

Microstructure of MgO-Al₂O₃-SiO₂ binders

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ABSTRACT

Magnesium (alumino)silicate hydrate (M-(A)-S-H) based binders are low-carbon alternatives to Portland cement, but their microstructure remains poorly understood. This study investigates the compressive strength and microstructure of paste samples with a fixed Mg/Si molar ratio of 1.5 and Al/Si molar ratios of 0 and 1.0 prepared using silica fume (MS) and metakaolin (MK), respectively. The results show that the MK system consistently achieved higher compressive strengths than the MS system. The addition of Na₂CO₃ increased the compressive strength of the MS system but decreased that of the MK system in the presence of excess phosphate. These results are supported by backscattered electron microscopy (BSE) and mercury intrusion porosimetry (MIP) analyses, which revealed increased pore volumes and sizes in the MS system than in the MK system. When Na₂CO₃ was added, the pore volumes and sizes of the MS system decreased, but no consistent changes were observed for the MK system.

KEYWORDS: *M-(A)-S-H, microstructure, pore structure, materials characterisation, low-CO₂ cement*

1. Introduction

Magnesium silicate binders are low-carbon alternatives to Portland cement since the raw material MgO can be derived from Mg-silicate minerals such as olivine without releasing chemically bound CO₂ through, for example, acid digestion combined with electrolysis (Scott et al., 2021). When reactive MgO is mixed with a silicate source (e.g., silica fume) and water, a binding magnesium-silicate-hydrate (M-S-H) phase is formed. M-S-H binders demonstrate high compressive strength (50 to 80 MPa), low pH, excellent fire resistance and potentially high durability (Bernard, 2022).

Due to the limited availability of silica fume, researchers have started investigating the replacement of silica fume with more widely available aluminosilicate sources such as calcined clays. It has been found that the use of metakaolin improves the mechanical properties through the formation of hydrotalcite and M-A-S-H (Shah et al., 2021). The addition of Na₂CO₃ has been found to enhance the mechanical properties further by promoting M-A-S-H formation (Bernard et al., 2023). However, the microstructure of both M-S-H and M-A-S-H binders has not yet been adequately studied, despite their importance to mechanical properties and durability. Therefore, this study investigated the compressive strength and microstructure of M-S-H and M-A-S-H binders, produced with MgO, silica fume (Al/Si = 0) or metakaolin (Al/Si = 1.0), sodium hexametaphosphate as a superplasticizer, and with and without Na₂CO₃, cured from 3 to 91 days. The microstructure was characterised using BSE, MIP and N₂ adsorption.

2. Methodology

Four pastes with a set Mg/Si molar ratio of 1.5 and Al/Si molar ratios of 0 (using MS) and 1.0 (using MK), with and without Na₂CO₃, were prepared according to the mix proportions in Table 1. Reactive MgO (CalMag 92/200, RBH), microsilica (920D, Elkem) and metakaolin (Argical M1200S, Imerys) were used as raw materials. Na₂CO₃ (anhydrous, ≥ 98% purity, VWR) was added at a concentration of 2.5 wt.% binder to all mixes. The water/binder ratio (w/b) was set to 0.68. Sodium hexametaphosphate

(NaHMP) (general purpose grade, Fisher Scientific) was added at varying concentrations to ensure comparable workability across all mixes (Jia et al., 2016). Before wet mixing, the raw materials were homogenised using a powder mixer. NaHMP and Na₂CO₃ were pre-dissolved in the mixing water. Mixing was then performed in a 30 L Hobart mixer for 3 min. All mixes were subsequently compacted in three layers in steel moulds of 50×50×50 mm³ and then covered with a plastic sheet. After 24 h, the samples were demoulded and cured in a fog room (21 °C, 98% RH) for 3, 7, 28 and 91 days. For each mix and curing age, four cubes were prepared, three for compressive strength testing and one for BSE, MIP and N₂ adsorption. For BSE observation, a prism of 40×20×8 mm³ was extracted from the cube while the remaining offcuts were crushed into granules of a few mm for MIP and N₂ adsorption. Hydration was stopped by immersing the samples in isopropanol for 15 min followed by diethyl ether for 5 min. The prism for BSE imaging was epoxy-impregnated and then polished to 0.25 µm. BSE imaging was performed using a Zeiss Sigma 500VP scanning electron microscope at 15 kV accelerating voltage and 8.5 mm working distance. MIP was performed on ~1 g of granules using a Quantachrome Poremaster 60 up to a pressure of 414 MPa to detect pore sizes of down to 3.6 nm. N₂ adsorption was performed on ~1 g of granules, pre-degassed under vacuum at 40 °C for 24 h, using a Micromeritics 3Flex analyser to determine the BET pore specific surface area (SSA) and mean pore diameter (d). Compressive strength testing was performed using a Controls cube crusher at a loading rate of 0.3 MPa/s.

Table 1: Mix proportions of the binders investigated. MS: silica fume; MK: metakaolin, NaC: sodium carbonate; NaHMP: sodium hexametaphosphate.

Sample ID	Materials (wt.%)						w/b (w/w)	Mg/Si (mol/mol)	Al/Si (mol/mol)
	MgO	MS	MK	Na ₂ CO ₃	Water	NaHMP			
MS_0	29.4	29.4	--	--	41.1	0.1	0.70	1.5	--
MS_NaC	28.6	28.6	--	1.4	40.1	1.2	0.68	1.5	--
MK_0	20.1	--	37.1	--	40.0	2.9	0.70	1.5	1.0
MK_NaC	19.8	--	36.5	1.4	39.4	2.8	0.68	1.5	1.0

3. Results and Discussion

Figure 1 presents the compressive strengths of all the systems investigated as a function of curing time. Irrespective of the binder, the compressive strength increased up to 28 days and then plateaued thereafter. MK_0 consistently had higher compressive strengths than MS_0, attributable to the formation of M-A-S-H and hydrotalcite (Shah and Scott, 2021). The addition of Na₂CO₃ increased the compressive strength in MS_NaC but reduced that in MK_NaC. Na₂CO₃ has been shown to accelerate the formation of M-S-H and M-A-S-H through destabilizing brucite (Bernard et al., 2023). However, in the case of MK_NaC, the formation of M-A-S-H might have been retarded by the presence of excess phosphate, as has been observed with M-S-H (Walling et al., 2015).

Figure 2 shows the BSE images of all systems at 91 days of curing. MS_0 is considerably more porous than MK_0. However, the spaces between MgO and silica fume or metakaolin particles appear to be occupied by M-S-H or M-A-S-H with no definite form. Platelet-like structures, likely to be hydrotalcite, are also observed in MK_0. The incorporation of Na₂CO₃ led to a densification of the microstructure in MS_NaC relative to MS_0, evident by the increased formation of M-S-H (and possibly brucite) in the pore space. This is supported by the presence of MgO particles with a dark rim, indicating an increased reaction of MgO. The effect of Na₂CO₃ in increasing porosity in MK_NaC relative to MK_0 is evident in the BSE images.

Figure 3 shows the cumulative pore size distributions measured by MIP at 7 and 91 days of curing. Overall, the results corroborate the BSE observations (Figure 2). The intruded pore volumes and pore sizes reduced with curing age and were larger in MS_0 than in MK_0. The addition of Na₂CO₃ reduced the pore volumes and pore sizes in MS_NaC, but no consistent effect was observed in MK_NaC, although the pore sizes seemed to increase.

Figure 4 shows the BET pore SSA and mean pore diameters measured by N₂ adsorption. Irrespective of the system, the pore SSA generally increased with curing age up to 28 days, presumably due to the increased formation of M-S-H or M-A-S-H, and their gel pores, similar to C-S-H in Portland cement

systems. However, the pore SSA decreased after 28 days of curing. The reason for this is unclear from the results obtained, but a similar observation has been reported with M-S-H synthesised at a high water/solid ratio of 45 between 1 and 3 years of curing (Bernard et al., 2019). The pore SSA was larger in MS_0 than in MK_0 after 28 days of curing, indicating that a larger amount of M-S-H had formed in MS_0 than M-A-S-H in MK_0. This result also suggests that the higher compressive strengths of MK_0 could be more of a result of physical pore filling by unreacted metakaolin particles. The incorporation of Na_2CO_3 increased the pore SSA in MS_NaC but decreased that in MK_NaC. A general opposite trend was observed with the mean pore diameters, such that the higher the SSA, the smaller the mean pore diameter, confirming the densification of microstructure by M-S-H or M-A-S-H gels.

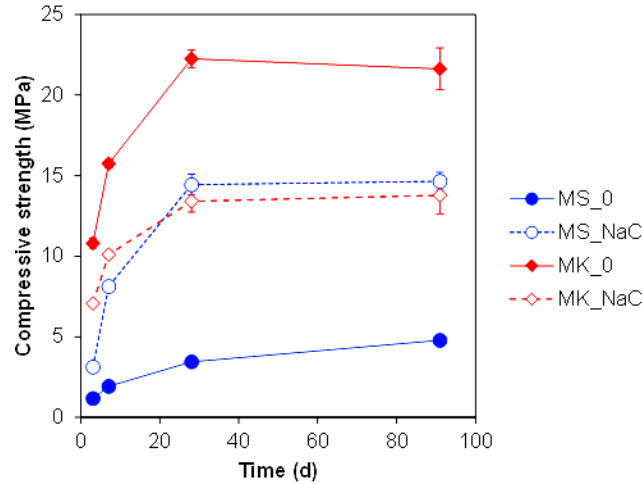


Figure 1: Compressive strength of all systems with curing age. Error bars represent \pm standard error.

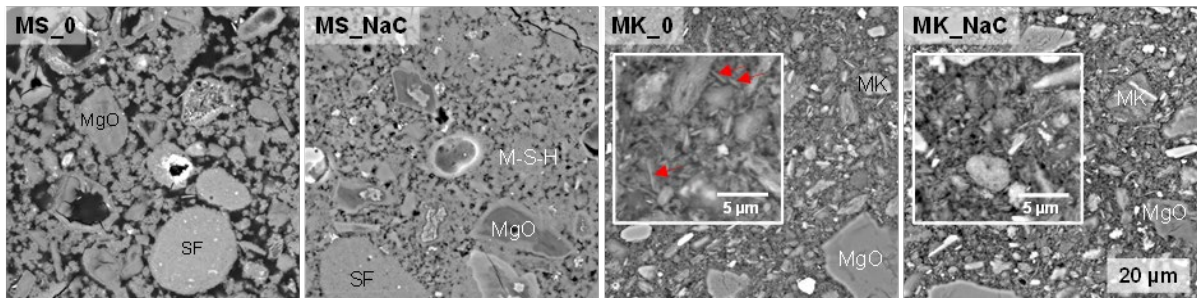


Figure 2: BSE images of all systems at 91 days of curing. Arrows indicate hydrotalcite-like structures.

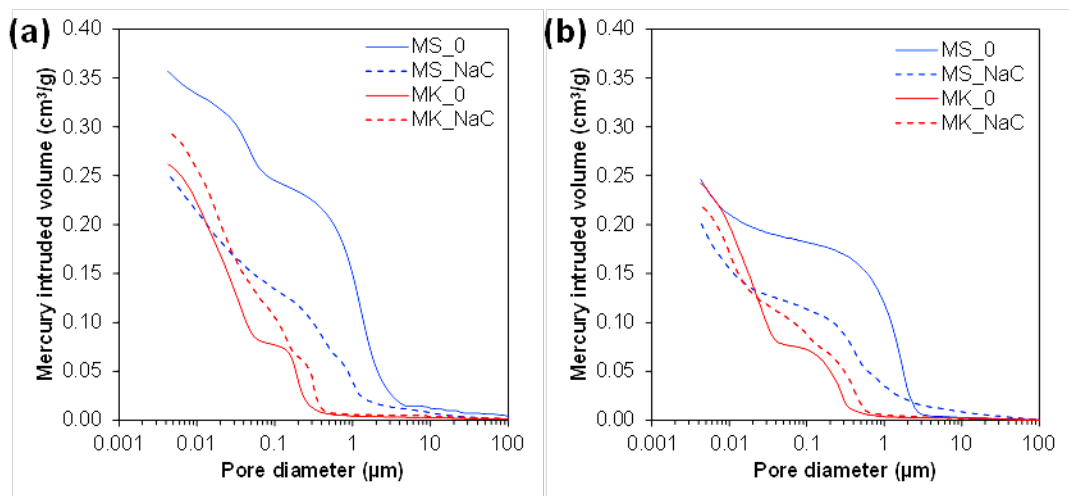


Figure 3: Pore size distribution of all systems at (a) 7 and (b) 91 days of curing measured by MIP.

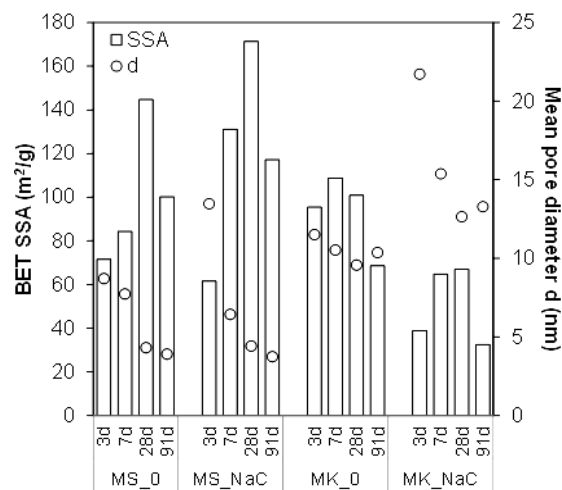


Figure 4: BET SSA and mean pore diameter (d) of all systems with curing age measured by N₂ adsorption.

4. Conclusions

The compressive strength and microstructure of M-S-H and M-A-S-H pastes with an Mg/Si molar ratio of 1.5 and Al/Si molar ratios of 0 (MS) and 1.0 (MK), with and without Na₂CO₃, were investigated. The MK system achieved higher compressive strengths than the MS system at all curing ages. Na₂CO₃ increased the compressive strength of the MS system but reduced that of the MK system, likely due to the presence of excess phosphate. BSE and MIP results showed higher pore volumes and larger pore sizes in the MS system than in the MK system, corroborating the compressive strength results. Na₂CO₃ reduced the pore volume and size distribution of the MS system but no consistent effects were observed for the MK system. However, the pore specific surface areas and mean pore diameters measured by N₂-BET suggest that a larger amount of M-S-H had formed in the MS system than in the MK system, with or without Na₂CO₃, indicating that the higher compressive strength of the MK system could be largely due to pore filling by metakaolin. Work is ongoing to correlate the microstructure and phase assemblages measured by XRD, TGA and NMR, and to understand the effect of phosphate on the formation of M-A-S-H.

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