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Performance and microstructure of $MgO-SiO_2$ concrete under different environments

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HIGHLIGHTS

- $MgO-SiO_2$ concrete was exposed to carbonation, H_2O, NaCl, $MgCl_2$ and $MgSO_4$ solutions.
- Compressive strengths were compared with PC concrete under the same environments.
- Strength of $MgO-SiO_2$ concrete did not deteriorate even after 180 days of exposure.
- Hydrate phases M-S-H and brucite were present even after long exposure durations.
- $MgO-SiO_2$ samples outperformed PC samples under $MgCl_2$ and $MgSO_4$ environments.

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ABSTRACT

This study investigated the changes in the performance and microstructure of $MgO-SiO_2$ concrete under exposure to different environments involving carbonation, NaCl, $MgCl_2$ and $MgSO_4$ 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 $MgO-SiO_2$ 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 $MgO-SiO_2$ formulations and their potential to be utilized in structural applications.

1. Introduction

Portland cement (PC) production is an energy intensive process and significantly contributes to global CO_2 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 $MgO-SiO_2$ 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 SiO_2 sources, sodium hexametaphosphate ($(NaPO_3)_6$, SHMP) is generally used to reduce the water demand of $MgO-SiO_2$ mixes, which results in lower porosity and higher compressive strengths [9]. When their water contents are reduced via the use of SHMP, $MgO-SiO_2$ 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 $MgO-SiO_2$ 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 $MgO-SiO_2$ 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 $MgO-SiO_2$ samples. A few studies [12,13] focusing on the durability

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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 $Ca(OH)_2$ 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 ($CaSO_4{\cdot}2H_2O$) is observed due to reaction of CH with SO_4^{2-} ions [18]. In addition to gypsum, ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$) 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 ($3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$) 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 MgO-SiO_2/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/m^3, 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 min to ensure that SHMP was fully dissolved. MgO was then slowly added into

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_2O_3	<0.7%	–	–
R_2O_3	–	10.0	–
K_2O	–	0.5	–
Na_2O	–	0.1	–
LOI	4%	1.1	<3%
Physical properties			
Particle size (%)	<74 μm 95% min	–	>45 μm 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	–