ROLE OF SODIUM HEXAMETAPHOSPHATE IN MgO/SiO₂ CEMENT PASTES

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ABSTRACT

The extent of reaction between magnesium oxide (MgO) and silica fume (SiO₂) is normally limited and mixes require high water contents to give suitable rheology. The use of considerably lower water contents and the formation of magnesium silicate hydrate (M-S-H) gel as a binding phase is made possible by adding sodium hexametaphosphate (Na-HMP) to the mix water prior to the addition of MgO and SiO₂. This results in the formation of extensive reaction products and cured samples with high compressive strength and low porosity. In this work, the effect of Na-HMP on the hydration of MgO/SiO₂ mixes is investigated using high water to solids ratio samples to allow monitoring of pH and the solution chemistry during hydration. It is shown that a relatively small amount of Na-HMP inhibits the formation of Mg(OH)₂ when MgO is hydrolyzed. It is proposed that this is due to adsorption of phosphate species on the MgO which inhibits the nucleation of the Mg(OH)₂. This gives rise to high Mg²⁺ species in solution and elevated pH (>12) conditions relative to when Mg(OH)₂ forms. In contrast, the phosphate does not suppress formation of M-S-H gel. In combination with the enhanced dissolution rate of SiO₂ at high pH, M-S-H gel can form quickly without competition for Mg²⁺ ions by Mg(OH)₂ precipitation. Incorporating the optimum concentration of Na-HMP into the mix water therefore transforms the properties of cement paste and mortar samples formed by reacting MgO and SiO₂.

Keywords: Dispersion (A), Hydration products (B), Microstructure (C), MgO (D), Silica fume (D)

1. INTRODUCTION

Cement systems forming magnesium silicate hydrate (M-S-H) have received increasing attention in recent years [1-4]. A mechano-chemical treatment has been used to react hydrous silicic acid and magnesium hydroxide in a hydrothermal reaction that formed M-S-H gel [5,6]. M-S-H gel was also formed by reacting Na_2SiO_3 and $\text{Mg}(\text{NO}_3)_2$ at room temperature with Mg/Si molar ratios in the range of 0.67-1.0 in research investigating the alkali (K, Cs) sorption potential of synthetic M-S-H gels [7,8]. The structure of M-S-H gel produced by reacting MgO and silica fume (SF) with water has recently been reported using x-ray diffraction, IR spectra, DTA-TGA-EGA and NMR studies[9-11,14].

It is very difficult to form useful cement pastes or mortars with good properties by reacting MgO with silica fume (SF) because very high water contents are required to give suitable rheology and mixing. This results in long setting times and low compressive strengths, typically less than 2 MPa [12]. Sodium hexametaphosphate(Na-HMP) is a hexamer of sodium metaphosphate, which is used in the ceramics and food industries and in nanotechnology as a deflocculant and/or sequestering agent [13-15]. The addition of Na-HMP to the mix water has been reported to significantly improve the rheology and properties of MgO/SF pastes and mortars and this enables the production of materials with high strength, high density and low porosity [10,13].

Although the beneficial effects of Na-HMP on MgO/SF systems are known, the changes induced by Na-HMP on the solution chemistry and hydration reactions have not previously been reported. The aim of this research was to investigate the effect of Na-HMP on the hydration of MgO/SF mixes and the formation of M-S-H gel. In a first set of experiments the effect of Na-HMP on the hydration of MgO is investigated. Subsequent experiments using MgO/SF mixes aimed to clarify how the addition of silica changes the reactions.

2. MATERIALS AND METHODS

2.1 Materials

MgO and sodium hexametaphosphate (Na-HMP) were obtained from the Chempur, Tianjin Guangfu

Technology Development Ltd, China. A commercially available silica fume was also used (SF, Elkem Materials Ltd, China). Chemical composition data for the raw materials as reported by the manufacturers is presented in Table 1. The median particle size of the MgO and silica fume was 3.8 μm and 0.3 μm respectively.

2.2 Effect of Na-HMP on the hydration reactions of MgO

The first set of experiments investigated the effect of Na-HMP on the hydration of MgO. 4 g of MgO was added to 100 ml of either distilled water or distilled water containing 0.2 g of Na-HMP to give the mixes. The pH during hydration was monitored (PHS-3C, Shanghai INESA and Scientific Instrument Company) and the concentration of Mg in solution was determined by inductively coupled plasma emission spectrometry (ICP-OES, Perkin Elmer Optima 2100 DV).

After 1, 7 and 28 days the granular residue was separated by filtration and soaked in absolute ethyl alcohol for 24 hours to inhibit further hydration reactions. It was then dried at 40 °C for 48 hours and the crystalline phases in the hydrated samples were determined by x-ray diffraction (XRD D/Max 2400V diffractometer with Cu K α radiation at a scan rate of 0.5°2 θ min⁻¹). The hydrated MgO residues were also characterised using field emission scanning electron microscopy (FE-SEM: NOVA Nano-SEM 450) on gold coated samples that had been sputter coated for 2 minutes using 15 mA and 30 Pa pressure.

2.3 Effect of Na-HMP on the formation of M-S-H gel

In a second set of experiments the reaction between MgO and SF in aqueous solutions containing different concentrations of Na-HMP has been investigated using the sample compositions shown in Table 2. The amount of Na-HMP was varied between 0 and 100 wt. % relative to the solids content and in order to ensure complete hydration a water/solids (W/S) ratio of 10 was used, where S is the total mass of MgO and SF. As in the initial MgO experiments, Na-HMP was first dissolved in distilled water for 20 minutes before mixing with MgO and SF. Samples were then stored at room temperature (25 $\pm$ 1 °C) in 250 ml sealed plastic bottles for up to 90 days. The solution pH was determined at various times during storage and the solutions were analysed by ICP-OES. Crystalline phases present

in the solid residues were determined by XRD using the same procedures as in the previous experiment. The solid residues were dried and gold coated prior to examination using field emission scanning electron microscopy (FE-SEM: NOVA Nano-SEM 450).

2.4. Thermodynamic modelling of the solution chemistry

The experimental measurements of pH and solution chemistry were compared as much as possible with predictions made using Visual MINTEQ 2.6[11], a windows implementation of the MINTEQA2 algorithm[12] for calculation of geochemical aqueous equilibria, which uses the thermochemical data contained within [20]. Unfortunately no information was found for the interaction of sodium hexametaphosphate with magnesium. While this limits the value of the calculations, it was decided to include the calculations as they still offer a useful point of reference for the experimental results.

3. RESULTS

3.1 Effect of Na-HMP on the hydration reactions of MgO

Figure 1 a) shows XRD data for MgO after hydrating in distilled water for 1, 7 and 28 days. Mg(OH)_2 forms rapidly and by 28 days the MgO is completely consumed. Figure 1 b) shows identical data but for MgO hydrated in distilled water containing a small amount of Na-HMP. This solution very effectively inhibits Mg(OH)_2 formation: MgO remains as the main crystalline phase present after 28 days and only a very limited amount of Mg(OH)_2 is formed.

The variation in solution pH during the hydration of MgO in the two solutions is shown in Figure 2. In distilled water the pH rapidly increases to approximately 10.5 and remains constant. When Na-HMP is present in the mix water the pH increases to about 12.0 within the first day and continues to increase gradually to ~12.5 after 28 days.

Figure 3 shows the variation in Mg^{2+} concentration in solution over a 28 day hydration period. The presence of Na-HMP significantly increases the concentration of Mg^{2+} in solution.

FE-SEM images of hydrated MgO particles in distilled water and Na-HMP solution are shown in

Figure 4. Figure 4 a-c) show MgO hydrated in distilled water. Some residual MgO remains in Figure 4a but crystalline $\text{Mg}(\text{OH})_2$ is the main phase present after 7 and 28 days hydration and this is shown in Figure 4b and 4c. Figure 4 d-f) show MgO particles which change in appearance with time, with particles becoming more agglomerated and consisting of very fine primary particles over time. The diameter of MgO primary particles appears to decrease from 0.5 μm at 1 day to $\sim 0.1 \mu\text{m}$ after 28 days.

3.2 Effect of Na-HMP on the formation of M-S-H gel

XRD data obtained from the solid residues extracted from the samples in Table 2 after 1, 7, 28 and 90 days are shown in Figure 5. After 1 day (Fig 5a), MgO is present and the extent of hydration is low. The broad peak centred at $\sim 22^\circ$ is due to the SF (amorphous silica). After 7 days (Fig 5 b), $\text{Mg}(\text{OH})_2$ is detected in all samples but the amount formed decreases with Na-HMP addition. In samples with very high Na-HMP additions, MSH-9, the phase hylbrownite ($\text{Na}_3\text{MgP}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$) [19] forms. After 28 days hydration (Fig 5c) the MgO peaks in MSH-1 through to MSH-4 have all but disappeared and more $\text{Mg}(\text{OH})_2$ has formed. Again the strength of the $\text{Mg}(\text{OH})_2$ peaks decreases with increasing Na-HMP addition. MgO is still detected and $\text{Mg}(\text{OH})_2$ is hardly present in MSH-5, MSH-6 and MSH-7. MgO and $\text{Na}_3\text{MgP}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$ are present in MSH-8 and MSH-9. Finally, after 90 days (Fig 5d), $\text{Mg}(\text{OH})_2$ is still present in MSH-1 through to MSH-4, while essentially only amorphous phases are detected in MSH-5, MSH-6 and MSH-7. The two amorphous peaks at $2\theta \sim 35^\circ$ and $2\theta \sim 60^\circ$ are associated with the formation of M-S-H gel [7,8].

The changes in pH over time for selected samples in Table 2 are shown in Figure 6 a). When the Na-HMP content is less than 1 wt. %, the pH value increases from ~ 11.0 to ~ 11.6 during the first 7 days and then the pH decreases, with the rate of decrease reducing after 28 days. MgO hydration releases OH^- contributing to the increase in pH. The consumption of SiO_2 and formation of M-S-H results in a reduction in pH due to a reduction in OH^- concentration, i.e. consumption of $\text{Mg}(\text{OH})_2$. When the Na-HMP content is between 2 wt. % and 10 wt. %, the peak value in pH is ~ 12 at 23 days. SF dissolution and M-S-H gel formation cause the pH to decrease. When the Na-HMP content exceeds 60 wt.%, the trends of pH value curves are different. The pH values decrease from 11.9 to 11.5 during the first 7 days, and then the pH increase to 12.2 at 90 days and $\text{Na}_3\text{MgP}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$ is formed by reaction between Na-HMP and MgO [19].

The variations in Mg^{2+} concentration in solution are presented in Figure 6 b). The total Mg concentration in solution is strongly enhanced by the presence of substantial amounts of Na-HMP.

Figure 6 c) shows the changes in silicate concentration in solution with hydration. The silicate concentrations increase to a maximum at ~7 days and then tend to decrease. In addition, silicate concentration increases with increases in Na-HMP concentration. The dissolution of SiO_2 in water at neutral pH is very low but increasing the pH increases silica dissolution and the silicate concentration is broadly in line with the variations in pH shown in Figure 6 a). After 7 days the silicate concentration decreases and this is related to the formation of M-S-H gel.

FE-SEM images of the residual granular samples with 0 (MSH-1) and 2 wt. % (MSH-5) addition of Na-HMP are shown in Figure 7. The spherical SF particles seem to fill the gaps between the blocky MgO particles after 1 day. The formation of $\text{Mg}(\text{OH})_2$ crystalline solid particles after 7 days is shown in Figure 7b) and SF particles have partially decomposed. There are no new crystalline phases formed in Figure 7f). After 28 days, M-S-H gel appears in Figure 7c) and Figure 7g). The difference is that M-S-H gel seems to be formed over the $\text{Mg}(\text{OH})_2$ particles in MSH-1 sample (Figure 7e)) while M-S-H gel grows between MgO particles in MSH-5 samples as in Figure 7f). In addition, the size of M-S-H gel in MSH-5 samples appears to be finer. After 90 days, the morphology of M-S-H gels is different due to Na-HMP as shown in Figures 7d) and 7h). Na-HMP contributes to the consumption of MgO, inhibition of $\text{Mg}(\text{OH})_2$ formation and dispersion of particles. The precursors of M-S-H gel are $\text{Mg}(\text{OH})_2$ and silicate if there is no Na-HMP, while the precursors are MgO and silicate if sufficient Na-HMP is present in the mix water. M-S-H gel produced in the presence of Na-HMP forms uniform fluffy spheres, while M-S-H gel formed without Na-HMP forms irregular flocculated particle as shown in Figure 7d). Na-HMP has excellent dispersing and chelating properties and this influences the morphology of the M-S-H gel formed.

4. DISCUSSION

Hydrolysis of MgO and dissolution of SF influences the formation of M-S-H gel. In order to investigate the effect of Na-HMP on M-S-H gel, the effect of Na-HMP on MgO hydration was

investigated. The aqueous dissolution of MgO and precipitation of magnesium hydroxide (Mg(OH)₂) has been extensively studied [15-17]. Protonation (Eq. (1)) and de-protonation (Eq. (2)) on the surface of MgO particle has been verified using zeta potential analysis [15]. Mg²⁺ and OH⁻ are released into solution gradually (Eq. (3)) and when Mg²⁺ and OH⁻ concentrations reach the saturation limit in solution, Mg(OH)₂ precipitation occurs (Eq. (4)). The chemical reactions involved are:

a) Dissolution of MgO:

b) Precipitation of Mg(OH)₂:

In the first set of experiments, where MgO was added to water, the pH and the amount of Mg²⁺ dissolved in solution have a fixed relationship because dissolution of MgO increases the pH (according to equations 1, 2 and 3) while precipitation of Mg(OH)₂ decreases the pH (equation 4). The line representing this relationship between Mg²⁺ dissolved and pH is shown in Figure 8 as line 1. Also shown in Figure 8 are the total dissolved magnesium ion concentrations (Mg²⁺, Mg(OH)⁺) in equilibrium with either magnesium oxide or magnesium hydroxide as a function of pH. These show that MgO is more soluble than Mg(OH)₂ and therefore the formation of magnesium hydroxide as the mix with water alone is expected. The pH should be close to the value predicted by the intersection of line (1) and the solubility curve for Mg(OH)₂, i.e. close to 10.5, as observed in the experiment.

When Na-HMP is added to distilled water, the measured Mg ion concentration and pH still follow line 1 in Figure 8 but have now equilibrated near the intersection with the MgO line, consistent with an absence in Mg(OH)₂ formation. Hence there is a very strong super-saturation of Mg ions. ICP-OES cannot distinguish between Mg²⁺, Mg(OH)⁺ ions and Mg chelated by hexametaphosphate. The hexametaphosphate reacts with Mg²⁺ to form soluble [Mg₂(PO₃)₆]²⁻_(soluble) and insoluble [6MgOH⁺·(PO₃)₆]⁶⁻_(insoluble). [Mg₂(PO₃)₆]²⁻_(soluble) remain in solution while the [6MgOH⁺·(PO₃)₆]⁶⁻_(insoluble) species precipitate onto the surface of MgO particle [17]. This [6MgOH⁺·(PO₃)₆]⁶⁻_(insoluble) layer forms a stable protective coating on MgO particles which prevents further hydrolysis of MgO [18]. The good agreement between the experimental pH and Mg concentrations and the expected pH and total

dissolved Mg in a calculation without phosphates, suggests that in this case a large part of the sodium hexametaphosphate has formed the insoluble variant and adsorbed on the MgO particles. In doing so it has inhibited the nucleation sites for magnesium hydroxide in analogy with the suppression of the nucleation of calcite from supersaturated Ca^{2+} solutions in the presence of Na-HMP [21].

For the experiments where silica fume is also present, it is clear that when excess Na-HMP is added, new phosphate phases are formed and as these are not of interest with respect to M-S-H formation. These mixes (MSH-8 and MSH-9) will not be discussed further.

The experimental results for pH and total dissolved Mg and Si are plotted in Figure 9 together with calculated equilibrium concentrations for quartz, periclase, brucite, sepiolite and chrysotile in water. The latter two were included as these crystalline materials have Mg:Si ratios similar to M-S-H gel [7, 8, 12].

For the mix without phosphate (MSH-1), XRD results indicate that $\text{Mg}(\text{OH})_2$ is formed first and the initial total dissolved magnesium concentrations are close to those expected for a solution in equilibrium with $\text{Mg}(\text{OH})_2$. As time progresses, the pH reduces and the Mg concentration in solution increases while M-S-H gel starts to form. For the mixes with substantial Na-HMP addition (MSH-5 and MSH-7), $\text{Mg}(\text{OH})_2$ hardly forms at all, and this is consistent with the observation that when sufficient phosphate is present its nucleation can be inhibited in the mix with MgO and phosphate above. The amount of magnesium in solution now appears to scale with the phosphate content irrespective of pH suggesting that at these levels of Na-HMP addition, the phosphate not only serves to adsorb on the MgO to suppress $\text{Mg}(\text{OH})_2$ nucleation but also forms a substantial amount of soluble chelates. The higher pH leads to faster silica dissolution and M-S-H gel forms again.

The pH and concentrations of Mg and Si in solution after 90 days for MSH-1 through to MSH-5 are fairly similar suggesting the observed values may be close to the equilibrium values over M-S-H gel. To investigate this, a fixed formula phase was added to the database to act as M-S-H gel:

and the formation energy varied to make the equilibrium concentrations agree reasonably (pK 95). It is clear from Figure 9 that this is indeed possible, suggesting the dashed curve is a good approximation

for the equilibrium of M-S-H gel. Not surprising for an amorphous phase, the solubility values found are higher than for the crystalline analogues sepiolite and chrysotile. It is recognized that this is a very simple description of what is essentially a material which can form with a range of Mg:Si ratios, and therefore the line is probably more a guide to the eye than an exact solubility. Nevertheless it gives some idea of the phase behaviour in water.

Once the M-S-H curve is added to the picture, it becomes clear that the rate of M-S-H formation is determined by the availability of magnesium species that can react, because the Mg concentration in many mixes is not equal to the concentration in equilibrium with MgO but to the concentration in equilibrium with M-S-H. Hence any available Mg ions quickly forms M-S-H gel. Only in MSH-5 and MSH-7 with substantial phosphate content is the amount of dissolved Mg much larger, but the fact that these concentrations do not alter as the pH shifts over the timescale of the experiment strongly suggests that most of this is chelated Mg, which is not available for reaction. However, the dissolution of silica appears to be quite slow because the silica concentration in solution is depressed relative to the equilibrium in the presence of quartz (Figure 9 b). If dissolution was in equilibrium the concentration should have been at least as high as the quartz line and probably higher since silica fume is not crystalline and hence more soluble. Instead, experimentally the concentration is lower, suggesting silica is also being consumed at a rate similar to its formation.

5. CONCLUSIONS

The presence of Na-HMP in solution inhibits $\text{Mg}(\text{OH})_2$ formation and increases the pH. It is proposed that the mechanism is inhibition of the nucleation sites by adsorption of phosphate species from the pore solution. When Na-HMP is added at less than 1 wt. %, $\text{Mg}(\text{OH})_2$ formation is not completely suppressed but when the Na-HMP content is increased to between 2 and 5 wt. %, the Mg^{2+} concentration in solution increases dramatically and protective layers of $[\text{6MgOH}^+ \cdot (\text{PO}_3)_6^{6-}]_{(\text{insoluble})}$ retard further hydrolysis of MgO and inhibit $\text{Mg}(\text{OH})_2$ formation. When silica fume is present the increased pH allows increased dissolution of SiO_4^{4-} ions into solution that react with the Mg^{2+} ions and water to form M-S-H gel. When the Na-HMP content exceeds 60 wt. %, Na-HMP reacts with MgO and the crystalline phase hyalbrownite ($\text{Na}_3\text{MgP}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$) is formed. Na-HMP not only improves the rheology of the mixes but also ensures that $\text{Mg}(\text{OH})_2$ formation is suppressed. The resulting higher pH

enhances M-S-H gel formation by increasing the solubility of silica fume.

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Table 1

Chemical composition of the raw materials (data from the supplier)

%	SiO ₂	Na-HMP	MgO	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	Na ₂ O	P ₂ O ₅	SO ₃	others
silica fume	94.7	-	1.2	0.2	0.7	0.2	1.7	0.3	0.4	0.4	0.1
MgO	-	-	98.0	-	0.02	<0.01	<0.01	0.05	<0.01	0.02	1.90
Na-HMP	-	98	-	-	-	<0.01	-	-	(n/a)	0.01	1.98

Table 2

Mix proportions of M-S-H gel specimens using a high W/S ratio of 10

Sample ID	MgO (g)	SF (g)	Water (g)	Na-HMP (wt. %)
MSH-1	4	6	100	0
MSH-2	4	6	100	0.2
MSH-3	4	6	100	0.5
MSH-4	4	6	100	1
MSH-5	4	6	100	2
MSH-6	4	6	100	5
MSH-7	4	6	100	10
MSH-8	4	6	100	60
MSH-9	4	6	100	100

Figure 1. Phase transformations during MgO hydration (a) MgO in distilled water, (b) MgO in distilled water containing 2 wt. % Na-HMP.

Figure 2. The variation in pH of solution over 90 days of MgO in distilled water with and without 2 wt. % Na-HMP.

Figure 3. Changes in the total Mg^{2+} concentration in solution with hydration time for MgO in distilled water with and without 2 wt. % Na-HMP.

Figure 4. FE-SEM images of the hydration products of MgO with and without 2 wt. % Na-HMP (a) MgO cured for 1 day,(b) 7 days,(c) 28 days and (d) MgO with Na-HMP cured for 1 day (e) 7 days, (f) 28 days.

Figure 5. Phase transformation during the hydration of MgO and SF with different contents of Na-HMP.

Figure 6. Changes in a) pH, b) Mg concentration, and c) silicate concentration in the solution versus hydration time for M-S-H samples.

Figure 7. FE-SEM images of hydration products of MgO with and without 2 wt. % Na-HMP addition (a) MSH-1 aged for 1 day, (b) MSH-1 aged for 7 days, (c) MSH-1 aged for 28 days, (d) MSH-1 aged for 28 days, (e) MSH-5 aged for 1 day, (f) MSH-5 aged for 7 days, (g) MSH-5 aged for 28 days, (h) MSH-5 aged for 28 days.

90 days, (e) MSH-5 aged for 1 day, (f) MSH-5 aged for 7 days, (g) MSH-5 aged for 28 days, (h) MSH-5 aged for 90 days.

Figure 8. Total dissolved Mg ion concentration in equilibrium with Mg(OH)₂ or MgO in water as well as relationship between pH and dissolved Mg ion concentration for hydrolysis of MgO (line 1). The experimental values are shown as symbols.

Figure 9. Total dissolved (a) magnesium and (b) silicon as a function of pH in equilibrium with either sepiolite, chrysotile, quartz, brucite or periclase in water as well as the experimental data and a proposed equilibrium concentration with M-S-H- gel. The symbols are the experimental results, the filled symbol is the 90 day result.