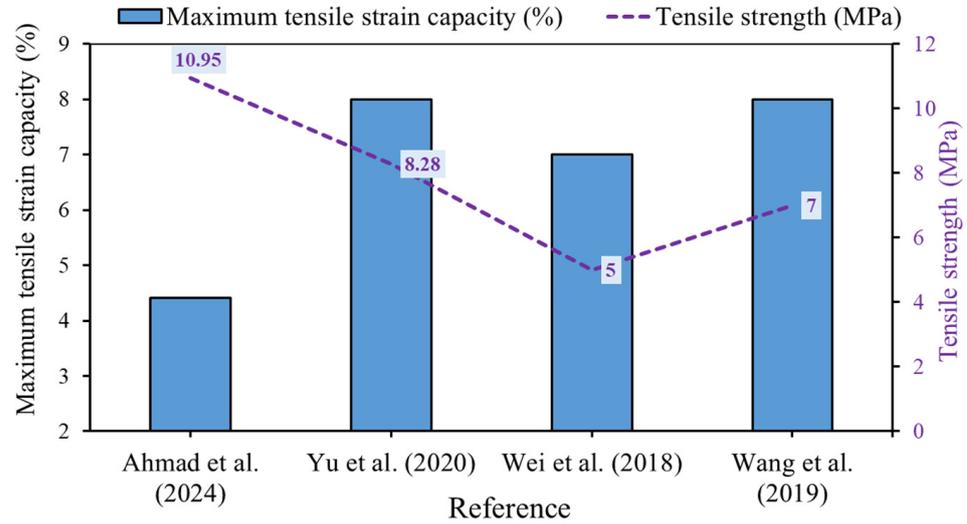


Figure 4. Tensile strengths and strain capacities of FRMOC reinforced with 2% PE fiber [1,2,31,81].

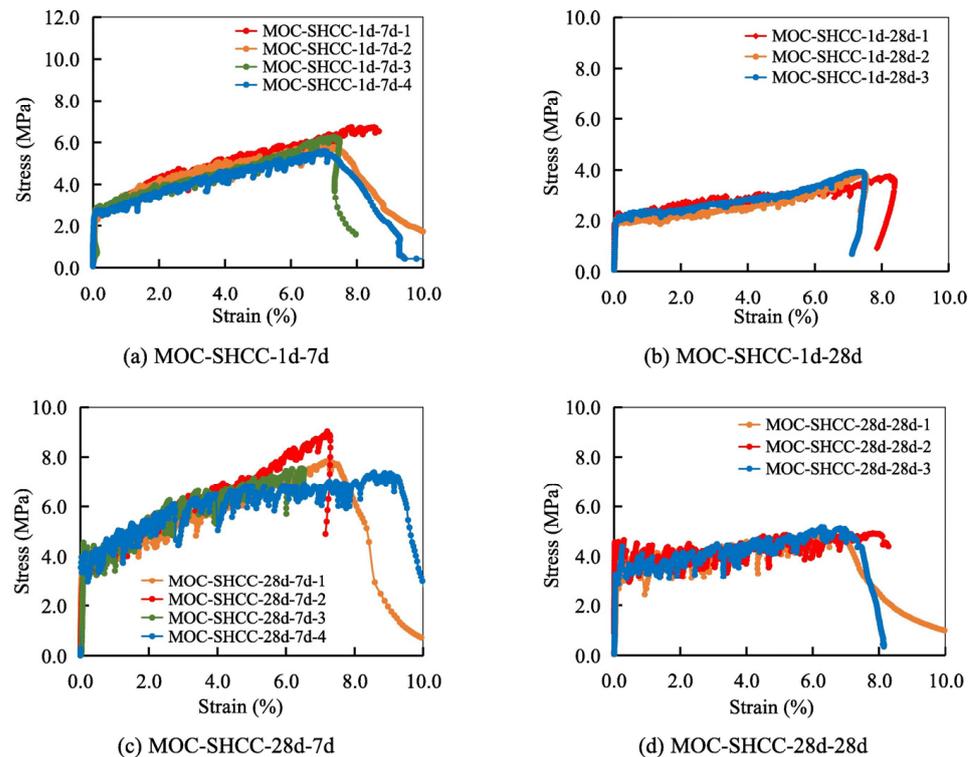


Figure 5. Tensile stress–strain curves of FRMOC [2].

In a recent investigation by Rawat et al. [35], the influence of 2% basalt fiber on the mechanical properties of MOC was explored, revealing enhancements in compressive and tensile strengths alongside a notable reduction in strain capacity. In a subsequent study aiming to optimize both tensile strength and strain capacity, Ahmad et al. [1] delved into the effects of hybrid fibers, specifically PE fiber and basalt fiber, on MOC behavior. They observed that all FRMOC composites exhibited strain hardening behavior, with those

containing 2% PE fiber demonstrating the highest tensile strength (10.95 MPa) and strain capacity (4.41%), potentially attributed to multiple cracking mechanisms illustrated in Figure 6. Moreover, as the proportion of PE fiber replaced by basalt fiber increased, a decrease in both tensile strength and strain capacity was observed. Their findings underscored the effectiveness of hybrid FRMOC reinforced with 1.25% PE fiber and 0.75% basalt fiber, exhibiting notable attributes such as high compressive strength (78.8 MPa) and tensile strength (8.49 MPa), alongside a substantial strain capacity (2.43%). The study also proposes further research into the utilization of FRMOC for cladding and facade applications.

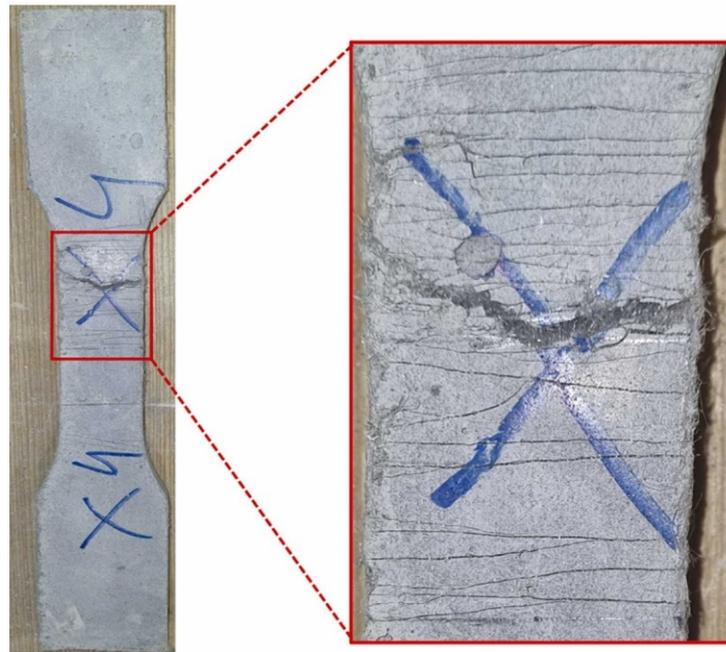


Figure 6. Multiple microcracking in FRMOC reinforced with 2% PE fiber [1].

6. Recent Developments in Water-Resistant MOC

The water resistance of MOC was one of the primary challenges limiting its application to mainly indoors. However, recent advancements in water-resistant MOC have widened the scope from interior to outdoor applications. The main reason for its poor water resistance was the conversion of compacted and dense hydrated phases into loose hydrated products such as brucite ($\text{Mg}(\text{OH})_2$), which results in significant strength reduction. Over the last decade, there has been a significant increase in research efforts to reduce or mitigate the water resistance issue of MOC, as illustrated in Figure 7. The figure depicts an annual summary of the number of articles published specifically on the water resistance of MOC as found on Google Scholar. It can be observed that in 2022, a maximum of 21 articles were published, followed by 18 articles each in 2021 and 2020, whereas in 2023, around 12 articles were published. This clearly shows the growing interest in this research topic, which is critical for construction applications.

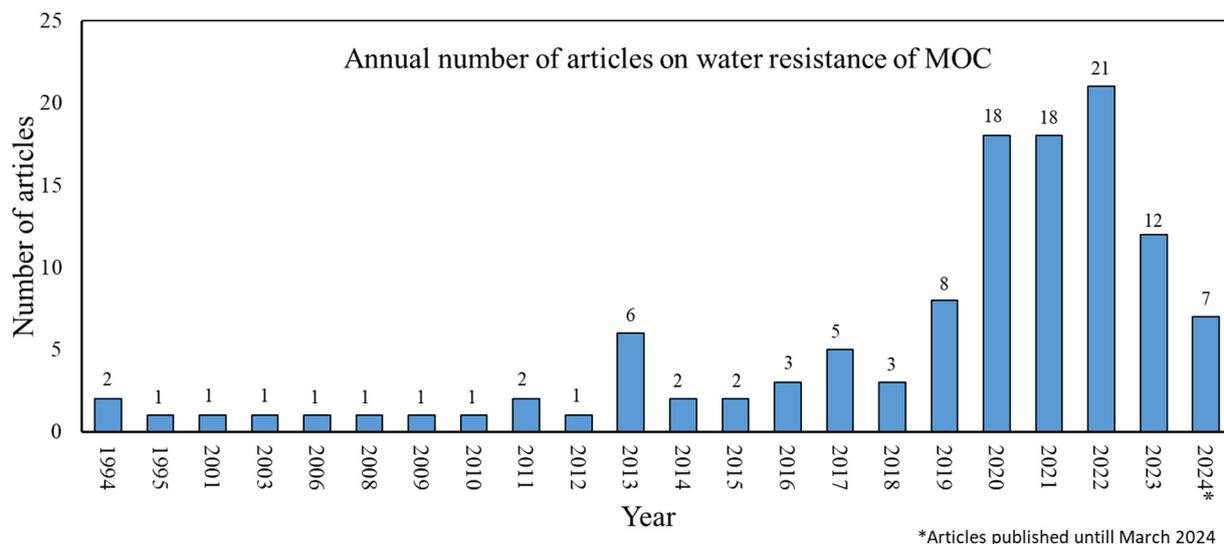


Figure 7. Yearly data on published studies focused on the water resistance issue of MOC.

The researchers have utilized a variety of SCMs to address this issue, including FA, silica fume, GGBFS, MK, alumina, nano silica, glass powder, sludge ash, and pulverized fuel ash, as well as soluble phosphates including PA, potassium phosphate, MFP, etc. [8,23,83]. The main aim of adding these admixtures and modifiers was to develop stable water-resistant hydrated products.

Lu et al. [84] doped 13 different additives individually in MOC to tackle the water resistance issue. Among them, seven were mineral additives (FA, GGBFS, baked clay, diatomite, silicate cement, coal gangue, and baked diatomite) and six were reagent modifiers (H_3PO_4 , $\text{Al}(\text{H}_2\text{PO}_4)_3$, H_3BO_3 , Na_2SO_4 , Na_3PO_4 , and K_3PO_4). The specimens were immersed for three months in water, and the loss in compressive strength after water exposure was compared for different additives. It was reported that a suitable combination of FA with PA, $\text{Al}(\text{H}_2\text{PO}_4)_3$, H_3BO_3 , or K_3PO_4 can be effective for improving water resistance with only a 10–20% reduction. Zhang et al. [85] incorporated aluminate minerals in MOC and revealed that the addition of aluminate minerals improved MOC water resistance by transforming phase 3 and phase 5 into stable water-resistant hydrated phases. Deng et al. [28] incorporated soluble phosphates (H_3PO_4 , $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{NH}_4\text{H}_2\text{PO}_4$) ranging from 0.5–1.0% by weight in MOC and studied its water resistance performance after 15, 30, 45, and 60 d water immersion. It was revealed that the strength retention coefficient was more than 0.8, which fulfills the minimal criteria for engineering applications. They attributed this to the presence of phosphate radical anions, which yielded a reduction in Mg^{+2} ions and thereby the primary phases remained unchanged after water soaking. Chan et al. [68] examined the water resistance characteristics of MOC with FA varying from 10–30% by weight of MgO. They reported that the strength retention coefficient was about 0.4 at 10% content, which increased to 0.65 and 0.85, respectively, at 20% and 30% FA content.

From 2008 to 2023, a significant number of investigations were conducted, and different researchers incorporated different types of SCMs, industrial byproducts, and soluble phosphate to enhance the MOC's water resistance performance. The SCMs include FA [22,86], silica fume [30], nano silica [67,87], rice husk ash [88], MK [80,89], and GGBFS [77]; the industrial byproducts include refuse floor tiles [88,90,91], incinerated sewage sludge [77,92], granite wastes [93], pulverized fuel ash [94], waste wood [95,96], plastic waste [97], agriculture and industrial waste [98], and waste gypsum [99,100], and modifier reagents like H_3PO_4 [39,67], $\text{Ca}(\text{H}_2\text{PO}_4)_2$ [101], MFP [48], tartaric acid [102] were added to MOC composites to enhance water resistivity of MOC. Zhang et al. [103] incorporated PA and phase-5 seed crystals in MOC cement to enhance strength and water resistance at the same time. They found that the addition of PA and phase-5 seed crystals reduced the porosity and made the MOC matrix more compact, leading to enhanced compressive

strength and water resistance, as shown in Figure 8. It can be seen from Figure 8a that with the addition of PA, a large number of crystals grew in the pores; however, some interspace still remained in the middle of pores. This was overcome with the addition of phase-5 seed crystals which lead to a compact microstructure (Figure 8b).

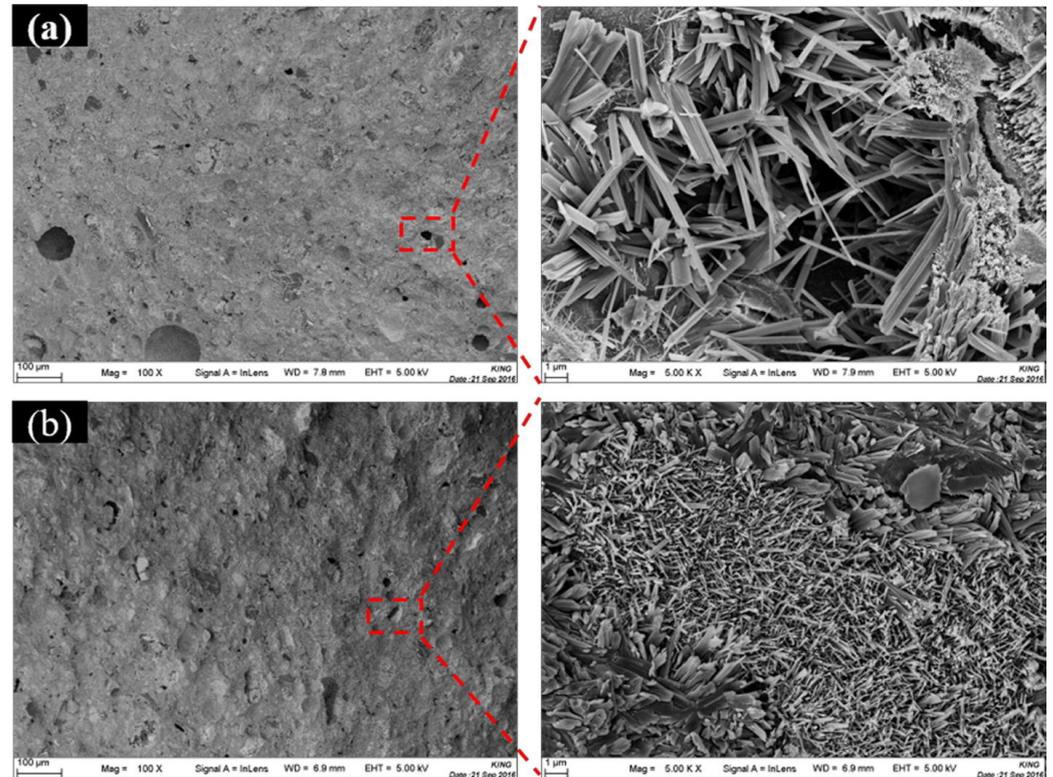


Figure 8. Morphology of MOC specimens reinforced with (a) only 1% (by weight) PA (b) 1% (by weight) PA + 1% (by weight) phase-5 seed crystals [103].

Similarly, Zhou et al. [104] found that phosphate may affect the hydration product composition during the hydration process and facilitate the development of stable water-resistant hydration products. Li et al. [23] also discovered that the MOC cement with KH_2PO_4 generated gel-like phase 5. In general, the existence of phosphate ions in PA contributes to its ability to increase the water resistance of MOC cement. It is believed that insoluble phosphate is generated, which hinders phase 5 from decomposition. Ionization of PA occurs when PA is added to MgCl_2 , as shown in Equations (6)–(8) [91].



A stable phase, i.e., $\text{MgPO}_4 \cdot 3\text{H}_2\text{O}$, with high water resistance is formed when HPO_4^{2-} reacts with Mg^{+2} in the solution. At the same time, $\text{MgPO}_4 \cdot 3\text{H}_2\text{O}$ can alter the interface regions to strengthen the conglutinated force of the phases, improving water resistance and compactness. The process by which soluble phosphate improves the water resistance of MOC also resembles that of PA. Likewise, Deng et al. [28] reported that phosphate ions might lower the Mg^{+2} concentration in the solution, resulting in more stable crystalline phases in water. Improvement in water resistance has also been observed with the addition of some acids, including tartaric acid (TA) [102], hydroxyacetic acid (HA) [105], and citric acid [106]. Figure 9 further provides a summary of the observations where water resistance was found to be improved by the addition of organic additives. It can be observed that these

chemical modifiers are effective in providing a higher softening coefficient. In particular, PA and HA have been found to have shown better effect in terms of strength retention. Nevertheless, the extent of improvement also depends on the raw MOC matrix composition. Also, though these modifiers improved the water resistance of MOC, there were some negative effects as well, such as the retarding impact of PA, which decreases the micro-level MOC compactness, leading to a decrease in strength [39].

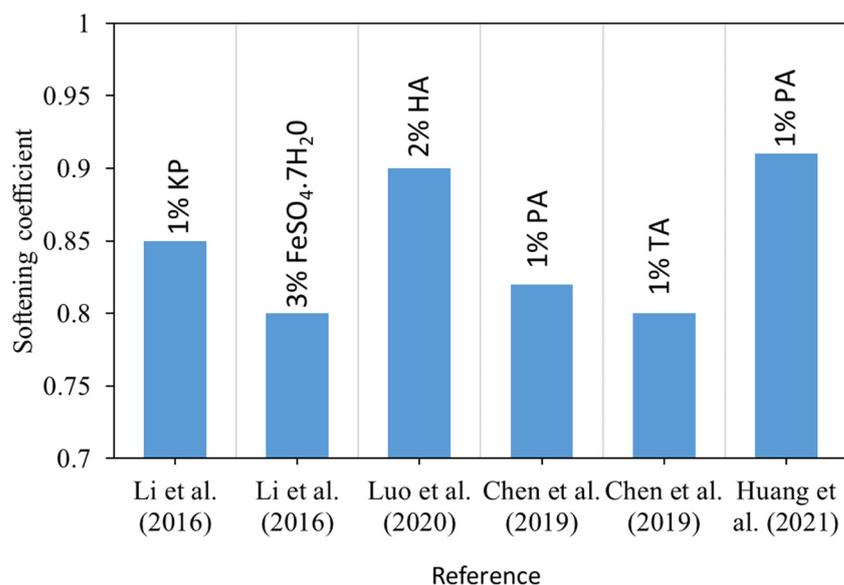


Figure 9. Softening coefficient of MOC with various organic additives (Note—KP: KH₂PO₄) [23,67,102,105].

Jirickova et al. [26] investigated the water resistance of MOC composites enhanced with nano-dopants like carbon nanotubes, alumina nanosheets, graphene nanoplatelets, and graphene oxide. They observed water resistance coefficients ranging from 62.7% to 74.8% after 24 h of water immersion. However, the study did not explore the water resistance characteristics of nano-modified MOC at longer curing duration. Similarly, Wang et al. [9] incorporated organic and inorganic additives into solidified-sludge-based MOC composites, revealing that these additives were effective in improving water resistance to a certain extent. Likewise, Sun et al. [107] incorporated 30% red mud and 1% potassium phosphate in MOC, revealing that approximately 85% strength retention was observed. All these admixtures improved the water resistance to a certain extent, but none of them could completely resolve the water-resistant issue of MOC. Recently, Guo et al. [19] made a significant contribution to the development of water-resistant MOC by incorporating a hybrid combination of 15% FA and 15% silica fume and found compressive strength retention up to 100% and 95% after 28 d and 56 d immersion in water. Similarly, Guo et al. [108] further extended the research by investigating the performance of MOC under ambient water (25 °C) and warm water (60 °C) and developed for the first time an optimized water-resistant MOC mix with a strength retention co-efficient of 1.08 and 0.9, respectively, at normal and warm water immersion. The optimized water-resistant MOC mix includes molar ratios of MgO/MgCl₂-9 and H₂O/MgCl₂-13, 30% FA, 0.5% PA, and 0.5% MFP. It was reported that this combination of ingredients leads to a compact microstructure with pores occupied with phase-5 crystals and some gel-like phase (Figure 10). This tightly bonded phase-5 crystals and gel-like phase helped in protecting the unstable crystalline phases leading to improvement in water resistance.

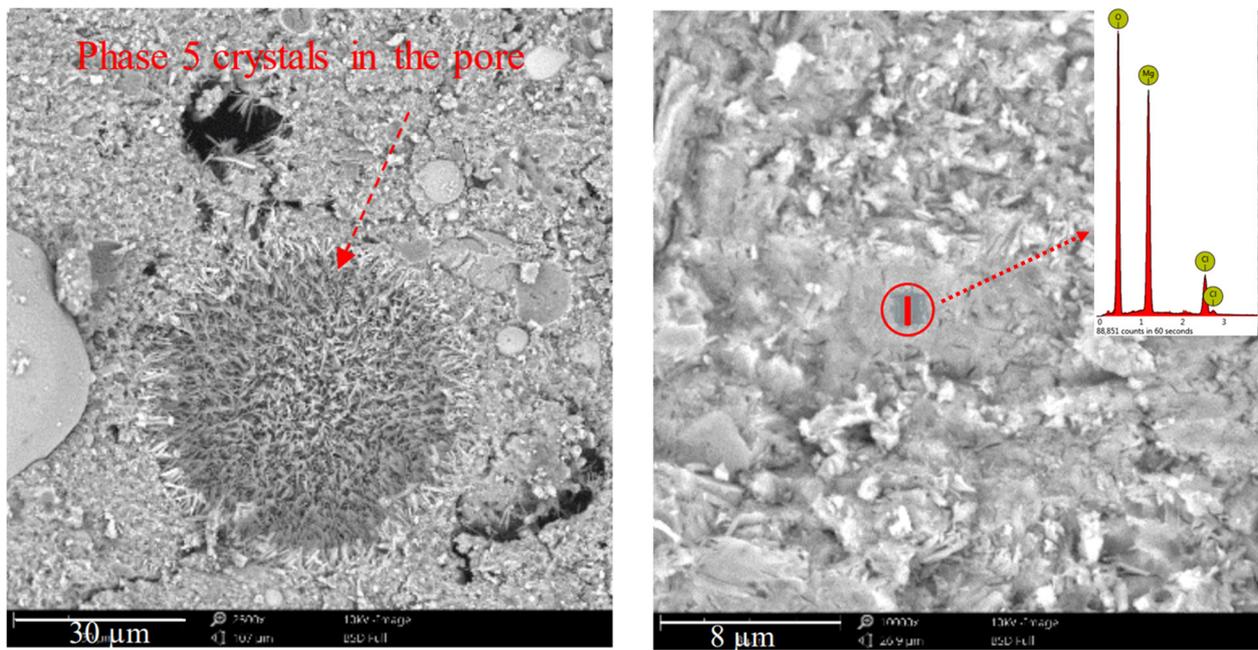


Figure 10. SEM micrographs with energy dispersive X-ray spectroscopy (EDS) of MOC matrix reinforced with 0.5% PA + 0.5% MFP + 30% FA [108].

The recent development and improvement in the water resistance of MOC can further be understood using Figure 11 which shows the effect of combination of SCM and chemical additives on the softening coefficient. It can be observed that FA is very effective in improving the water resistance and when it is combined with suitable organic additives, it can greatly enhance the resistance with even over 100% strength retention at 28 days. Overall, this substantial improvement in water-resistance of MOC has broadened the scope of MOC to outdoor engineering applications, and the increased ongoing research efforts are likely to further extend its practical implementation.

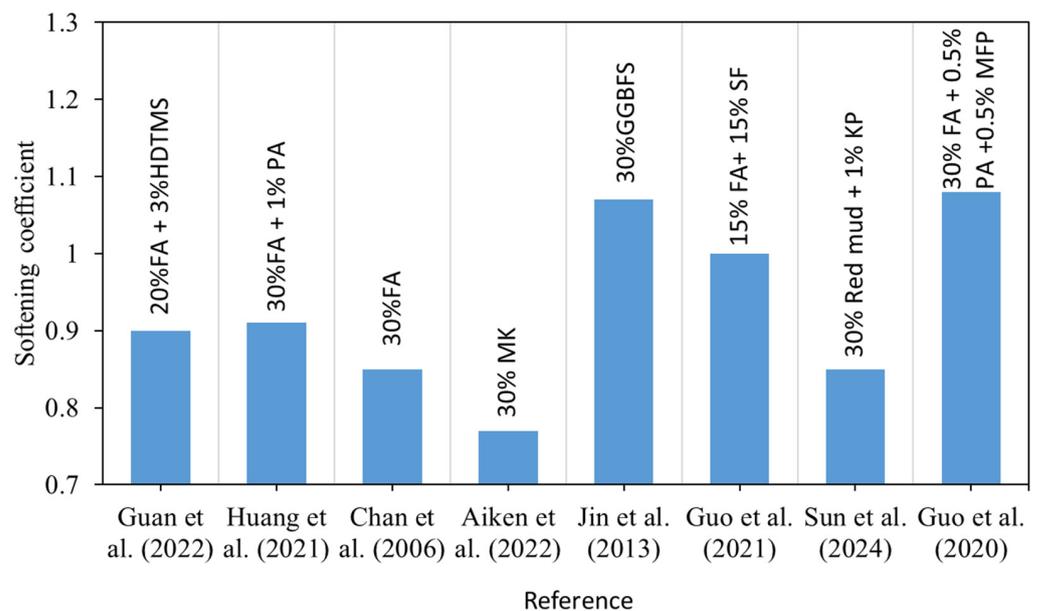


Figure 11. Softening coefficient of MOC with various SCM and additives [19,66–68,74,75,107,108].

7. Application of MOC as a Fire-Resistive Material

MOC has been regarded as inherently fire-resistant in past studies [11,34,109]. Regarding the fire-resisting mechanism of MOC, there is very limited literature available, and the complete understanding of its mechanism is still uncertain and needs further investigation. Chang et al. [110] conducted a study on the elevated temperature behavior of pure MOC mixes, noting a complete loss in compressive and flexural strength as temperatures rose from 100 to 500 °C. To enhance the elevated temperature performance of MOC, Rawat et al. [35] investigated the incorporation of hybrid fibers (basalt fiber and polypropylene fiber) into MOC. Results showed a substantial deterioration in compressive strength, ranging from approximately 30% to 87% at 400 °C and over 95% at 800 °C (Figure 12), with no observed cracks or spalling. Tensile strength was entirely lost at 600 °C, accompanied by a significant mass loss exceeding 30%, indicating notable matrix decomposition. The study suggested future research incorporating various admixtures into MOC to generate more thermally stable hydration phases.

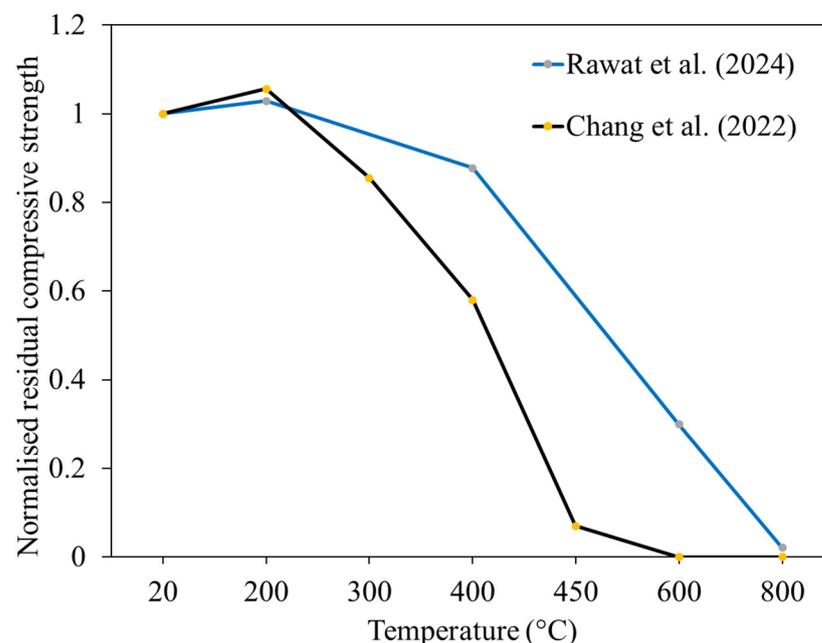


Figure 12. Residual compressive strength of MOC reported in previous studies [35,110].

Moreover, a few studies regarding the use of MOC as a fire-resistive coating material were also conducted, depicting the potential of MOC to resist high temperatures without deteriorating the interior substrate [11,34]. Montle and Mayhan [36] studied the performance of MOC as a fire-resistive coating material, and MOC was found to have good insulating properties due to the presence of water of hydration which acts as an insulating agent when used as a coating material. Further, they mentioned that when a cementitious composite coated by MOC was heated to a temperature of 301 °C, the chemically bonded water within the composite was released, but not discharged outside due to the presence of the MOC coating. Due to the insulating effect of hydration water of MOC, the discharge of entrapped high-water content required a huge amount of energy, approximately 1000 Btu per pound. They also suggested that MgO acted as an excellent reflector, hence, the cement structure remaining after the loss of water of hydration was still an integrally sound structure due to the presence of MgO. Similar findings were also reported by Thompson et al. [111] and Aiken et al. [34]. Walling and Provis [11] further reported that MOC binders had good heat resistance because of the significant amount of crystalline water (typically about 35% hydrated water by weight) in MOC phases, which is difficult to liberate and requires a lot of energy. This large amount of crystalline water, along with the capacity of MgO to effectively reflect heat, were found to be the two main contributors to its better thermal resistance.

Xia et al. [109] studied the thermal performance of MOC using comprehensive microstructural analysis such as X-ray diffraction analysis (XRD), thermal gravimetric analysis (TG), infrared spectroscopy (IR), differential scanning calorimetry (DSC), and derivative thermogravimetry (DTG). It was revealed that dehydration occurred up to 200 °C, whereas the crystals were completely decomposed to MgO up to 600 °C with the liberation of HCl (Figure 13). Further, they reported that both phase 3 (3.1.8) and phase 5 (5.1.8) disintegrate through stepwise dehydration, followed by degradation and dissociation to MgO and HCl by 600 °C.

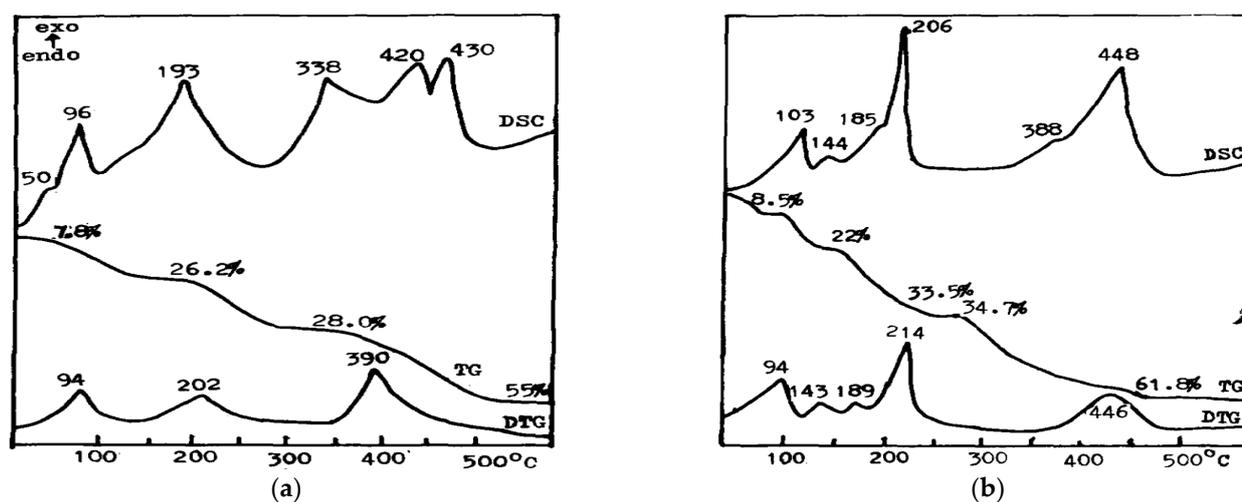


Figure 13. TG, DTG, and DSC curves of the (a) phase 5 and (b) phase 3 [109].

Table 1 further presents the thermal-analytical findings of the MOCs, indicating that it is transformed into MgO when subjected to 500 °C. Xia et al. [109] further stated that the release of HCl during heating must be considered when using MOC binders for fire protection in household applications. In summary, the literature indicates the potential of MOC as a fireproof coating material, but its use in the construction industry requires a thorough investigation to assess its strength and resilience at elevated temperatures.

Table 1. Thermal-analytical behavior of the MOCs [109].

No	DSC (°C)	Enthalpy (kJ mol ⁻¹)	DTA (°C)	TG (wt.%)	Products
Phase 5 (5Mg(OH)₂·MgCl₂·8H₂O)					
1	96	76.58	90	7.8	5Mg(OH) ₂ ·MgCl ₂ ·6H ₂ O
2	145		140	13.5	5Mg(OH) ₂ ·MgCl ₂ ·4H ₂ O
3	193	363.4	202	26.4	5Mg(OH) ₂ ·MgCl ₂
4			250	27.0	5Mg(OH) ₂ ·MgCl ₂
5	378		390	44.0	5Mg(OH) ₂ ·MgCl ₂ + MgO
6	420	607.0	430	54.5	MgO
Phase 3 (3Mg(OH)₂·MgCl₂·8H₂O)					
1	103	78.36	94	8.5	3Mg(OH) ₂ ·MgCl ₂ ·6H ₂ O
2	144		149	19.0	3Mg(OH) ₂ ·MgCl ₂ ·4H ₂ O
3	185		189	22.0	3Mg(OH) ₂ ·MgCl ₂ ·4H ₂ O + 3Mg(OH) ₂ ·MgCl ₂
4	206	286.9	216	33.5	3Mg(OH) ₂ ·MgCl ₂
5			250	34.7	3Mg(OH) ₂ ·MgCl ₂
6	388				3Mg(OH) ₂ ·MgCl ₂ + MgO
7	448	666.4	446	61.8	MgO

8. Application of MOC in Solid Waste Management

Previous research has demonstrated that MOC exhibits strong bonding capabilities with various industrial byproducts, including sewage sludge ash (ISA), PFA, marble floor, phosphogypsum (PG), flue gas desulfurization gypsum (FDG), asbestos, expanded clays, and wood particles, and it exhibits rapid setting with a notable early strength gain [6,82,92,93,99]. The disposal of these industrial byproducts in landfills can have detrimental effects on the environment and human health. Therefore, MOC may serve as an environmentally friendly alternative, reducing waste accumulation and contributing to a more sustainable environment.

He et al. [92] incorporated different percentages of ISA, a byproduct of wastewater treatment plants, ranging from 10 to 30% as a partial replacement of MgO to improve the resistance performance of MOC. Their findings revealed that the inclusion of ISA resulted in enhanced water resistance and reduced expansion of MOC mortar resulting from the improved stability of phase 3 and phase 5 in water. ISA served as a source of soluble silicon (Si) and aluminum (Al), leading to the development of an amorphous gel of M-Cl-A-S-H type, which enhanced the stability of phase 3 and phase 5, consequently improving water resistance. He et al. [94] further conducted a comparative analysis to investigate the impact of both ISA and PFA on the water resistance of MOC. They found that both ISA and PFA enhanced the water resistance of MOC, with the ISA-modified MOC paste demonstrating superior water resistance compared to the PFA-modified paste. The improvement was attributed to the development of an amorphous phase (Mg-A-S gel) resulting from the reaction between MgO and the active phases in ISA or PFA. This amorphous gel interspersed with Phase 5 and converted it to fibroid-like phases leading to a more stable and dense structure, thereby contributing to enhanced water resistance (Figure 14).

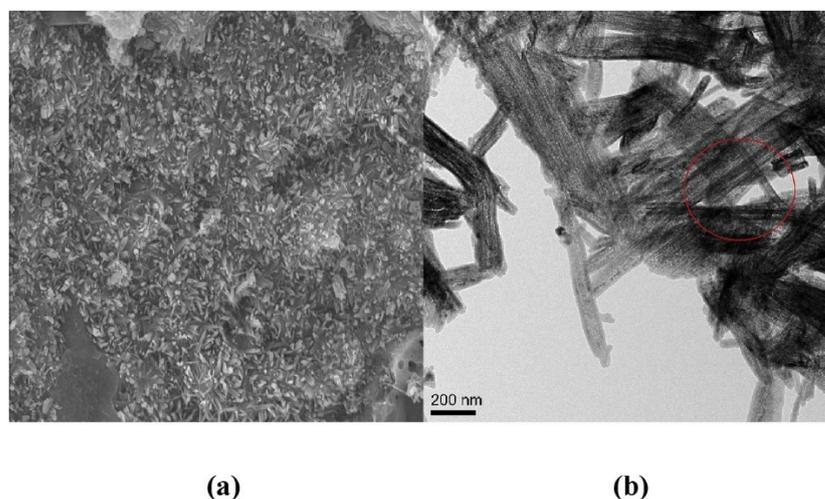


Figure 14. Fibroid-like phases observed through (a) SEM and (b) transmission electron microscopy (TEM) of ISA-modified MOC [94].

Wang et al. [77] conducted a study on the behavior of solidified waste sludge using GGBFS-incorporated MOC. They observed that the inclusion of GGBFS prevents the strength retraction of MOC-solidified sludge and promotes the formation of C-S-H gels through alkaline activation, resulting in improved long-term strength and durability of the solidified sludge. Similarly, Jianli et al. [112] studied the impact of MOC on the solidification and stabilization of sewage sludge and found that MOC effectively solidified the waste sludge, mitigating sludge handling and disposal challenges. Gu et al. [99] incorporated recycled waste gypsum containing PG and FDG ranging from 10 to 30% (by weight) as a partial replacement of MgO. This was aimed at considering the huge annual production of PG and FDG in China amounting to approximately 30 million tons which is discarded as

solid waste rather than being efficiently recycled. They reported that the incorporation of PG and FDG induced the formation of phase 3. Moreover, the presence of phosphate impurities in PG and FDG facilitated the nucleation of phase 5 and phase 3, thereby improving their water stability. Therefore, it was inferred that the utilization of waste gypsum in MOC not only improves the performance, but also supports the recycling of waste resources, promoting environmental sustainability.

9. Application of MOC and Wood as a Composite Building Material

Wood–cement composites are currently produced in several countries worldwide, primarily in the form of panels, owing to their exceptional exterior characteristics [113]. The primary challenge in the manufacturing of wood–cement composites lies in the chemical incompatibility between cement and wood, with OPC often inhibiting the setting and hardening of cement in most cases [114]. The inhibitory compounds primarily encompass certain sugars, a portion of hemicelluloses, and associated disintegration byproducts. The extent of inhibition is influenced by various factors, including the type of wood species, its geographical origin, the tree part used, the season of wood cutting, cement type, wood-to-cement ratio, and other related factors [115,116]. Past studies have indicated that, in contrast to OPC, MOC exhibits good compatibility with wood, suggesting its potential as an alternative for OPC in the production of wood–cement boards, particularly for wood species that are poorly compatible with OPC [82,96,114,115].

Research indicates that wood–MOC composites having an increased wood fiber dosage exhibit reduced thermal conductivity, increased bending resistance, greater residual bending resistance following water immersion and exposure to elevated temperatures, and improved noise reduction properties [82,96,114,117]. Despite an increase in water absorption associated with higher wood fiber dosage, it remains at a relatively low level when mixed with MOC [64]. He et al. [96] discovered that integrating rice husk ash into wood-fiber-reinforced MOC improved both the mechanical strength and water resistance of the material, thereby enhancing its environmental sustainability and making it an eco-friendly alternative to traditional resin-based and OPC-based particle boards. Alternative approaches suggest the utilization of MOC and wood via an extrusion process to produce lightweight composite building materials [82]. Simultaneously, MOC can serve as an effective alternative to adhesive solutions employed in wood-based building materials. For instance, Jin et al. [113] suggested that the use of MOC as an inorganic adhesive offers viable and sustainable binding agents for plywood applications. Zhou et al. [118] developed an environmentally friendly and high-performance MOC-based formaldehyde-free adhesive containing hybrid combinations of organic–inorganic adhesives, demonstrating that MOC deposited on the surface of fibers formed connections through hydrogen bonds in wood, leading to enhancement in wood-based composites' mechanical characteristics. Furthermore, the incorporation of MOC enhanced the flame-retardant properties of the plywood. He et al. [114] demonstrated that greenhouse gas emissions (GHG) related to wood–MOC-based boards containing ISA were around 71% lesser in contrast to plywood manufacture, and similar to the resin-based board. Moreover, the human toxicity of MOC–wood-modified boards was 58% lower in contrast to normal resin-based board manufacture, which involves the use of extremely toxic organic resins. In summary, the above-mentioned studies clearly illustrate that combining MOC with wood for panel production results in reduced GHG emissions, reduced formaldehyde emissions or formaldehyde-free options, and improved product durability with enhanced resistance to decay, fungi, and pests. Therefore, MOC may facilitate the production of sustainable and environmentally friendly wood-based building materials, providing a green construction approach for the next generation.

10. Conclusions

The review primarily emphasizes recent progress in MOC, specifically highlighting advancements such as the development of water-resistant MOC and ductile FRMOC.

It also discusses various curing methods and explores the impact of different additives and the reactivity of MgO on MOC behavior. Furthermore, the review delves into the potential applications of MOC in fire-resistant coatings, solid waste management, and its incorporation into wood–MOC-modified composite building materials. Based on the present study, the recent advancements in MOC can be summarized into the following key points:

- Different mineral admixtures and chemical reagents such as acids and soluble phosphates were added to the MOC over the past few decades, and it was found that they improved the water resistance performance up to a certain level. Moreover, recently, a water-resistant MOC mix (molar ratios of MgO/MgCl₂-9 and H₂O/MgCl₂-13, 30% FA, 0.5% PA, and 0.5% MFP) was discovered with a strength retention co-efficient of 1.08 and 0.9, respectively, at normal (25 °C) and warm water (60 °C) immersion. This discovery potentially broadens the scope of MOC to outdoor applications.
- Controlled curing conditions such as a temperature of 24 ± 1 °C and relative humidity of 60 ± 5% were identified as suitable for curing MOC composites. Additionally, accelerated CO₂ curing demonstrated significant enhancements in the strength and water-resistant characteristics of MOC. This improvement was attributed to the formation of an insoluble amorphous gel and the densification of the microstructure.
- The addition of 2% PE fiber was effective in improving MOC composites' ductility with tensile strength ranging from 5 to 10.95 MPa and tensile strain capacity within the range of 4.41 to 8% without compromising the overall performance of MOC. This demonstrates the potential of FRMOC for utilization in structural applications.
- MOC exhibits promising potential in non-structural applications such as cladding or coating considering its superior ability to withstand high temperatures without compromising the integrity of the underlying substrate. However, existing literature revealed a complete loss in mechanical properties for MOC exposed to temperatures between 600–800 °C, highlighting the need for further research to enhance its fire resistance capabilities, especially for structural applications.
- MOC also exhibits strong bonding potential along with rapid hardening and a significant early strength gain with various industrial byproducts such as sewage sludge ash, pulverized fuel ash, phosphogypsum, and flue gas desulfurization gypsum. Hence, MOC may serve as an environmentally friendly alternative, reducing waste accumulation and contributing to a more sustainable environment.
- MOC also demonstrates good compatibility with wood as opposed to OPC, and this further establishes MOC as a green and sustainable material for the development of lightweight wood-based composite building materials.

11. Recommendation and Future Research Directions

The current study further identifies potential avenues for future studies to expand the scope of MOC in engineering applications. The main areas are outlined below.

- Though past studies have reported that MOC is inherently fire resistant, the extent of strength retention post fire exposure remains unclear. Therefore, a systematic investigation into the fire performance of MOC is needed to broaden the understanding in this area and further improve the performance as needed.
- Concerning the reactivity of MgO, it has been determined that MgO calcined within the range of 800–900 °C yields optimal results for MOC production. Nevertheless, further investigation is needed to elucidate the underlying mechanism of the impact of varying reactivities on MOC performance.
- The effect of CO₂ curing on MOC performance has not been extensively investigated and requires more in-depth study to elucidate the underlying mechanisms effectively and its potential to improve water resistance.
- The lightweight, high-strength, and ductile nature of FRMOC suggests the potential to be used for lightweight infrastructural applications. However, the performance needs to be further improved before it can be implemented and hence, more research efforts

should be directed towards evaluating the potential of MOC in attaining high tensile performance. Additionally, the use of FRMOC as cladding panels necessitates further large-scale testing studies to ensure its suitability and efficacy.

- Currently, the investigation into the advancement of MOC–wood composite is very scarce despite the potential it has shown in comparison to the OPC-based alternatives. Therefore, detailed investigations are needed to further enhance the industrial applications of MOC-based wood composites, aiming to establish them as eco-friendly alternative to OPC-based composites.

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