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Performance and microstructure of MgO-SiO₂ concrete under different environments

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Abstract

This study investigated the changes in the performance and microstructure of MgO-SiO₂ concrete under exposure to different environments involving carbonation, NaCl, MgCl₂ and MgSO₄ solutions for up to 180 days. Compressive strength results were compared to Portland cement (PC)-based concrete samples subjected to the same environments. Microstructural analysis performed via FESEM, XRD and TG/DTG indicated a lack of change in the composition of MgO-SiO₂ samples. The sustained mechanical performance and the clear presence of hydrate phases such as brucite and M-S-H even after longer exposures highlighted the resistance of MgO-SiO₂ formulations and their potential to be utilized in structural applications.

Keywords: MgO; SiO₂; M-S-H; durability; strength; microstructure

1 Introduction

Portland cement (PC) production is an energy intensive process and significantly contributes to global CO₂ emissions [1]. The environmental impacts of PC have driven the need for alternative building materials, such as reactive magnesium oxide (MgO) cement. Reactive MgO cement involves the use of reactive MgO, which is produced under lower calcination temperatures than PC (i.e. 700 vs. 1450 °C) [2], can be obtained from waste materials such as reject brine [3, 4] and can be recycled at the end of its use [5]. Magnesium silicate hydrate (M-S-H), the hydration product that forms via the reaction of an Mg-based source (e.g. MgO, Mg(OH)₂) with a silica source (e.g. microsilica), is known to lead to strength gain within MgO-SiO₂ systems [6]. M-S-H based mixes have several applications ranging from waste encapsulation [7] and refractory castables [8] to building materials [6].

The main factors influencing the properties of M-S-H include the chemical and physical properties of the precursors, mix composition, curing conditions and pH of the pore solution. In addition to MgO and SiO₂ sources, sodium hexametaphosphate ((NaPO₃)₆, SHMP) is generally used to reduce the water demand of MgO-SiO₂ mixes, which results in lower porosity and higher compressive strengths [9]. When their water contents are reduced via the use of SHMP, MgO-SiO₂ pastes were reported to reach compressive strengths of ~70 MPa at 28 days [6]. The formation of M-S-H continues until either of the magnesia or silica sources is fully consumed in the hydration reaction [10].

In addition to their strength development and associated reaction mechanisms, the durability of MgO-SiO₂ samples in the long term needs to be thoroughly assessed in order to enable their use on a large scale. Previous studies [9, 11] reported the formation of shrinkage cracks in MgO-SiO₂ samples, which was overcome by the inclusion of sand in the mix composition. Other than these, there are no studies in the literature on the durability aspects of MgO-SiO₂ samples. A few studies [12, 13] focusing on the durability of MgO samples under acid and sulfate conditions have reported the superior performance of samples with MgO over samples containing only PC. The lack of any significant reduction in the strength of mixes containing MgO was attributed to the hydration product of MgO, i.e. brucite (Mg(OH)₂), not

entering any detrimental reaction with acids or sulfates [13]. However, these studies did not involve any mixes containing SiO_2 and mainly focused on carbonated MgO samples or blends of PC and ground granulated blast furnace slag (GGBS) with MgO. Understanding the long-term performance of MgO- SiO_2 samples should also involve a comparison to existing PC-based samples, on which there is a wide range of literature.

Differing from MgO- SiO_2 systems, PC consists of four main phases, namely tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). Calcium silicate hydrate (C-S-H) and calcium hydroxide (CH) are the main hydration products observed in PC-based samples, whose hydration leads to a high internal pH (i.e. 12-13). Constant access to a high humidity or water curing plays a vital role for the strength development of PC samples as the continuation of the hydration reaction requires humidity. Water cured samples have been reported to perform up to 23% better than air cured samples [14].

When PC samples are exposed to carbonation, CO_2 penetrates and dissolves in the pore solution, producing HCO_3^- and CO_3^{2-} ions, which lowers the pH. Dissolution of $\text{Ca}(\text{OH})_2$ releases Ca^{2+} ions, which combines with CO_3^{2-} ions to form CaCO_3 . The volume of CaCO_3 is larger than that of CH and thus carbonation may result in lower porosity and increased compressive strength, depending on the mix design and curing conditions [15]. However, carbonation can also lead to the decalcification of C-S-H, which results in carbonation shrinkage and formation of cracks [16]. Additionally, the reduction in pH due to carbonation leads to the depassivation of the protective layer around steel reinforcement, thereby causing corrosion [17].

When PC samples are subjected to sulfate attack, formation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is observed due to reaction of CH with SO_4^{2-} ions [18]. In addition to gypsum, ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) can also form via the reaction between gypsum and C_3A or via the reaction of sulfate ions with calcium aluminate hydrate (C-A-H) [19]. Formation of gypsum and ettringite is an expansive process, which compromises volume stability and results in cracks and strength reduction [20]. Alternatively, one of the main outcomes of chloride attack is the corrosion of

reinforcement bars, which leads to significant problems in the performance and aesthetic properties of reinforced concrete structures [21]. However, chloride ions by themselves are not as detrimental as other environments such as those involving sulfates [22]. Exposure of PC samples to chloride may result in the formation of Friedel's salt ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$) and calcium oxychlorides [22], which causes hydraulic pressure in cement matrix [23]. In the presence of Mg^{2+} ions, formation of brucite or M-S-H due to reaction of MgCl_2 with decalcified C-S-H can also be observed [24], which can lead to a porous structure [25].

Several recent studies [26-29] investigated the blends of MgO-SiO_2 and PC mixes (i.e. resulting in the formation of M-S-H and C-S-H) in terms of the hydration process and evolution of hydration products at different ages. These studies have shown that the properties of the final products are highly dependent on the initial $\text{MgO-SiO}_2/\text{PC}$ ratio, which in turns determines the pH of the system. While the reaction mechanisms, properties and mechanical performance of MgO-SiO_2 systems have been previously investigated, the durability aspects of this binder system under severe environments remain to be reported. In line with this gap in the literature, this study aims to investigate the performance of MgO-SiO_2 based binders under different environments, whose influence on strength development was evaluated via a comparison of MgO-SiO_2 and PC-based concrete samples subjected to the same environments. The prepared samples were subjected to sealed, under water, carbonation, sodium chloride (NaCl), magnesium chloride (MgCl_2) and magnesium sulfate (MgSO_4) environments for up to 180 days. This was followed by an assessment of their mechanical performance via compressive strength testing at different durations and pH measurements. The strength results of MgO-SiO_2 samples were supported with a detailed microstructural analysis at different stages of exposure. The formation of phases was investigated via X-ray diffraction (XRD) and thermogravimetric/derivative thermogravimetric analysis (TG/DTG), while microstructural observations were performed via field emission scanning electron microscopy (FESEM).

2 Materials and Methodology

2.1 Materials

Reactive MgO (commercial name “calcined magnesite 92/200”), microsilica (MS, commercial name “940U”) and PC were acquired from Richard Baker Harrison (UK), Elkem Materials (Singapore) and Lafarge Cement (Singapore), respectively. The properties of MgO, PC and microsilica (MS) are as listed in Table 1. The superplasticizer, SHMP, was obtained from VWR (Singapore). The aggregate used was saturated surface dry (SSD) gravel with a particle size of 4.7–9.5 mm and a density of 2.61 kg/m³, supplied by Buildmate (Singapore).

2.2 Mix compositions

Table 2 presents the mix compositions of the samples prepared in this study. In line with the findings of a preliminary study [30], M samples were composed of MgO and MS at a ratio of 1.5:1. P samples were composed of PC as their main binder component. Both M and P samples were composed of 40% binder and 60% coarse aggregates (4.7-9.5 mm) by mass. Fine aggregates were not included in this mix design to avoid any quartz contamination during microstructural analysis. Both M and P systems were prepared with a constant water/binder (w/b) ratio of 0.4. M samples included 2% (i.e. of the total binder content) of SHMP to improve their fluidity, in line with the findings of previous studies [31, 32].

2.3 Sample preparation and curing conditions

M samples were prepared with the addition of SHMP into the predetermined amount of water in a mixing bowl, which was thoroughly mixed for about 20 minutes to ensure that SHMP was fully dissolved. MgO was then slowly added into the mixing water in small portions while mixing, followed by the slow addition of MS. The mixing procedure continued for about 10 minutes after all the powders were added to prepare a thoroughly mixed paste. P samples were prepared in a similar manner, in which PC was slowly introduced into the predetermined amount of water and

carefully mixed to ensure complete homogeneity. Coarse aggregates were introduced into both mixes after the binder component was thoroughly mixed.

The prepared concrete mixes were cast into 50x50x50 mm cubic molds and consolidated by using a vibrating table for around 10 minutes and trowel finished. The cube samples were demolded after 24 hours, weighed and kept under sealed conditions for up to 28 days to ensure adequate curing. After 28 days of curing under sealed conditions, the prepared samples were subjected to five different durability environments in addition to a control (sealed) environment. The details of the durability environments are as follows: (i) sealed/control (C) under 95% relative humidity (RH) and ambient CO₂ concentration; (ii) carbonated (CA) under 95% RH and 10% CO₂ concentration; (iii) under water (W); (iv) under sodium chloride (SC) solution at 10 mg/L concentration; (v) under magnesium chloride (MC) solution at 10 mg/L concentration; (vi) under magnesium sulfate (MS) solution at 10 mg/L concentration. All conditions were maintained under an ambient temperature of 28±2 °C.

2.4 Methodology

2.4.1 Compressive strength

The compressive strengths of all concrete samples were measured by uni-axial loading in triplicates after the initial 28 days of curing, and at 28, 56, 90 and 180 days of exposure to different durability conditions. The equipment used was a Toni Technik Baustoffprüfsysteme machine, operated at a loading rate of 55 kN/min.

2.4.2 pH test

Samples extracted from the cubes after compressive strength testing were dried and ground into powder form for pH measurements. To measure the pH of extracted samples, 2 grams of powdered samples were dissolved in 10 grams of distilled water. After an hour of mixing, the solids were filtered through vacuum and the pH

was measured by using a Horiba pH meter F-52 with an accuracy of ± 0.01 . All the measurements were conducted in triplicates and the average values were recorded.

2.4.3 XRD, TG/DTG and FESEM analyses

Samples extracted from the cubes after compressive strength testing were stored in acetone for 7 days to stop hydration, followed by vacuum drying for another 7 days. The vacuum dried samples were ground into powder form in preparation for XRD, TG/DTG and FESEM analyses. XRD data was collected via a Bruker D8 advance instrument using Cu K α radiation (40 kV, 30 mA) with a scanning rate of 0.02° 2 θ /step from 10 to 80° 2 θ . TG/DTG was conducted on a Perkin Elmer TGA 4000 equipment from 30 to 900 °C with a heating rate of 10 °C/min under nitrogen flow. The quantification of the formed phases within each sample was performed via the deconvolution of the DTG curves using Gaussian functions and the calculation of the area corresponding to different decomposition reactions under each deconvoluted curve. The morphologies of the formed phases within the prepared samples were investigated via FESEM images obtained by a JEOL JSM-7600F equipment. The vacuum dried samples were coated with platinum prior to FESEM analysis.

3 Results and Discussion

3.1 Compressive strength

The compressive strengths of M and P samples exposed to different durability conditions for up to 180 days are shown in Figures 1 and 2, respectively. Before being subjected to different durability conditions, the 28-day compressive strengths of M and P samples were recorded as 65 and 55 MPa, respectively. The higher initial 28-day strength achieved by M samples in comparison to P samples was associated with the water content used in both mixes. Although the w/b ratio was kept constant at 0.4 for consistency within both M and P systems, this water content led to slightly wet mixes for P samples, as the amount of water required by PC to achieve a standard consistency is lower than MgO (i.e. 0.28 vs. 0.64) [33, 34]. While

the formation of M-S-H was the main source of strength within M samples in addition to the relatively small contribution of the formation of brucite, the strength development of P samples was attributed to the formation of calcium-silicate-hydrate (C-S-H) and calcium hydroxide (CH).

When subjected to curing under a sealed environment for up to 180 days, the control (C) samples within both M and P systems exhibited a continuous strength gain, which was an indication of the continuation of the hydration reaction after 28 days of initial curing. M samples demonstrated an increase in strength up to 90 days by reaching 84 MPa, which remained relatively stable until 180 days. Alternatively, P samples showed a continuous increase in strength up until 180 days and reached 74 MPa. These strength values obtained under the control environment were used as a benchmark value to compare the performance of each system under various durability environments.

The use of carbonation (CA) was favorable in terms of the compressive strength development of both M and P samples. Amongst all the durability conditions they were subjected to, M samples achieved the highest strengths (80 MPa from 56 days onwards) under carbonation throughout the 180 days of curing. The strength gain exhibited by these samples was associated with the formation of Mg-based carbonate phases that are known to be the main source of strength within carbonated MgO systems [35-37]. Alternatively, P samples exhibited a continuous strength gain under carbonation and reached over 90 MPa at 180 days. Similar to M samples, this increase in strength was attributed to the expansive formation of carbonate phases under these elevated carbonation conditions.

M samples subjected to under water (W) curing revealed the lowest strengths amongst all the durability conditions. The strengths of these samples remained at around 65 MPa during the entire testing period of 180 days, which was similar to the strength observed after 28 days of initial curing. The lack of further strength development after 28 days of initial curing could be due to the leaching of ions in water, which was previously reported for M-S-H samples cured under water [33]. The adverse effect of water curing on M samples could be an indication of dimensional stability issues [38]. M-S-H samples were reported to display shrinkage cracks

during drying due to the loss of water from the M-S-H gel structure [38], while cracks due to volume expansion as a result of brucite formation could occur under wet conditions. On the contrary, P samples cured under water demonstrated a steady strength development and outperformed the control sample by reaching 80 MPa at 180 days. For P samples, the increase in compressive strength was due to the continuation of the hydration reaction in the presence of water, as expected.

When subjected to sodium chloride (SC) solution, M samples revealed the second lowest strength values after the W environment throughout the entire duration. M samples exhibited a very limited strength development up to 90 days and reached ~72 MPa, which remained stable until 180 days. These values were lower than those of the control sample, which achieved ~16% higher strengths than those subjected to SC at 180 days. The lower strength development under SC environment could be attributed to the limited formation of M-S-H and the development of a new phase (e.g. MgCl_2 , $\text{MgCl}_2 \cdot (\text{H}_2\text{O})_x$ or $x\text{Mg}(\text{OH})_2 \cdot y\text{MgCl}_2 \cdot z\text{H}_2\text{O}$) from the Mg^{2+} ions released from the sample and Cl^- from the testing solution. Similar to M samples, SC environment inhibited strength gain in P samples, which could only achieve ~8 MPa of strength increase after the initial 28 days. P samples kept under SC environment for 180 days revealed a strength value of 63 MPa, which was notably lower than samples under C, CA and W environments. These lower strengths of P samples under SC could be due to the dissolution of C-S-H and CH, and the formation of calcium chloride (CaCl_2) [23].

Under magnesium chloride (MC) environment, M samples exhibited a gradual increase in strength up to 90 days and reached a compressive strength value of ~77 MPa, after which a slight reduction in strength to ~74 MPa was observed at 180 days. Compared to the control sample at 180 days, a ~12% reduction in strength was observed under MC environment. Alternatively, P samples exhibited a significant decrease in strength under MC environment, which was immediately obvious from the first few days of exposure. The compressive strength of P samples reduced by ~16% on average when compared to the initial 28-day strength and remained at ~46 MPa for the entire testing period. The detrimental effect of MC solution on P samples could be attributed to the depletion of CH (i.e. $\text{Ca}(\text{OH})_2 + \text{MgCl}_2 \rightarrow \text{Mg}(\text{OH})_2 + \text{CaCl}_2$) and decalcification of C-S-H (i.e. $\text{C-S-H} + \text{MgCl}_2 \rightarrow$

CaCl₂ + M-S-H) [39]. The notably lower performance of P samples under MC environment in comparison to SC environment suggested that the type of cation (e.g. Mg²⁺) in the solution played a significant role in the chemical reactions taking place. Additionally, calcium oxychloride (3CaO·CaCl₂·15H₂O), which generates hydraulic pressure on the cement matrix, could form in the presence of Cl⁻ ions [40]. The higher durability performance of M samples could be associated with the lower solubility of the hydrate phases in MgO-SiO₂ systems, when compared to those in PC systems (i.e. the solubility of brucite is 0.009 g/L at 18 °C, while this value is 1.23 g/L for CH [41, 42]).

Under magnesium sulfate (MS) environment, M samples achieved a considerable increase in compressive strength, reaching ~77 MPa at 180 days, which was ~8% lower than the control sample. However, when compared to W, SC and MC environments, samples subjected to MS environment revealed higher strengths at all times, which could be due to the increased amount of Mg²⁺ ions in solution that could have contributed to the formation of M-S-H [43]. The compressive strength values of P samples under MS environment was affected in a similar manner to those subjected to MC, albeit not at the same scale. P samples kept under MS environment indicated an average of ~2% reduction in strength when compared to the initial 28-day strength, which was better than those observed in MC environment. This low reduction in strength could be attributed to the formation of gypsum and ettringite, and the decline in the amount of CH [25].

Collectively, the changes in the strength development of each system demonstrated the durability of M and P samples individually under different conditions. While both sets of samples continued to gain strength under sealed (C) and carbonation (CA) environments due to the densification of the sample structure via the continuation of hydration and carbonation reactions, the use of under water (W) curing as well as SC, MC and MS solutions led to variations in sample performance. Both systems indicated a slight increase in strength in SC solution. Under water curing was beneficial for the strength development of P samples, which benefitted from the continuation of hydration; whereas M samples demonstrated a lack of strength gain that could be associated with dimensional stability issues. When compared to P samples, M samples revealed higher resistance under MC and MS solutions, which

was attributed to the formation of M-S-H and brucite under the increased concentration of Mg^{2+} and their lower solubility values in comparison to Ca-based hydrate phases. Despite the slight reduction observed under MC and MS environments, the compressive strengths of all M samples were almost the same at 90 and 180 days, indicating that most the reactions took place within 90 of exposure. Therefore, further microstructural analysis was conducted on M samples exposed to different conditions for 28 and 90 days.

3.2 pH

The pH values of M and P samples exposed to different durability conditions for 90 days are shown in Figure 3. The initial 28-day values (I-28) of M and P samples before the start of durability testing were recorded as 10.6 and 12.7, respectively. Previous studies [7, 10] showed that a pH value of around 10 was observed in MgO-SiO₂ samples after 28 days of hydration. The slightly higher pH values observed for M samples in this study could be attributed to the presence of impurities in MgO and formation of brucite, which has a pH value of ~10.5. For PC systems, hydration results in a pH value between 12 and 13 [42], which was in line with the initial measurement. When the pH values of M and P samples were compared over the 90 days of exposure, M samples had significantly lower pH values than P samples under all durability conditions due to the different binders used in each system.

When compared to the control sample at 90 days, M samples revealed very similar pH values under most of the durability conditions such as CA, MC and MS, which could be an indication of the stability of formed phases under each of these conditions. The only two conditions that indicated the largest deviation was the SC solution and under water curing. When subjected to SC, an increase in pH was observed; whereas those cured under water led to slightly lower pH values than the control. This reduction in pH could be attributed to the leaching of ions under water. The higher pH value of M samples under SC environment, which was also observed in MC solution to a smaller extent, could indicate the formation of a new phase, which could explain the reduction in strength compared to the control sample.

Alternatively, a significant reduction in the pH values of P samples subjected to MC environment was observed, which was in line with the lowest strength results of these samples. Other than the MC environment, most other environments revealed similar pH values to the control. The slight reduction observed under CA was in line with the progress of the carbonation reaction. Although not at the same scale as the MC solution, P samples subjected to SC and MS solutions also led to lower pH values than the control, which explained the lower strengths of these samples in comparison to the control sample at 90 days. When compared to M samples, P samples generally revealed larger deviations from the pH of the control sample, which could be an indication of the higher stability of M samples under the tested conditions.

3.3 Microstructure

Figures 4 and 5 show the FESEM images of M samples after being subjected to different durability conditions for 28 and 90 days, respectively. Both figures also include the FESEM image of the initial sample at 28-days (I-28) to illustrate the microstructure of M samples before they were subjected to any of the testing environments. The formation of M-S-H gel that established a continuous network, along with spherical pores attributed to the presence of silica particles, could be observed in the I-28 sample. A similar microstructure was revealed by the control sample (C) at 28 and 90 days, during which the presence of M-S-H layer dominated the microstructure. This was an indication of the continuation of the hydration reaction, thereby explaining the gradual increase in the compressive strength of the control sample over time.

M samples subjected to carbonation (CA), shown in Figures 4(c) and 5(c), possessed a similar microstructure to the control sample, with some densification as a smaller amount of silica was observed. Formation of any carbonate phases such as hydrated magnesium carbonates (HMCs) was not observed by FESEM, which suggests that the conversion of Mg-phases such as M-S-H to carbonates was limited even after 90 days of carbonation. These findings differed from those reported in a previous study [44], where the formation of HMCs was widely observed and

399 associated with strength gain in MgO-SiO₂ samples subjected to carbonation
400 immediately after casting. The lack of HMC formation in this study was associated
401 with the introduction of carbonation after 28 days of curing in a sealed environment,
402 after which the diffusion of CO₂ through the dense hydrate network and its reaction
403 with hydrate phases was limited.

404
405 When M samples were subjected to under water (W) curing, a reduction in the
406 continuity of M-S-H layer was observed in Figures 4(d) and 5(d). This reduction in M-
407 S-H was accompanied with an increase in the amount of individual particles, which
408 could be identified as brucite and MgO. Delayed formation of brucite may have led to
409 dimensional stability problems, thereby resulting in the formation of cracks, as can
410 be seen in Figure 6(b). These changes in the microstructure could explain the
411 hindered strength development of these samples. Similar to under water curing, M
412 samples subjected to SC environment led to a disintegrated microstructure at 28
413 days (Figure 4(e)), resulting in the disturbance of the continuous M-S-H previously
414 observed in the I-28 sample. However, a different scenario was revealed at 90 days
415 (Figure 5(e)), during which the formation of a new phase with a distinct morphology,
416 involving particles with larger sizes and rough surfaces, was observed.

417
418 As seen in in Figures 4(f) and 5(f), M samples subjected to MC environment led to
419 similar microstructures as the control sample at both curing durations, where a
420 continuous and dense layer of M-S-H was generally observed. Under MS
421 environment (Figures 4(g) and 5(g)), the formation of a new phase, identified by
422 round, dark and bulky spherical particles, was seen around the sample
423 microstructure. The presence of these particles was more pronounced at 90 days,
424 showing that their formation continued under the longer exposure to MS
425 environment. The dispersed formation of these distinct phases around the
426 continuous layer formed by M-S-H gel could explain the lower strength results of
427 these samples when compared to the control sample at 90 days.

428
429 Figure 7 shows the FESEM images of P samples subjected to different durability
430 conditions for 90 days for comparison purposes. Samples cured under C, CA and W
431 environments (Figures 7(a), (b) and (c)) revealed similar microstructures, showing
432 the continuous formation of a gel-like structure attributed to C-S-H and small sized

CH particles with clear edges. Samples subjected to SC, MC and MS environments (Figures 7(d), (e) and (f)) presented less continuous microstructures coupled with the formation of phases with different morphologies, which had a detrimental effect on the mechanical performance in line with the compressive strength results presented earlier. In addition to their less continuous morphologies, the bulky structure shown in Figure 7(d) and the formation of needle-like ettringite observed in Figure 7(f) could explain the reduction in compressive strength revealed by P samples.

3.4 XRD

The XRD diffractograms of M samples exposed to different durability conditions for 28 and 90 days are shown in Figures 8 and 9, respectively. There were notable similarities in the XRD patterns of most samples at 28 and 90 days. The presence of unhydrated MgO (i.e. periclase) and brucite was observed in all samples, along with the presence of amorphous M-S-H at $\sim 20\text{-}30^\circ$, $\sim 35^\circ$, and 60° 2 Theta. Additionally, quartz was observed in most samples due to the contamination from coarse aggregates in the preparation of powder samples for XRD analysis. The main unreacted periclase peaks, located at 43° and 63° 2 Theta, indicated that the hydration of MgO was not complete at both durations, which was in line with the findings of earlier studies [8, 44].

When compared to the periclase peak within the I-28 sample, the intensity of this peak reduced in all samples subjected to different conditions. This reduction was more pronounced at 90 days, indicating the continuation of the hydration reaction after the initial 28 days of curing. Alternatively, no obvious change in the presence of brucite peaks was observed in most samples, except for a slight increase revealed by M samples subjected to under water curing. This increase could be an indication of the higher degree of brucite formation within these samples, which could explain the formation of cracks and lower strength results of these samples than others at later ages. Differing from brucite, the presence of the main hydrate phase of MgO-SiO₂ systems, M-S-H, could explain the strength development of M samples over time. The lack of any notable change in the characteristic peaks of M-S-H, even after

90 days of exposure, was an indication of its stability under various conditions including carbonation, sulfate and chloride attack.

3.5 TG/DTG

TG plots of M samples exposed to different durability conditions for 28 and 90 days are presented in Figures 10(a) and (b), respectively. The total mass loss obtained in all samples was mainly due to the decomposition of brucite and M-S-H, which were the two main hydration products observed within the MgO-SiO₂-H₂O system. In line with the findings of previous studies [6, 8, 44], all samples followed a systematic mass loss throughout the temperature range they were exposed to, during which a steep decrease around ~400 °C was revealed, which referred to brucite dehydroxylation. Other than brucite, the following decomposition reactions were observed in the thermal decomposition of MgO-SiO₂-H₂O systems [6, 29]:

1. 30-300 °C: Loss of interlayer water of M-S-H
2. 300-750 °C: Decomposition of brucite and separation of hydroxyl groups in M-S-H
3. 750-900 °C: Dehydroxylation of silanol groups

Most samples, except for those subjected to under water (W) curing, revealed similar mass loss values at 28 days (Figure 10(a)). The notably lower total mass loss of W sample at 28 days, which could be attributed to the inhibition of the further formation of hydration products due to the rapid brucite formation and leaching of ions from the hydrate phases [33], was reflected in its lower compressive strengths. Differing from the trend observed in 28 days, all samples revealed similar mass losses at 90 days (Figure 10(b)), which suggested that M samples were not significantly affected by various durability environments they were subjected to even after 90 days. The increase in the mass loss of samples cured under water at 90 days could be associated with the increased formation of brucite at later ages, which was also observed earlier in the XRD patterns.

For a detailed investigation of the decomposition of the different phases, the deconvoluted first derivatives of the TG curves (DTG) were generated. The DTG plots generally represented similar patterns in all samples subjected to different durability conditions. All samples exhibited three main bands of decomposition reactions, which partially overlapped. The decomposition during 30-300 °C was associated with the loss of interlayer water of M-S-H and the dehydration of the physically bound water, while the decomposition peak centered around 400 °C was characteristic of brucite dehydroxylation. Lastly, the broad hump occurring just after the brucite decomposition (~550 °C) was indication of M-S-H dehydroxylation. When compared to the control sample, the similar DTG curves of all samples under different durability environments even after 90 days could be an indication of the stability of the hydration products (e.g. M-S-H and brucite) under different conditions.

Figures 11 and 12 show the deconvoluted DTG curves of M samples under different durability conditions for 28 and 90 days, in addition to those of the I-28 sample. The original data (represented by the black dots) was included as well as the cumulative fit (represented by the thick solid line) for each sample, showing that a good fit was obtained in all cases. These two sets were accompanied with the deconvoluted curves, whose combination formed the cumulative fit. Each deconvoluted curve, represented different decomposition reactions observed during thermal analysis. The two curves at up to 300 °C represented the dehydration of interlayer water of M-S-H and dehydration of physically bound water within all samples. It is known that M-S-H loses physically bound water in this temperature range, therefore this range can be attributed to the adsorbed water in the sample as well as the loss of interlayer water in M-S-H. The relatively tall curve around 400 °C indicated the dehydroxylation of brucite in all samples. The remaining curves were used to describe the dehydroxylation of M-S-H over the whole temperature range. This range also included the mass loss associated with the loss on ignition of the raw materials, which could have led to the overestimation of the mass loss due to M-S-H dehydroxylation. However, as all samples included the exact same binder and initial mix composition, the effect of loss on ignition on mass loss should be relatively constant within all samples.

The mass loss values revealed from the deconvolution curves of M samples under different durability conditions at 28 and 90 days are listed in Table 3. All samples exhibited a total mass loss in the narrow range of 19.5-22.2% at both curing durations, except for the W sample at 28 days, whose mass loss remained at 13.9%. When compared to other samples, this limited mass loss was associated with the rapidly formed brucite that could cover the unreacted MgO/silica particles, inhibiting the further formation of hydration products within this sample at 28 days. However, an increase in the mass loss of this sample to 21.1% was observed at 90 days, which could be an indication of increased brucite and M-S-H formation. The delayed formation of these hydrate phases within this sample could have resulted in dimensional stability problems, which was also reflected in its low compressive strength results.

All other samples achieved higher mass loss values than the I-28 sample at 28 days, indicating the continuation of hydration after the 28 days of initial curing. Amongst these, those subjected to carbonation (CA) revealed the highest mass loss (21.9%) at 90 days, which could be attributed to the slight formation of carbonate phases under the presence of diffused CO₂. However, the presence of any carbonate phases did not appear in the form of a significant separate peak in DTG curves, which could be due to the overlap with other phases and the relatively small content of these carbonates, whose presence could also not be detected earlier in XRD and FESEM analyses. The challenge in the identification of carbonate phases via microstructural analysis could be attributed to their formation on mainly the sample surfaces (i.e. especially challenging after 28 days of initial sealed curing), while sample preparation for microstructural analyses involved the extraction of powders from all sample depths. Alternatively, samples subjected to SC environment revealed the lowest mass loss at both durations, which could explain their lower strengths results. This outcome could be attributed to the adverse effect of sodium chloride in the hydration of MgO-SiO₂ samples. The appearance of an additional small peak at ~500 °C in the DTG plot of SC sample at 90 days (Figure 12(e)) suggested the formation of a new phase, which was in agreement with earlier observations.

Similar to the trend observed in the total mass loss values, mass loss due to the dehydroxylation of brucite and M-S-H was within a narrow range in most samples at

both curing durations. While the mass loss due to the decomposition of brucite remained relatively stable over time, a slight reduction in the mass loss due to the dehydroxylation of M-S-H was observed from 28 to 90 days of exposure in most samples. This reduction, albeit small, could be an indication of the changes in the amount of M-S-H at longer exposure durations. However, the lack of any significant change in the mass loss values over time could suggest that the hydration products did not undergo a notable change under the various durability environments used in this study.

4 Conclusions

This study investigated the mechanical performance and microstructural development of MgO-SiO₂ (M) concrete samples subjected to different durability environments over a 180-day period, following 28 days of initial curing. Samples exposed to carbonation, under water curing, and NaCl (SC), MgCl₂ (MC) and MgSO₄ (MS) solutions were compared with the control sample kept under sealed conditions for the same duration. The changes in the mechanical performance of M samples were also compared to corresponding PC (P) samples, which were subjected to the same durability environments. The pH and strength results were supported with microstructural analyses involving XRD, TG/DTG and FESEM.

Control samples kept under sealed conditions led to 180-day strengths of 84 and 74 MPa for M and P samples, respectively. Subjecting the samples to carbonation was beneficial for both M and P samples, resulting in high compressive strengths, which were attributed to the densification of microstructure. M samples experienced hindered strength development under water curing, potentially due to volume stability issues; while P samples exhibited a notable strength development as water curing enhanced the hydration of PC. Under SC environment the strength development of both M and P samples were lower than those of corresponding control samples. Under MC and MS environments, M samples revealed continuous strength development over time. However P samples subjected to these two conditions experienced a reduction in their strength.

The results of this study showed that MgO-SiO₂ based concrete samples were overall durable under several aggressive environments, some of which were detrimental for PC samples. Under none of the durability environments used in this study, the strengths of M samples were lowered below the initial 28-day value. The maintenance of strengths obtained by M samples in most conditions were associated with the stability of their hydrate phases, namely brucite and M-S-H. This was confirmed by microstructural analysis, which indicated a lack of any significant change in sample composition even at longer durations. The sustained mechanical performance, coupled with the clear presence of brucite and M-S-H even at longer durations, suggested that these phases did not decompose under any of the durability environments.

These outcomes highlight the potential of MgO-SiO₂ formulations to be utilized in structural applications. Optimization of the mix design and fresh properties of MgO-SiO₂ mixes can result in the production of workable mixes with desirable mechanical properties and durability under various environments. These outcomes can lead to formulations that can be a potential alternative to PC-based mixes in certain practical structural applications, once the interaction of this binder system with various reinforcement systems are fully examined. This can extend the use of this novel binder system in different structural applications including the use of reinforcement that is compatible with lower pH systems (e.g. glass or polymer fibers). Further studies on the volume stability and changes in the chemical composition of MgO-SiO₂ samples under other aggressive environments would further increase the knowledge about their long-term durability.

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752

List of Tables:

Table 1 Chemical composition and physical properties of MgO, PC and MS (provided by suppliers).

	MgO	PC	MS
Chemical composition			
MgO	>91.5%	0.9	-
CaO	1.6%	66.2	-
SiO ₂	2.0%	20.9	>90%
Al ₂ O ₃	<0.7%	-	-
R ₂ O ₃	-	10.0	-
K ₂ O	-	0.5	-
Na ₂ O	-	0.1	-
LOI	4%	1.1	<3%
Physical properties			
Particle size (%)	<74µm 95% min	-	>45µm 1.5% max
Bulk density (kg/dm ³)	-	-	0.20-0.35
Specific gravity (g/cm ³)	-	3.1	-

Table 2 Mix compositions used in this study.

Sample	Dry mix (wt.%)				SHMP
	MgO	PC	MS	Coarse aggregates	
M	24	-	16	60	2%
P	-	40	-	60	-

Table 3 Allocation of mass loss obtained from the thermal decomposition of M samples under different durability conditions, based on the deconvoluted DTG curves at 28 and 90 days.

Sample	Curing duration (days)	Mass loss (% of original mass)			Total
		Adsorbed water (dehydration)	Brucite (dehydroxylation)	M-S-H (dehydroxylation)	
I-28	28	4.8	2.8	11.9	19.5
C	28+28	6.1	2.7	12.0	20.8
CA		6.5	2.7	12.7	21.9
W		4.0	2.0	7.9	13.9
SC		5.0	2.8	11.8	19.6
MC		6.5	2.5	13.2	22.2
MS		5.8	2.2	12.3	20.3
C	28+90	6.5	2.3	11.5	20.3
CA		6.8	3.5	11.6	21.9
W		6.5	2.7	11.9	21.1
SC		5.4	2.5	11.6	19.5
MC		6.4	2.7	11.2	20.3
MS		7.4	2.2	11.1	20.7

List of Figures:

Figure 1 Compressive strength of M samples under different conditions

Figure 2 Compressive strength of P samples under different conditions

Figure 3 pH values of M and P samples under different conditions at 90 days

(a)

(b)

(c)

(d)

(e)

(f)

(g)

Figure 4 FESEM images of M samples under various conditions: (a) I-28, (b) C, (c) CA, (d) W, (e) SC, (f) MC and (g) MS at 28 days

Figure 5 FESEM images of M samples under various conditions: (a) I-28, (b) C, (c) CA, (d) W, (e) SC, (f) MC and (g) MS at 90 days

(a)

(b)

Figure 6 Images showing samples under (a) control and (b) water environments at 90 days

(a)

(b)

(c)

(d)

(e)

(f)

Figure 7 FESEM images of P samples under various conditions: (a) C, (b) CA, (c) W, (d) SC, (e) MC and (f) MS at 90 days

Figure 8 XRD diffractograms of M samples at 28 days

Figure 9 XRD diffractograms of M samples at 90 days

(a)

(b)

Figure 10 TGA curves of M samples at (a) 28 days and (b) 90 days

Figure 11 Deconvolution of DTG curves of M samples under various conditions: (a) I-28, (b) C, (c) CA, (d) W, (e) SC, (f) MC and (g) MS at 28 days

Figure 12 Deconvolution of DTG curves of M samples under various conditions: (a) I-28, (b) C, (c) CA, (d) W, (e) SC, (f) MC and (g) MS at 90 days