

## STRENGTH DEVELOPMENT OF MORTARS USING A MAGNESIUM SILICATE HYDRATE BINDER SYSTEM UNDER DIFFERENT CURING CONDITIONS

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### Abstract

A magnesium silicate hydrate (M-S-H) binder system was studied to develop low CO<sub>2</sub> emission cementitious materials. The binder system contained 60% magnesium oxide and 40% silica fume. M-S-H mortar mixtures were prepared with a fixed water content of  $w/c=0.40$ , compared to a control mix using Portland cement (PC). A polymer-based superplasticizer was used to improve the workability of the M-S-H mixtures. Samples were cured at different moist and curing temperatures for compressive strength tests performed at 7, 28 and 90 days. It is found that curing conditions have a significant influence on the strength development of mortar mixtures using M-S-H binder systems. Ambient conditions increase early strength for M-S-H binders, however, reduces long-term strength over 90 days. This curing regime surprisingly results in higher strengths at 28 and 90 days age for M-S-H samples compared to PC. Heated treatment increases early strength, however, decreases the long-term strength of M-S-H samples over 90 days curing period. M-S-H binders have slow strength development compared to PC. The highest compressive strengths of M-S-H samples cured in different regimes at 7, 28, 90 days were 50, 53 and 71 MPa while PC samples cured in water at 21°C at these ages had higher strengths of 55, 75, and 86 MPa, respectively.

### Keywords:

Magnesium silicate hydrate, magnesium oxide, silica fume, M-S-H gel, brucite, curing conditions, ambient conditions, oven-dried curing, heated treatment

## 1 INTRODUCTION

The material calcination up to 1450°C for Portland cement production is attributed to be energy-intensive and cause a negative impact to the environment. As such, there has been a trend to develop low-energy-consumption binder systems that incorporate high volume of waste-related constituents, including M-S-H binder systems.

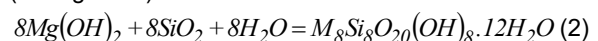
The M-S-H binder systems use reactive magnesium oxide which is calcined at 700-1000°C (Thomas 2014). Such decarbonation process at low temperature releases less CO<sub>2</sub> from burning fossil fuel than the production of Portland cement [Harison 2007]. Another method to produce magnesium oxide using magnesium silicates has been developing by Novacem which is claimed to eliminate the CO<sub>2</sub> emissions from raw materials processing [Gartner 2011]. The other constituent of M-S-H binders is amorphous silica which is available in various forms of industrial by-products or waste materials such as silica fume, rice husk ash, fly ash and natural pozzolans.

Research on cementing properties of M-S-H binder systems revealed a number of distinct properties compared to Portland cement. The chemical reactions for the formation of M-S-H gel were proposed by a number of authors [Wei 2006, Li 2014, Zhang 2014]

whereby the M-S-H gel was formed in a similar mechanism as the pozzolanic reaction in Portland cement. The first stage is the hydration to form magnesium hydroxide from magnesium oxide:



The secondary reaction is then followed to form magnesium silicate hydrates, following the equation (Zhang 2014):



Studies of the microstructure revealed a poor crystalline structure of M-S-H gel. The Mg/Si molar ratio of M-S-H gel was found to vary in a wide range in between 0.67 to 1.50 [Kalousek 1954, Mitsuda 1977, Brew 1995, Nied 2016] while the Ca/Siratio of the C-S-H gel of Portland cement is approximately 1.75 with a variable stoichiometry range of 1.2 to 2.1 [Taylor 1997, Richardson 1999].

The hydration of M-S-H binders generally required very high water demand for chemical reactions and workability due to containing a high volume of reactive silica with its very high surface area [Zhang 2009, Walling 2015]. The compressive strength of the M-S-H binder systems is highly dependent on material sources and mix proportions [Jin 2014]. A wide range of MgO/SiO<sub>2</sub> ratios was tested in literature to optimize

the compressive strength of the binder systems. Zhang [Zhang 2014] assumed that the low Mg/Si ratio systems (MgO/SiO<sub>2</sub>=40/60 by mass) resulted in the optimal formation of M-S-H gel, which was responsible for strength, and reported some M-S-H pastes obtained 28-day compressive strength in excess of 60 MPa. On the other hand, Wei [Wei 2006] suggested high MgO/SiO<sub>2</sub> ratios in which MgO content accounted for 60-70% of the binder composition resulted in optimal strength. These studies confirmed comparable strengths of M-S-H samples to control samples using PC. Tran [Tran 2017] reported a ternary binder system containing magnesium oxide, silica fume and crushed quartz obtaining the compressive strength of over 85 MPa.

Curing is important to improve mechanical and durability of the concrete materials. However, on the debut of developing M-S-H binder systems, little research has been found on the effect of different curing regimes on the strength development of M-S-H binder systems. By far, most previous studies on M-S-H binder systems controlled curing conditions at high humidity (RH≥95%) and temperature at or near 21°C.

### Significance

The experimental data of this paper is significant to develop a potential construction material using M-S-H binder system which is capable to produce cementitious materials of normal to high strength. The curing effect of differing humidity and heated treatment which has not been found in literature will be examined to provide further understanding of the strength development of M-S-H binder systems.

## 2 MATERIALS AND METHODS

### 2.1 Materials

#### Binder

M-S-H binder systems were composed of magnesium oxide and amorphous silica. Light burnt magnesium

oxide was provided by Calix (Australia) with a particle size  $d_{50}=9\mu\text{m}$ . Condensed silica fume (SF) supplied by SIKA NZ includes agglomerates of particle size  $d_{50}=100\mu\text{m}$  although the original silica fume particles had particle size  $d_{50}=0.1\mu\text{m}$ .

Control samples were prepared using Ultracem cement which is a general purpose Portland cement (Type GP) provided by Holcim New Zealand.

#### Aggregate

Normal sand which is primarily siliceous in nature was sourced locally to produce mortar samples. The sand was sieved to a maximum particle size of 2.36mm and meets the requirement of ASTM C33.

#### Superplasticizer

A third-generation polymer-based superplasticizer supplied by Sika (NZ) was used and expected to provide extremely high water reduction for M-S-H binder systems.

### 2.2 Mix proportions

As one of the most disadvantages of M-S-H binders using silica fume was the very poor workability due to the inclusion of high silica fume content, most previous studies of M-S-H binders used high w/c ratios of 0.50 or above even with the presence of superplasticizers [Wei 2006, Jin 2014, Walling 2015]. To develop durable cementitious materials with M-S-H binders, it is necessary to reduce the water content w/c to below 0.50, however, such experiments have been scarcely reported. Therefore, w/c=0.40 was selected in this study aiming at testing strength capacity for durable M-S-H cementitious materials with the use of polymer-based superplasticizer to improve workability.

A binder composition containing 60% MgO and 40% SF was selected for M-S-H mortar samples. The sand/binder ratio for both M-S-H and PC samples was 1.0. The M-S-H samples required a superplasticizer content of 3% binder for workability. Mix proportions and curing conditions of samples are shown in Table 1.

Table 1: Mix proportions of M-S-H and PC mortar samples

Mix labels	Binder			S/B Ratio	w/c	Super-plasticizer (% binder)	Curing regime
	MgO	SF	PC				
SF40-A	0.6	0.4	-	1.0	0.40	3%	A
SF40-W28d	0.6	0.4	-	1.0	0.40	3%	W28d
SF40-W90d	0.6	0.4	-	1.0	0.40	3%	W90d
SF40-D50-3d	0.6	0.4	-	1.0	0.40	3%	D50-3d
SF40-D100-3d	0.6	0.4	-	1.0	0.40	3%	D100-3d
SF40-W60-1d	0.6	0.4	-	1.0	0.40	3%	W60-1d
SF40-W60-3d	0.6	0.4	-	1.0	0.40	3%	W60-3d
PC-A	-	-	1.0	1.0	0.40	-	A
PC-W21	-	-	1.0	1.0	0.40	-	W21

### 2.3 Samples preparation and curing regimes

Samples were cast in cube molds 50×50×50 mm and cured under differing conditions as follows:

- A (Ambient condition): Samples were cured in an environmental chamber with a relative humidity RH=50% and a standard temperature at 21°C.

- W28d: Samples were cured in water at 21°C for 28 days followed by curing regime A until testing date.
- W90d: Samples were cured in water at 21°C over 90 days curing period.

- D50-3d: Unsealed samples were cured in oven at 50°C for 3 days followed by curing in water at 21°C until testing date.
- D100-3d: Unsealed samples were cured in oven at 100°C for 3 days followed by curing in water at 21°C until testing date.
- W60-1d: Samples were cured in hot water at 60°C for 1 day followed by curing in water at 21°C until testing date.
- W60-3d: Samples were cured in hot water at 60°C for 3 days followed by curing in water at 21°C until testing date.

## 2.4 Testing methods

Compressive strength tests were performed as per ASTM C 109-02. The tests were undertaken at 7, 28 and 90 days age. The result for each test is the average result of compressive strengths of three samples.

## 3 RESULTS AND DISCUSSION

### 3.1 Effect of moist curing to M-S-H binder systems

Fig. 1 presents the compressive strength of samples under different moist curing conditions.

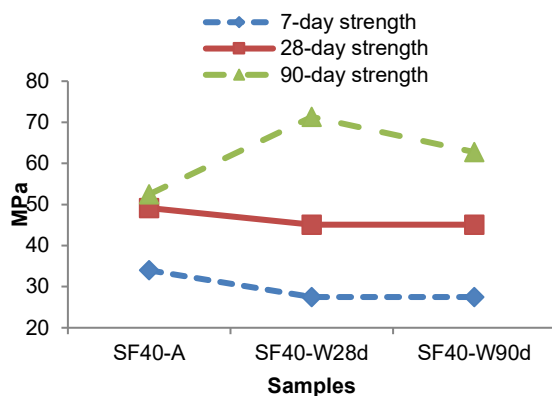


Fig. 1: Compressive strength versus (vs.) different humidity of curing conditions.

At the early age of 7 days, it is surprising that sample SF40-A achieved the highest compressive strength, indicating the ambient condition results in better strength than water curing method. The dominance of brucite as the main hydration product at this early age considerably contributed to strength. The improved crystallinity of brucite in low humidity curing is attributed to the higher strength of samples cured in ambient condition compared to water curing at 7 days. The difference of M-S-H gel volume formed in different curing conditions is insignificant at this early age. It appears that the bound water in brucite is sufficient for the continuing hydration of magnesium oxide and reaction between brucite and silica to form M-S-H gel in ambient-cured samples.

Over the 28 days, the strength increased impressively to approximately 50 MPa (sample SF40-A). Ambient curing conditions probably provide sufficient water for M-S-H gel formation and the low humidity improves crystallinity of brucite. Water curing as observed in SF40-W28d and SF40-W90d samples can provide more water for the formation of M-S-H gel however affected the crystallinity of brucite and therefore obtained a lower strength.

The dramatic 90-day strength increase in samples cured in water (SF40-W28d and SF40-W90d) reveals that the formation of M-S-H gel is significant from 28 days age. The pozzolanic reaction of brucite and silica develops at a low rate at the early age up to 7 days but improves considerably from 28 to 90 days period. The highest compressive strength over a long-term period of 90 days was over 70 MPa, achieved with samples immersed in water for 28 days before curing in ambient condition. On the other hand, long-term strength of samples cured in ambient conditions remained stable after 28 days. The formation of M-S-H gel in these samples is less than in samples cured in water, indicating that the binding effect of brucite is not as significant as M-S-H gel in MgO-SiO<sub>2</sub> mixtures.

### 3.2 Effect of oven-dried curing to M-S-H binder systems

Fig. 2 presents the compressive strength of samples under different temperatures of curing conditions.

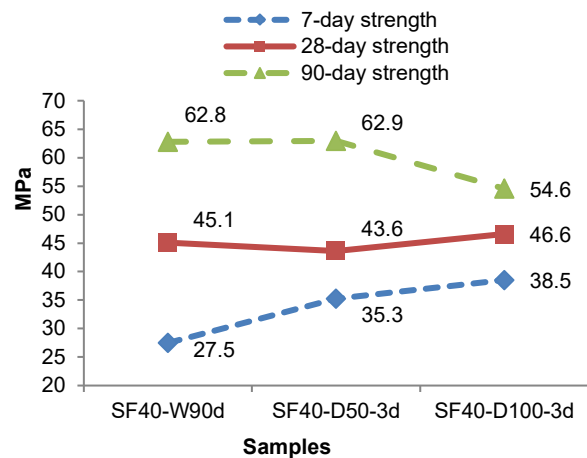


Fig. 2: Compressive strength vs. curing at different temperatures.

Both early and long-term strengths were influenced by oven-dried curing. Early strength at 7 days age of all samples cured in 50°C and 100°C was improved compared to water-cured samples at 21°C (SF40-W90d). Furthermore, higher temperature (100°C) resulted in higher early strength. The highest 7-day strength achieved by oven-dried curing was 40MPa, increased by 45% compared to water curing at standard temperature (21°C).

Despite increasing early strength, the oven-dried curing did not improve 28-day and 90-day compressive strength significantly compared to water-cured samples. Oven-dried curing at 100°C even reduced 90-day strength considerably from 63 MPa to 55 MPa.

### 3.3 Effect of hot water curing to M-S-H binder systems

The coupled effect of moist and oven-dried curing can be tested by using steam or hot water curing. Fig. 3 presents the compressive strength of samples under hot water curing at 60°C for 1 and 3 days in comparison to standard temperature (21°C). Hot water curing improves 7-day and 28-day strengths considerably, however reduced 90-day strength. In addition, a longer curing period in hot water for 3 days resulted in higher strengths at 7 and 28 days age, but also decreased 90-day strength by a greater extent, compared to a short period of hot water curing for 24h. Samples cured in hot water developed strength at a higher rate compared to water curing at standard temperature. The increase of heating duration in water

at high temperature also resulted in the increase of strength development rate.

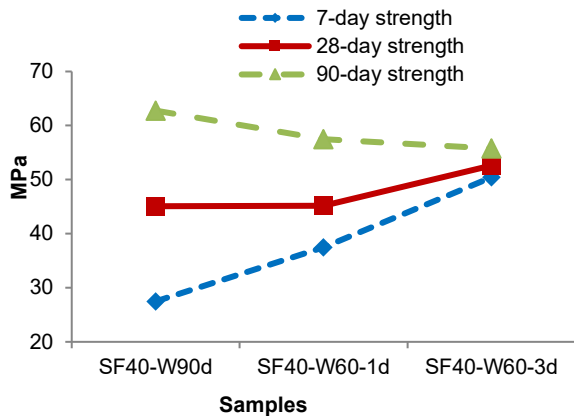


Fig. 3: Compressive strength vs. curing in hot water (60°C). Strength comparison of M-S-H and Portland cement mortar samples

Fig. 4, 5, 6 compares compressive strengths between M-S-H and Portland cement mortars. Surprisingly, M-S-H samples cured in ambient conditions achieved higher strength than PC samples at the ages of 28 and 90 days, despite a lower strength at 7 days age (Fig. 4).

The strengths of M-S-H samples cured in other curing regimes were lower than that of control Portland cement samples cured in water at 21°C (Fig.5, 6). The highest compressive strength of M-S-H samples cured in different regimes at 7, 28, 90 days were 50 MPa (SF40-W60-3d), 53 MPa (SF40-W60-3d), and 71 MPa (SF40-W28d) while PC samples at these ages had higher strength of 55, 75, and 86 Mpa, respectively.

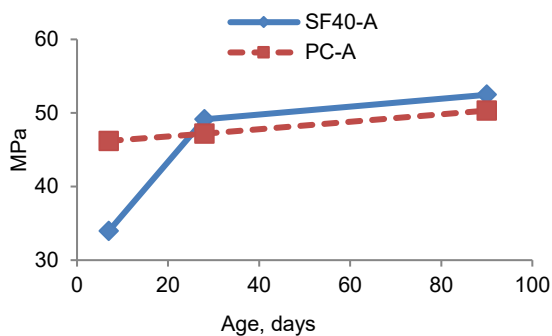


Fig. 4: Compressive strength of M-S-H and PC samples (Ambient curing).

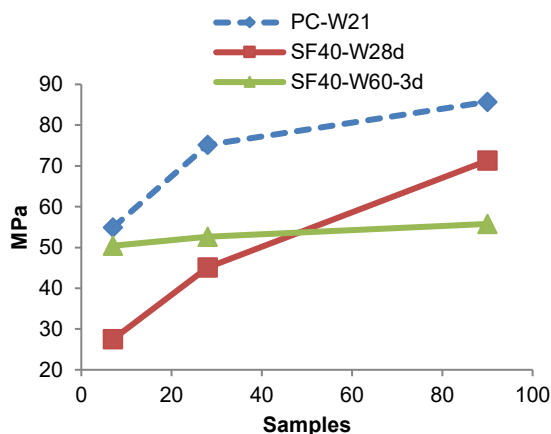


Fig. 5: Compressive strength of M-S-H and PC samples (Water curing).

Ambient conditions and heat treatment resulted in high strength development rates which reduced long-term strength at 90 days age of M-S-H samples (mix SF40-A and PC-A). Due to heated treatment for a long period up to 3 days, the SF40-W60-3d samples also experienced high strength development rate. Water curing at 21°C for M-S-H samples resulted in slow strength development than PC samples, indicating slow pozzolanic reactions to form M-S-H gel in M-S-H binder systems.

#### 4 CONCLUSION

Based on selected materials and experimental results in this study, the following conclusions can be derived:

1. Ambient curing condition increases early strength for M-S-H binders due to the improved crystallinity of brucite, however reduces long-term strength at 90 days age as a result of insufficient water for hydration to form M-S-H gel.
2. Similar to PC, water curing is crucial to develop long-term strength of M-S-H binder. The slow pozzolanic reactions to form M-S-H gel possibly explain the slow strength development of M-S-H binder systems.
3. Heated treatment for M-S-H samples increases early strength but decreases long-term strength at 90 days age. Higher temperature curing results in higher early strength but also reduces long-term strength to a greater extent.
4. M-S-H samples cured in ambient condition surprisingly have higher 28-day and 90-day strength than PC samples. Beside those exceptions, strength of M-S-H samples cured in various conditions is lower than the PC samples cured in water at 21°C.

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