

## **PORE SOLUTION ANALYSIS OF MAGNESIUM SILICATE HYDRATE BINDER SYSTEMS**

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### **SUMMARY**

Magnesium silicate hydrate binder has been developed recently as an alternative to Portland cement. In this study, the pore solutions of magnesium silicate hydrate (M-S-H) paste samples were extracted to analyze pH and ion concentrations and compare to XRD analysis. Mixtures contained reactive magnesium oxide and natural microsilica (MS) with MgO/silica mass ratio varied between 40-60%. M-S-H binders generally have alkaline pore solutions with pH values strongly influenced by the reactivity and alkalis content of the raw materials. The pH was found to decrease during 90 days testing period. Reactive silica (MS) mixed with MgO resulted in pH of 10.50-11.00 at 2 days age and the pH reduced over time to below 10.50 after 90 days. Ion concentrations analysis showed the dominance of sodium, potassium, calcium, magnesium and silicon ions in the pore solutions. The ion concentrations were influenced by the pH of the pore solution and the solubility of the binder constituents. The formation of M-S-H phases have been confirmed from the combination of pH, ion concentrations and XRD analysis. The unexpected high Mg concentrations observed after 90 days curing may be detrimental to the durability of the binders and will need further studies.

### **INTRODUCTION**

M-S-H binder systems are among potential sustainable cements due to the use of reactive magnesium oxide calcined at low temperatures (700-1000°C) and utilization of industrial by products, natural pozzolan and waste materials such as silica fume, fly ash, rice husk to name a few. There are other benefits of using M-S-H binders for the immobilization of nuclear wastes (Zhang et al. 2012; Walling et al. 2015). A developing technology which involves CO<sub>2</sub> sequestration if successful can be applied to produce carbon neutral magnesium-based binders in the future (Pacheco-Torgal 2014). Since cementing properties of M-S-H binder were reported with strengths of over 50 MPa (Wei et al. 2006), an increasing number of publications have been found in the last decade concerning the characterization of the microstructure and mechanical properties of M-S-H binder systems. Zhang et al. (2014) developed low pH M-S-H binder systems obtaining strengths of over 60 MPa. Marmol et al. (2016) produced 70 MPa fiber-cement with MgO-SiO<sub>2</sub> systems incorporating cellulosic reinforcing elements. By using quartz fillers, Tran and Scott (2017) proposed ternary mortar mixtures of MgO-SiO<sub>2</sub>-quartz filler resulting in strengths exceeding 85 MPa. Chen et al. (2017)

produced cement pastes with compressive strengths in excess of 105 MPa by using a combination of CFB slag, reactive MgO and silica fume. Mitsuda and Taguchi (1977) and Brew and Glasser (2005) have laid the foundations for the understanding of microstructure and reaction mechanisms of M-S-H binders. Li et al. (2014) and Zhang et al. (2014) also examined chemical reactions forming M-S-H phases at room temperature. It is known that the composition of the cement pore solution is essential as it reflects the hydration processes and determines which hydrate phases are stable and can thus potentially precipitate and vice versa (Vollpracht et al. 2016). Hence, the pore solution analysis is very useful for understanding cement's deleterious reactions and durability (Hooton et al. 2010). This study will analyze the pore solutions extracted from M-S-H cement paste, which has not been reported in the literature.

## EXPERIMENTAL PROGRAMME

### Materials

M-S-H binder systems generally consist of reactive magnesium oxide and amorphous silica. A source of light burnt magnesium oxide, calcined at temperatures of approximately 700°C was selected for this study. This highly reactive MgO was provided by Calix (Australia) with a particle size  $d_{50}=9\mu\text{m}$ . Microsilica 600 (MS), a natural amorphous silica source, was quarried from a local site in New Zealand and marketed by Microsilica New Zealand Ltd (2017). A third-generation polymer-based superplasticizer supplied by Sika (New Zealand) was used to reduce high water demand of M-S-H binder systems.

The chemical compositions are shown in Table 1.

Table 1. Chemical compositions of MgO and silica sources

Sample	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	LOI	SO <sub>3</sub>	Total
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
M (MgO)	11.36	0.02	0.57	0.33	0.02	71.67	4.06	0.13	0.13	0.02	11.67	-	99.98
MS	85.14	0.95	6.31	0.41	0.01	<0.05	0.13	0.29	0.77	0.07	3.96	-	98.04

### Mix proportions and sample preparation

A series of samples for pore solution expression were prepared from freshly-mixed cement paste using deionized water. Mix proportions are shown in Table 2.

Table 2. Mix proportions of samples for pore solution expression

No.	Samples	Binder composition	w/b	SP (liquid % binder)	Test age and methods			
					2d	7d	28d	90d
1	MS60	0.4MgO+0.6MS	0.60	1.0	pH, ICP-MS	pH, ICP-MS	pH, ICP-MS	pH, ICP-MS
2	MS50	0.5MgO+0.5MS	0.60	1.0	pH, ICP-MS	pH, ICP-MS	pH, ICP-MS	pH, ICP-MS
3	MS40	0.6MgO+0.4MS	0.60	1.0	pH, ICP-MS	pH, ICP-MS	pH, ICP-MS	pH, ICP-MS
10	MS60	0.4MgO+0.6MS	0.40	3.0		XRD	XRD	XRD

The pastes were stored and sealed in 50 ml cylindrical laboratory tubes immediately after mixing, and cured at room temperature of approximately 20 °C until testing dates. To extract the pore solution, samples were taken out of the tubes and immediately placed into the apparatus followed by the compression procedure. Paste samples after extraction can be seen in Figure 1.



Figure 1. Paste samples after expression

The collected pore solution of each mixture was filtered and sealed in a container to prevent reactions with atmospheric carbon dioxide. The pH was measured within 1 h of collection using a pH benchtop meter (Thermo Scientific Orion Star A211). Ion concentrations of the pore solutions were analyzed using the Agilent 7500cx ICP-MS instrument. To verify the pore solutions analysis results, mixtures of MgO and MS were also prepared for XRD analysis.

## RESULTS AND DISCUSSION

### Pore solutions' pH development

Figure 2 shows the control pH of each individual material measured at testing ages compared to pH of the pore solutions of each mixture.

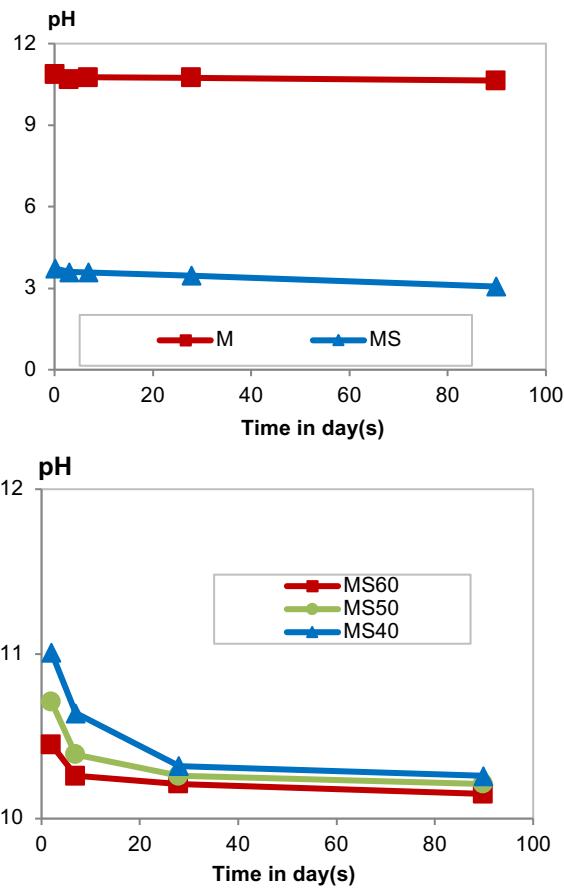


Figure 2. Left: pH of raw material solutions (solid/water = 5/50 g/ml), right: pH of the M-S-H binder pore solutions

pH of M-MS mixtures decreased over the 90 days period. The pH of the pore solutions is determined by the chemical compositions of the raw materials. It was shown that the reference MS solution has the lowest pH between 3.0 and 4.0 over the 90 days compared to other silica solutions. This low pH resulted in a wide range of pH-values of the pore solutions at 2 days and 7 days age as MS content increased from 40 to 60%.

M-MS mixtures showed a pH range of 10.20 to 11.00. As pH of MgO solution remains stable, the pH decrease of the pore solutions illustrates reactions of MS and  $\text{Mg}(\text{OH})_2$  (brucite) forming M-S-H phases.

#### Alkali concentrations of the pore solutions ( $\text{Na}^+$ , $\text{K}^+$ , $\text{Ca}^{2+}$ )

Figures 3, 4, 5 shows the alkali concentrations in the pore solutions extracted from M-MS paste samples. Due to the consumption of water during the hydration process and also a release of alkalis incorporated into binder constituents the alkali concentrations slightly increase over time, although a part of the alkalis is bound in the hydration products (brucite and M-S-H phases).

The concentrations of sodium, potassium and calcium depend on the total content of  $\text{K}_2\text{O}$ ,  $\text{N}_2\text{O}$  and  $\text{CaO}$  of the binders. The sodium and potassium concentrations in M-MS mixtures reached up to 400 and 120 mg/L while calcium concentrations were below 30 mg/L.

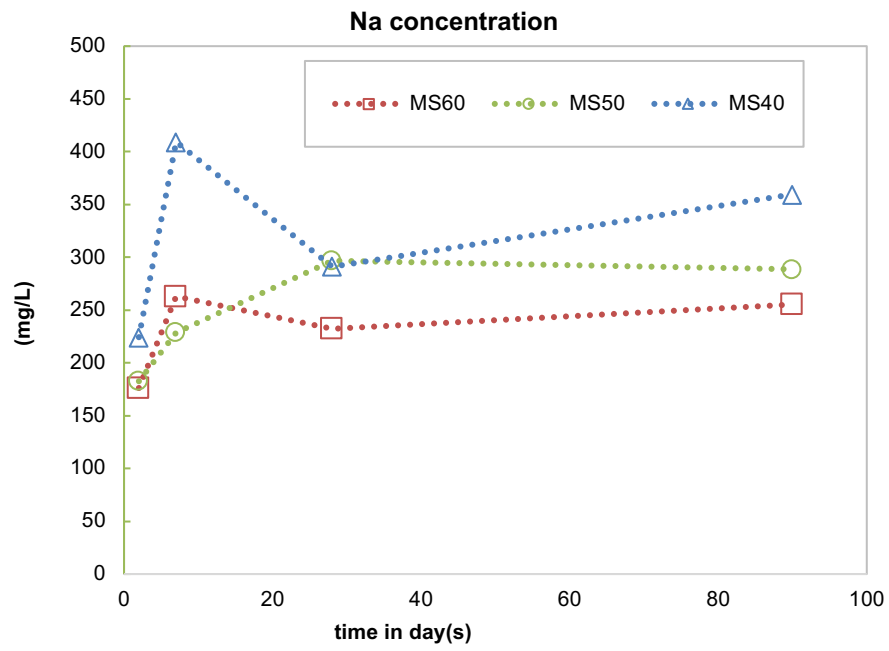


Figure 3. Na concentrations of the pore solutions

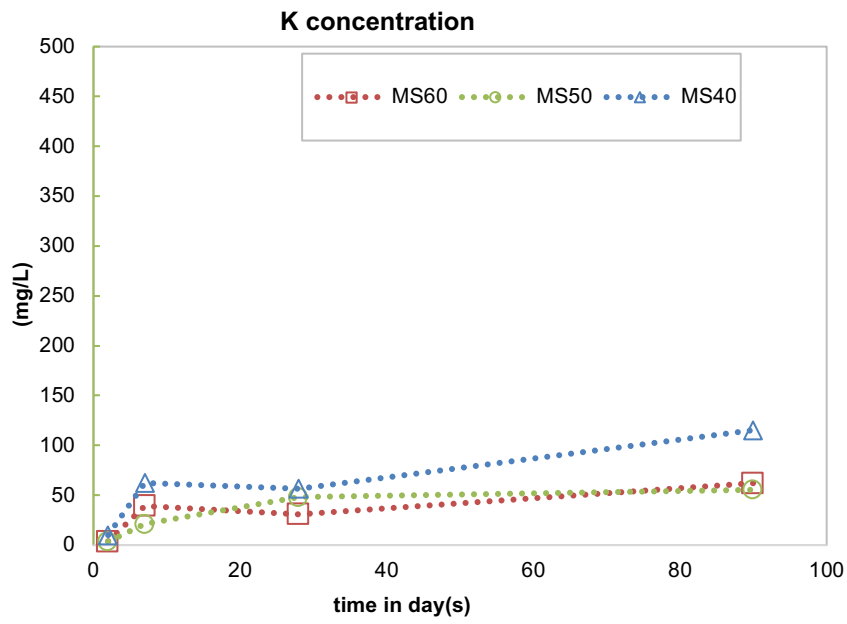


Figure 4. K concentrations of the pore solutions

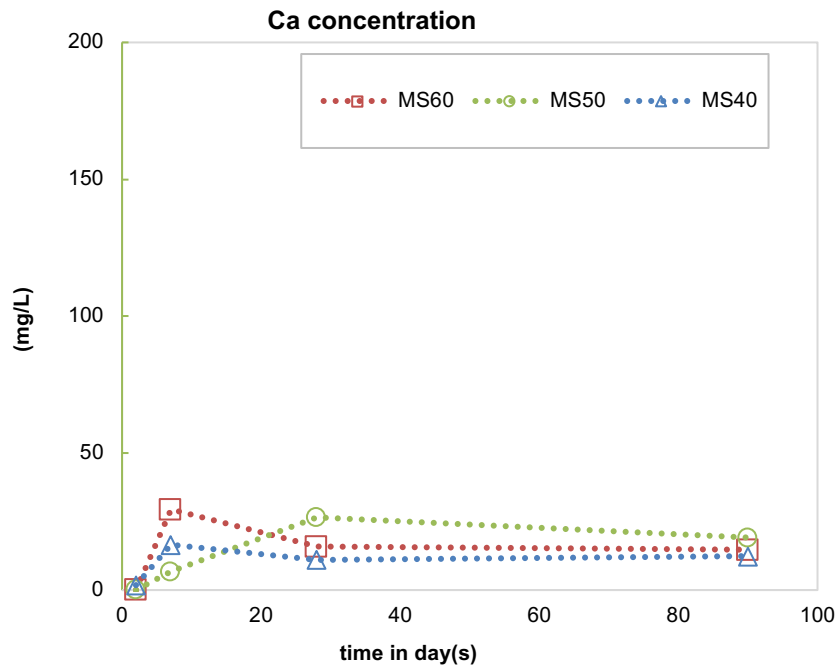


Figure 5. Ca concentrations of the pore solutions

#### Magnesium concentrations of the pore solutions

Figure 6 shows Mg concentrations in the M-MS mixtures over 90 days period. During the early age, Mg concentrations were pretty low which were attributed to the limited solubility of MgO in water. An increase of the Mg concentrations in the pore solution was observed over time. The presence of MS has a strong influence on the dissolution of hydrated MgO after 7 days.

The measured concentrations at 7 days were in between 20 and 100 mg/L, then rose to 50÷200 mg/L at 28 days and further increased to 150÷250 mg/L. The increase in Mg concentrations suggests the depletion of brucite to react with MS to form M-S-H phases.

Mg concentrations are also influenced by MgO/MS ratios. The variation of the concentration reflects the change of MS content. High amounts of MS can reduce pH faster to increase dissolution of MgO. The increase in Mg concentrations of mixtures containing higher MS content also indicates the high reactivity of MS as a supplementary cementitious material.

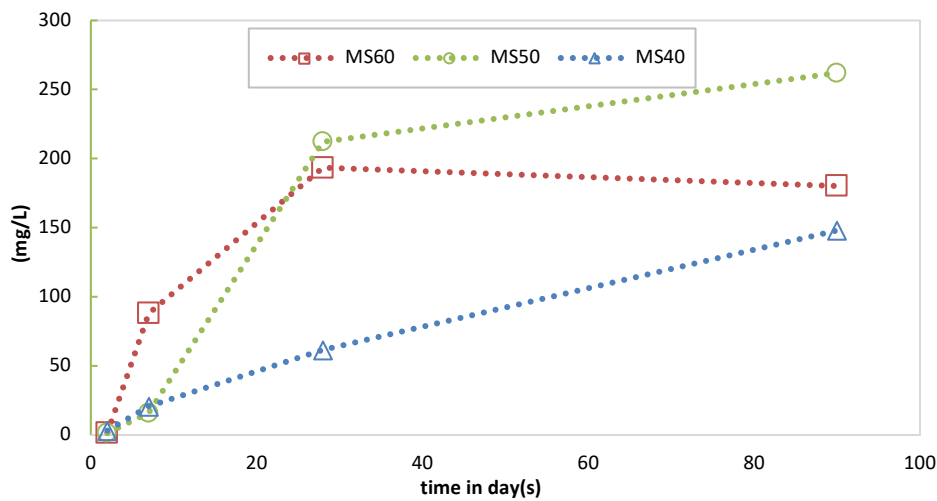


Figure 6. Mg concentrations (mg/L) in M-MS mixtures

#### Silicon concentrations of the pore solutions

Silicon concentrations of M-MS mixtures are shown in Figure 7. The Si concentrations are correlated to the solubility of silica which is affected by the pH and alkalis content in the mixtures. The pore solutions have high pHs at early age due to the high content of MgO and the availability of other alkalis (NaO, K<sub>2</sub>O, CaO) in the binder. As a result, the Si concentrations increased to the highest values after 7 days (150 mg/L), then decreased to the low value (100 mg/L) over 90 days. It was observed that different MgO/SiO<sub>2</sub> ratios only result in marginal difference of Si concentrations over 90 days, probably due to the high content of silica (40-60%). The decrease of Si concentrations suggests that most of the silica has reacted with brucite to form M-S-H phases over time.

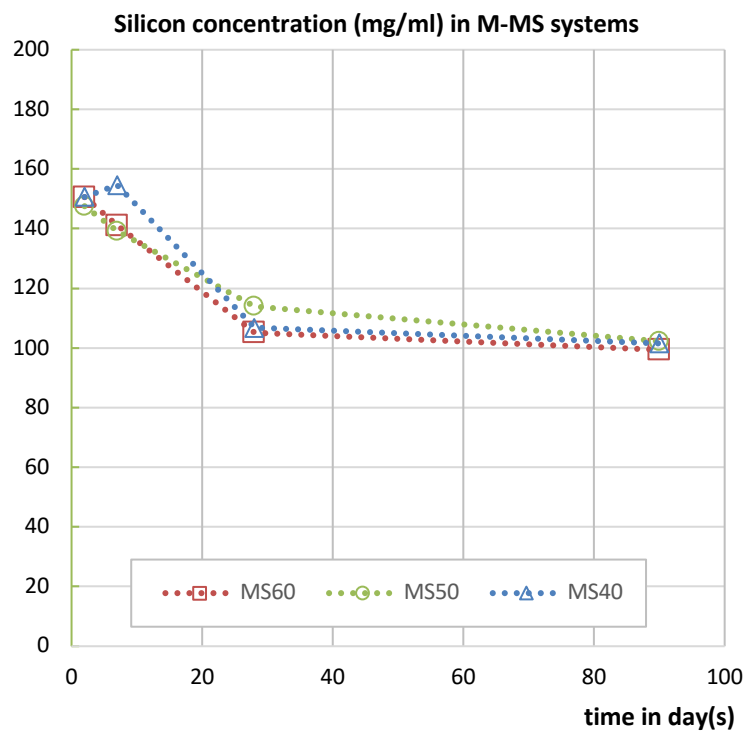


Figure 7. Si concentration (mg/L) in M-MS systems



### 3.5 XRD analysis

Figure 8 presents XRD spectra of M-MS mixtures with  $\text{MgO}/\text{SiO}_2 = 40/60$ . The raw materials before mixing with water were denoted by age 0 while the hydration development was analyzed at 7, 28, and 90 days.

It was found that curing duration has a significant effect on the type of hydration products of M-SF mixtures. Most of the  $\text{MgO}$  was consumed in the first 7 days, illustrated by the reduction in intensity of  $\text{MgO}$  peaks and the presence of brucite's peaks at  $2\theta = 18^\circ, 38^\circ, 51^\circ, 59^\circ$ . This is consistent with other studies (Vandeperre et al. 2008; Jin and Al-Tabbaa 2013). According to previous studies (Gollop and Taylor 1992; Temuujin et al. 1998), three major broad peaks at  $20\text{--}30^\circ, 32\text{--}39^\circ$ , and  $58\text{--}62^\circ$   $2\theta$  can be assigned to M-S-H phases. The peaks related to M-S-H gels were found at 7 days age, although it was not clear. M-S-H phases developed further after 28 days and all brucite reacted with MS after 90 days.

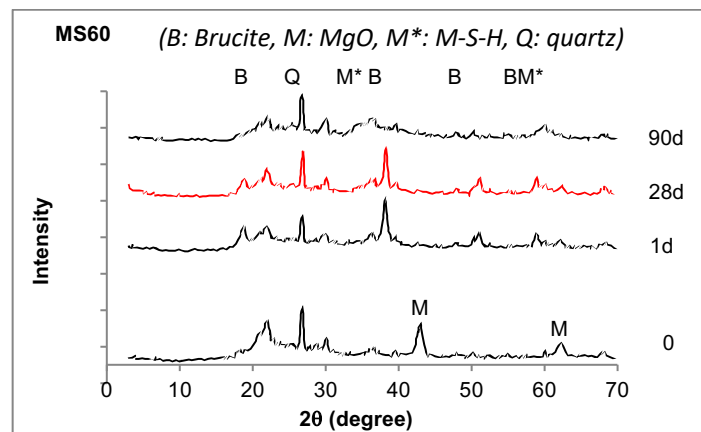


Figure 8. XRD patterns of M-MS mixtures ( $\text{MgO}/\text{MS} = 40/60$ )

It was found that the XRD results are consistent with the pH development of the pore solutions. The high pH at early age up to 7 days can be attributed to the dissolution of  $\text{MgO}$  to form brucite. As reactions of brucite and accelerate at later stage, the brucite content decreases which also reduces the pH. The XRD results confirmed the formation of M-S-H phases over time, which can be supported by the decrease of pH and Si concentrations after 7 days age. Although XRD results have shown a high degree of reactions of brucite and MS, there are still high Mg concentrations in the pore solution after 90 days, possibly result from the dissolution of hydration products including M-S-H and/or brucite at this later stage. This unexpected result requires further study of the durability of the M-S-H binders over the long term.

### CONCLUSIONS

The pore solutions of M-S-H binders are naturally alkaline with the pH decreases over time and strongly depends on the reactivity and alkalis content of the raw materials. For binders using highly reactive silica, pH values reach the peaks after 2 days and in the range of 10.50 – 11.70. The pH decreases over time to well below 10.50 after 90 days. XRD results of the samples are well correlated with the pore solution analysis. Dominant ions available in the  $\text{MgO}$ -silica mixtures include sodium, potassium, calcium, magnesium and silicon. Ion concentrations at 90 days age are in between 100-300 mg/L (Mg) and 100 mg/L (Si). One unanticipated finding was the high Mg



concentrations after 90 days curing period. The increase in Mg concentrations at later stage may adversely affect the durability of the M-S-H binder systems in aggressive environments and will be an interesting topic for future research.

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