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SOLID SOLUTION AND HYDRATION BEHAVIOUR OF MAGNESIUM-BEARING TRICALCIUM SILICATE PHASE

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ABSTRACT

Saturation solubility of MgO in tricalcium silicate (C_3S) and the hydration kinetics of magnesia-bearing tricalcium silicate phase have been studied. MgO-doped C_3S was obtained by repeated firing of calcium carbonate and quartz in the stoichiometric ratio of 3:1 in the presence of varying amounts of MgO from 0.5 to 5% by weight. Elemental analysis and X-ray diffraction studies have revealed that up to 1.5% MgO goes in solid solution at 1450°C and the rest precipitates as periclase. Presence of 1% MgO marginally slows down the rate of hydration of tricalcium silicate up to about 20 h and then increases sharply to overtake the hydration rate of pure C_3S. Complete hydration could be achieved in 28 days for the doped sample, against 83% for the undoped C_3S in the same period. The study has been found useful in understanding the relationship between modified chemical/mineral composition and the hydration behaviour of magnesia-doped C_3S phase. © *1998 Elsevier Science Ltd*

Introduction

Minor constituents present in cement raw mixes enter cement minerals and affect their reactivity and hydraulic behaviour. In a large number of studies on cement minerals doped with cationic impurities (1–3) such as Ti, Mn, Cr, Ba, Sr, etc., it is reported that these alter the crystal structure of C_3S. It is also known that these form solid solutions depending upon their saturation solubilities, and significantly affect the hydration kinetics of the doped phases.

The present investigation concerns the extent of dissolution of MgO (which is a common associated mineral in limestone) in C_3S and its influence on the kinetics of hydration of the C_3S phase.

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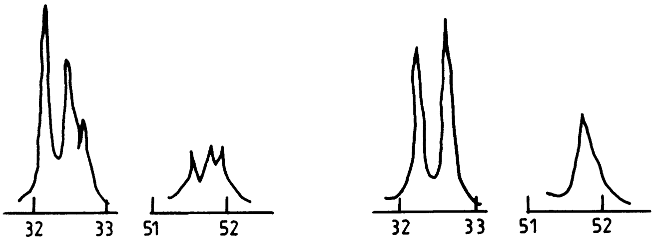

FIG. 1.
X-ray diffractogram of C_3S doped with MgO.

Experimental

Preparation of Specimens

Pure tricalcium silicate and its solid solutions with magnesia were made by solid state reactions at 1450°C. The starting materials were analytical reagent grade calcium carbonate, quartz, and light magnesium oxide. Calcium carbonate and quartz were ground to a fine powder and homogenised with magnesia in anhydrous acetone. The dried mass was pressed into pellets and fired at 1450°C for 3 h in a platinum dish. The sintered pellets were ground to pass 63 micron and reformed into pellets and fired again at 1450°C for 3 h. Samples were cooled at room temperature, $\sim$ 27°C .This process was repeated until the free lime reduced to $< 0.1\%$ in the pure C_3S. The final products were ground to pass a 45-micron sieve. The powdered samples were examined by XRD to check the completion of reaction. The doped specimens (0.5, 1.0, 1.5, 2, and 5% MgO) contained 0.42, 0.98, 1.30, 0.86, and 0.75% free lime, due to displacement by Mg ions, as reported by Locher (4). No C_2S was present in any of the specimens. Hydration studies were performed over a period of 1 h to 28 days on the pure C_3S and C_3S doped with 0.5, 1, 2, and 5% MgO. The hydration was carried out at ambient temperature between 27 ± 2°C, employing a water/solid ratio of 0.5. Hydration was arrested by crushing and immersing the specimen in acetone and drying in a vacuum desiccator at the specified ages. The hydrated samples were ground to pass 45 micron sieve, and investigated using the techniques of free lime, XRD, DTA-TGA, and chemical analysis.

XRD Studies

A Regaku D Max/III C model was used. Polymorphic forms detected in the X-ray diffractograms with different concentrations of dopant have been presented in Figure 1. The unreacted C_3S was quantitatively determined. The percentage of reacted C_3S was calculated and is shown in Figure 2.

Rate of hydration with varying % MgO was calculated using formula:

$$\frac{\text{Reacted moles } C_3S \times 100}{\text{Starting moles} \times \text{hours}}$$

This is reported in Figure 3. Hydration rate with age was calculated and is presented in Figure 4.

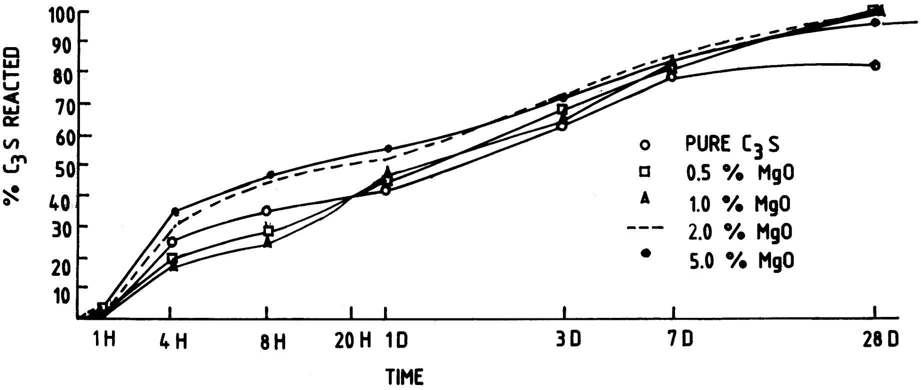

FIG. 2.
Degree of hydration of pure and doped C_3S.

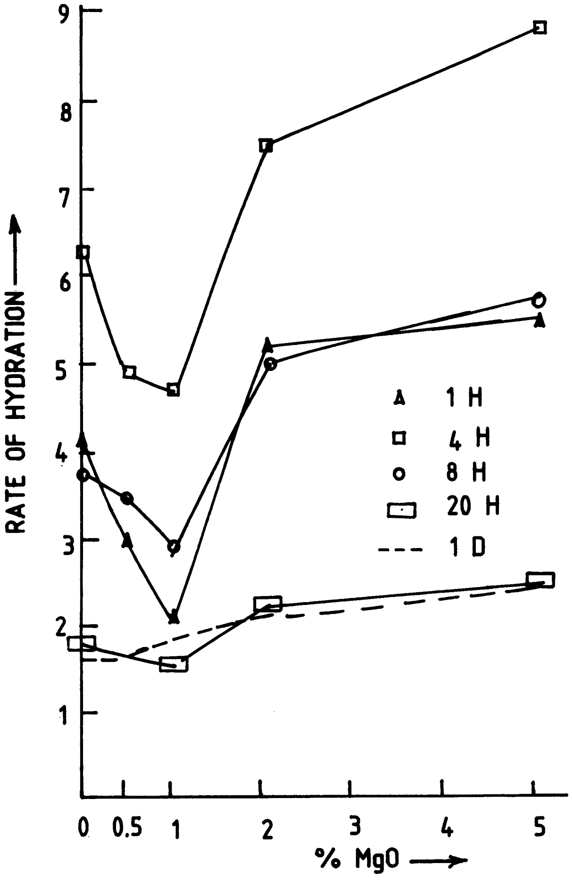

FIG. 3.
Rate of hydration per %MgO.

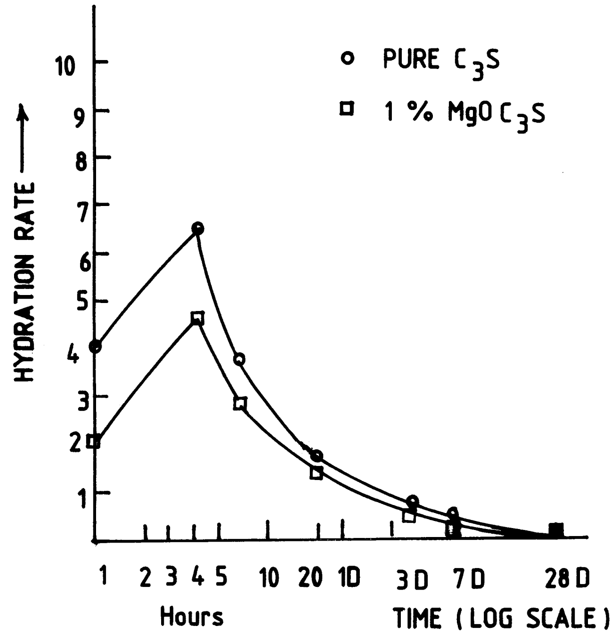

FIG. 4.
Rate of hydration.

Chemical Analysis.

Free lime "$Ca(OH)_2$" was estimated using ethylene glycol extraction method (6) in the samples hydrated from 1 h to 28 days at different intervals. Data is reported in Figure 5.

Distribution of MgO in Tricalcium Silicate

The amount of unreacted MgO was estimated by complexometry after extracting the samples with ammonium nitrate (7). Samples of tricalcium silicate containing 0.5, 1, 1.5, 2, and 5% MgO were extracted with ammonium nitrate in anhydrous mixed solvent containing a 5:1 mixture of ethanol and glycerol. After the extraction, magnesia was estimated by difference, by titrating CaO and CaO+MgO with 0.01 M EDTA solution (Ethylene diamine tetra acetic acid disodium salt). The results are reported in Table 1.

Weight Loss

A Mettler Thermal Analyser (TA–1) was used. Weight of sample = 50mg, and heating rate = 6°C/min. in air(static) atmosphere.

Weight loss at 1000°C was obtained from the TG curve (Fig. 6), after making corrections for weight loss at 110°C and considered as combined water.

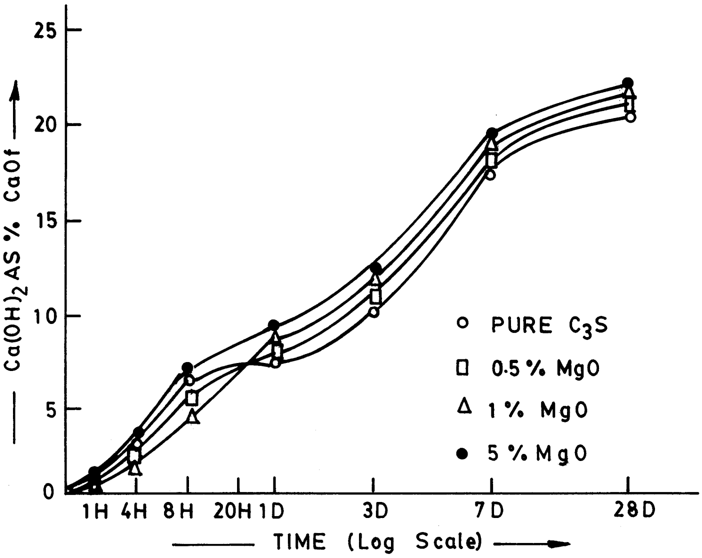

FIG. 5.
Free lime per age of hydration.

Results and Discussion

Solid Solution of MgO in Tricalcium Silicate

MgO forms solid solution with C_3S, and the extent of dissolution depends upon the saturation solubility. In order to establish the solubility of MgO in the C_3S phase, the free MgO was extracted from the doped samples using ammonium nitrate,and determined by complexometry. The results reported in Table 1 indicate that the entire MgO beyond 1.5% could be extracted in all the cases, indicating a saturation solubility of 1.5% by weight (0.086 mole/mole of C_3S). Beyond this limit, the excess MgO remains unreacted and is present as crystalline periclase.

Woermann et al. (8) proposed the formula $(Ca_{1-x}Mg_x)_3SiO_5$, where $x < 0.0125$ at 1550°C, for the solid solution of MgO in C_3S. Locher (4) reported that Mg^{2+} ions replace an equal

TABLE 1
Amount of MgO in C_3S solid solution (as determined by complexometry).

Sample	Periclase (%)	% MgO fixed in C_3S
1. C_3 doped with 0.5% MgO	Nil	0.5
2. C_3 doped with 1.0% MgO	Nil	1.0
3. C_3 doped with 1.5% MgO	Nil	1.5
4. C_3 doped with 2.0% MgO	0.50, 0.49, (AV 0.50) 0.51	1.5
5. C_3 doped with 1.5% MgO	3.50, 3.51, (AV 3.50) 3.48	1.5

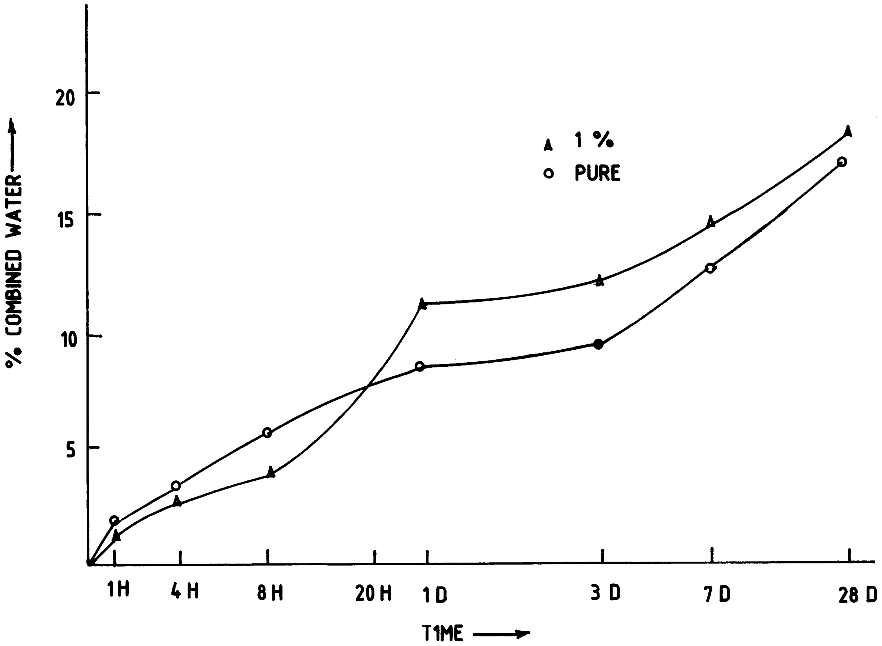

FIG. 6.
Percentage combined water of pure and 1% MgO C_3S.

number of Ca^{2+} ions in the C_3S lattice and the solubility limit under different temperature conditions differs and is 2.5% MgO at 1500°C. In addition, CaO dissolves small quantities of MgO (9). Thus, crystals of the solid solutions Ca_3SiO_5–"Mg_3SiO_5" and (Ca,Mg)O can co-exist. Koyangi et al. (10) reported that C_3S can take up less MgO, namely, only 1.0 to 1.5%. Solubility of MgO in C_3S at different temperatures, as reported by various authors, is shown in Table 2.

Luginina (13) reported a value of 1.9% MgO in alite. Alite ($Ca_{54}Mg_2AlSi_{16}O_{90}$) has MgO up to 1.62%. The discrepancy in the amount of MgO that goes into pure tricalcium silicate and alite is due to the fact that during heating an equilibrium occurs between the MgO taken up in solid solution of alite and the total MgO present in the system (4). This equilibrium depends on the following factors:

TABLE 2
Solubility of MgO in C_3S.

Researcher	Solubility %	Temperature °C
Locher (4)	1.5	1420
Woermann et al. (11)	1.5	1425
Spohn et al. (12)	1.6	1450
This study	1.5	1450

1. MgO concentration in the sample;
2. Temperature treatment;
3. Nature and amount of foreign ions present in the system.

According to Luginina et al. (13), the increase in MgO concentration is accompanied by a steady increase of its content in alite and aluminoferrite. The solubility of MgO also depends upon the basicity of the raw mix. With increase in mix basicity, the ability of MgO to be retained in the alite crystal decreases. For these reasons the amount of MgO that goes into solid solution of commercial clinker has been reported to be variable.

XRD studies were carried out on the unhydrated pure and doped C_3S phase containing 0.5, 1.0, 1.5, and 2% MgO. The XRD study also indicates that MgO is dissolved in the C_3S phase. The periclase peak could be detected only in 2% doped specimen, indicating that up to 1.5% MgO may have entered the solid solution, at 1450°C.

Addition of MgO in C_3S phase has a significant effect on the polymorphic form of C_3S. Nagashima (14) obtained triclinic (T_I) form with MgO content of 0–0.5%, T_{II} form for 0.5–1.5% and monoclinic (M_I & M_{III}) for MgO 1.5 to 2.0%. Mascolo et al. (15) reported T_I polymorphic form for MgO content of 0.45%, monoclinic M_I form for 1.0% MgO, and monoclinic inverted for MgO content of 2.01%.

Our study reveals triclinic polymorphic form for up to 1.5% MgO, and monoclinic in the case of 2.0% MgO. XRDs are shown in Figure 1.

The high-temperature polymorphs of C_3S cannot be stabilised by quenching. A foreign ion introduced into C_3S crystal lattice can either substitute for Ca^{2+} or Si^{4+}, or can occupy a hole. The lattice energy is modified and one of the polymorphic forms is stabilised at room temperature. These transformations are of a displacive type. Their structures are so similar that a very small displacement of the atoms is sufficient to transform one phase into another without breaking the primary coordination bonds (16).

Mg^{2+} substitutes for Ca^{2+} and stabilises T_I,T_{II}, and M_{III} at room temperature (17). A part of the magnesium ions added replaces calcium ions in the alite lattice, another fraction of the magnesium is included in the lattice of alite, other than by occupying Ca^{2+} ions (18).

Hydration Studies Of Doped And Undoped C_3S

The results of the XRD study on the hydration of pure C_3S and MgO- doped specimens reveal that the percentage of tricalcium silicate that reacts with water is very much less during the 1st h and is at a maximum between 1 and 4 h (Fig. 2). The rate of hydration is fastest between 1 and 4 h (Fig. 4). Up to a period of 20 h the percentage of C_3S reacted with is at a minimum in the case of C_3S doped with 1% MgO, in comparison to pure C_3S, 0.5%, 2%, & 5.0% MgO-doped samples (Fig. 2). The rate of hydration with variable percentage MgO (Fig. 3) also indicates that the hydration rate is at a minimum when the MgO content is 1%. Beyond 1% MgO, there is a clearly increasing trend in the rate of hydration (Figs. 2 and 3). These findings are supported by the results for hydrated lime (expressed as CaO_f) (Fig. 5) and combined water (Fig. 6).

Samples containing MgO $>$ 1.5% show the presence of MgO_f, as well as some CaO_f. Free lime in unhydrated C_3S containing 2 and 5% MgO is less than that in the 1.5% sample. Hence, 2% and 5% MgO samples are expected to show a higher rate of hydration, which is evident from Figures 2 and 3. Secondly, as revealed in the study, C_3S containing up to 1.5%

MgO is triclinic, whereas the 2% and 5% MgO samples are monoclinic. The monoclinic form of C_3S hydrates more rapidly than triclinic (19). Yamaguchi et al. (20) also reported that monoclinic alite hydrates slightly faster than triclinic. Because of these factors, there is a higher rate of hydration of the 2 and 5% MgO (Figs. 2 and 3) samples in comparison to samples containing MgO less than 1.5%. In this way, MgO affects the hydration indirectly.

Sersale (21) studied the behaviour of Al-, Fe-, and Mg-bearing alites and found that the entrance of foreign ions in the C_3S lattice increases reactivity towards water. It was established that 1% MgO leads to a hydration degree higher than that of 0.45% and 2.01% MgO alite, from 1 to 28 days.

Our study, however, reveals that 1% MgO slows down the hydration rate at up to 20 h as compared to 0.5% MgO. After this period, the 1% MgO specimen overtakes the hydration rate of pure C_3S and 0.5% MgO C_3S (Figs. 2 and 3). Tricalcium silicate with 2.0% and 5% MgO has a higher hydration rate, leading to higher degree of hydration, as compared to pure C_3S, 0.5%, and 1% MgO-doped specimens over the ages of 1 h to 28 days.

These findings are supported by the work of Valenti, who studied the hydration kinetics of pure tricalcium silicate in comparison with synthetic alite bearing magnesia for the period up to 24 h (5) and from 1 to 28 days (22). He found a lower degree of hydration in respect to pure C_3S during the first 24 h. For the period from 1 to 28 days, he showed that the introduction of 0.45% to 1.81% MgO into C_3S causes the hydration degree to be respectively greater than the corresponding alite.

The results of our study are also supported to some extent by the work carried by Thompson et al. (23). He studied the reactivity of variable MgO amounts in C_3S by monitoring the heat of hydration during the first 35 h. For alites containing up to 1% MgO, a decrease of reactivity in comparison with pure C_3S was observed.

Conclusions

Magnesia has a limited solubility in tricalcium silicate phase and a maximum of 1.5 wt.% goes into solid solution at 1450°C.

Magnesia at different concentrations affects the rate of hydration differently. It slows down the hydration, particularly in the first 20 h. The decrease is sharp in up to 1.0% MgO. The rate of hydration study also reveals that the increase in rate of hydration is steep until 4 h of age.

Magnesium also modifies the polymorphic forms of tricalcium silicate phase. The triclinic form is stabilized by MgO contents of up to 1.5% and the monoclinic form with the 2% and 5% concentrations studied. The monoclinic form of C_3S hydrates faster than triclinic. Thus, MgO affects the hydration process indirectly.

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