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Communication

Effect of TiO_2 on the hydration of tricalcium silicate

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Abstract

The hydration kinetics of titania-bearing tricalcium silicate phase have been studied. TiO_2-doped tricalcium silicate (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 titanium dioxide from 0.5 to 6% by weight. The study revealed that the presence of up to 2% TiO_2 has an inhibiting effect on the rate of hydration of C_3S. One percent TiO_2 in C_3S marginally slows down the rate of hydration of tricalcium silicate up to approximately 2 days and then increases sharply to overtake the hydration rate of pure C_3S. Higher percentages of TiO_2 (>2%) in C_3S have a higher hydration rate than C_3S containing up to 2% TiO_2 from 1 h to 28 days. This is achieved by modification of the polymorphic form of C_3S and by the formation of $CaOTiO_2$ in the CaO-SiO_2-TiO_2 system.

Keywords: Ca_3SiO_5; TiO_2; Hydration; Polymorphism; $CaOTiO_2$

1. Introduction

The presence of small quantity of TiO_2 (<0.5%) is known to increase the hydraulic activity of cement [1] because of the distortion of the belite and alite crystal lattice as a result of the substitution of the Si^{4+} ion by the Ti^{4+} ion and formation of corresponding solid solutions [2]. In the $CaOTiO_2$ system there is formation of $CaOTiO_2$ and $3CaOTiO_2$, which possess hydraulic properties [3].

In a previous work [4] it was noticed that tricalcium silicate remained triclinic in presence of up to 2% TiO_2, formed monoclinic with 4 to 5%, and adopted rhombohedral form with 6% TiO_2 at 1450°C. There was $CaOTiO_2$ formation in the $CaOSiOTiO_2$ system at the same temperature.

The present work aims at studying the hydration kinetics of TiO_2-doped tricalcium silicate because TiO_2 stabilizes various polymorphic forms and there is formation of titanium compound (titanate) in the $CaOSiO_2TiO_2$ system in comparison to pure C_3S.

2. Methods

2.1. Preparation of specimens

Pure tricalcium silicate and its solid solutions with titania were made by repeated firing of calcium carbonate and quartz [4] in the stoichiometric ratio of 3:1 in presence of various amounts of TiO_2 (0.5, 1, 2, 4, and 6% by weight) until free lime reduced to 0.1% in the pure C_3S at 1450°C. All the materials used were of analytical reagent grade.

2.2. Hydration study

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, 4, and 6% TiO_2. The specimens were ground to 45-μm sieve and hydrated with distilled water at a water/cement ratio of 0.5, and the respective pastes were sealed in plastic vials. The hydration was carried at ~27 ± 2°C. After the respective planned duration, hydration was arrested by crushing and immersing the specimens in acetone and drying the specimens in a vacuum desiccator. The hydrated samples were ground to pass through 45-μm sieve and were investigated using the techniques of chemical analysis, X-ray diffraction (XRD), and differential thermal analysis–differential thermogravimetric analysis (DTA-TGA).

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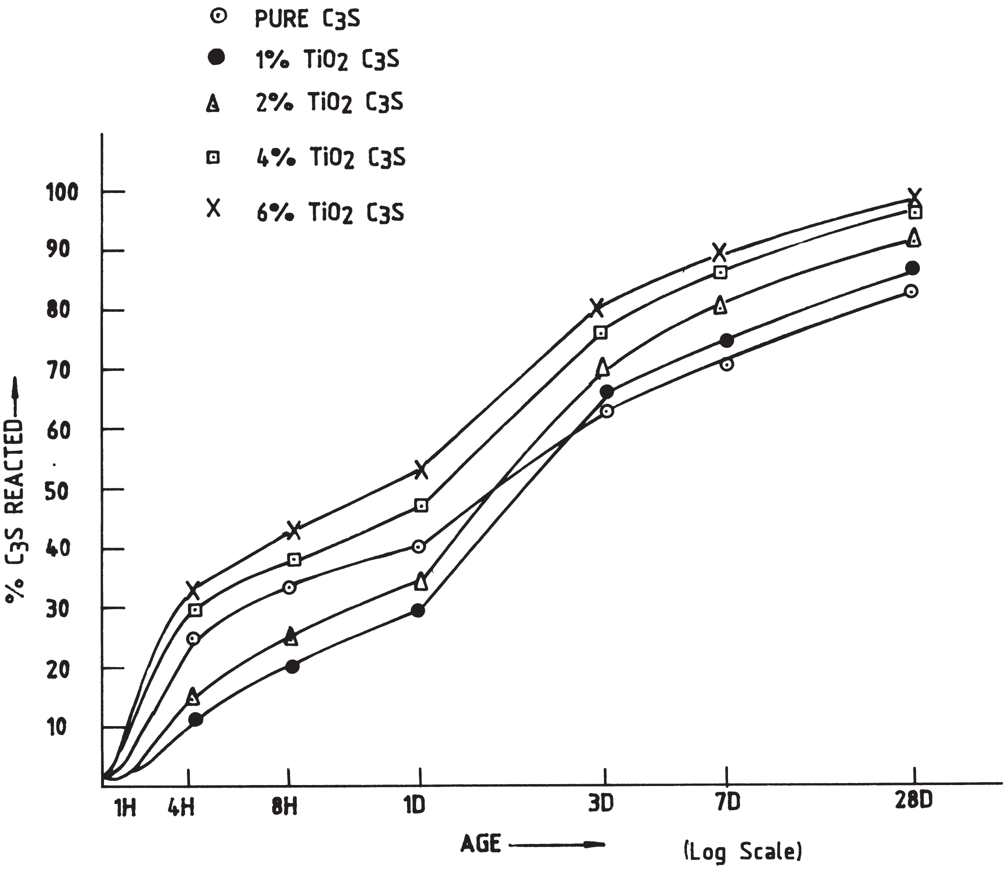

Fig. 1. Degree of hydration.

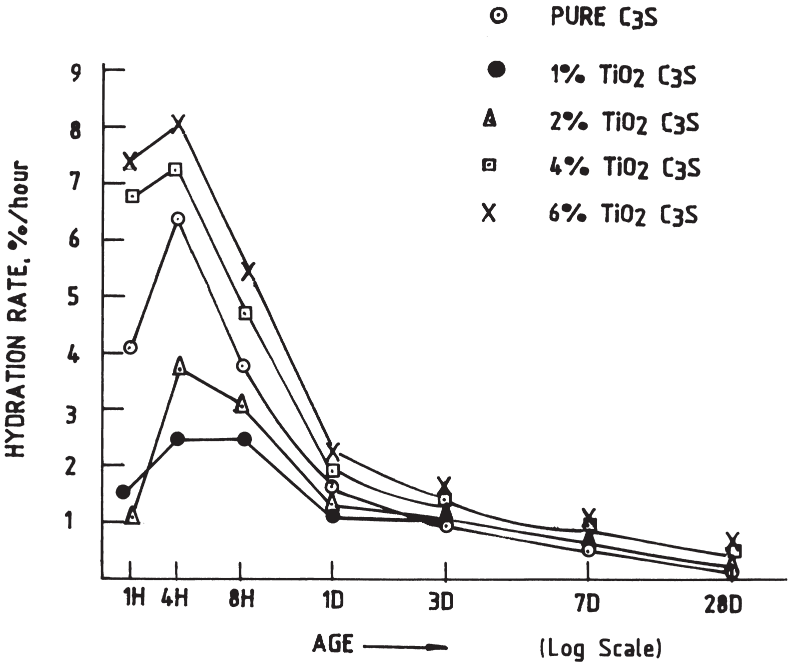

Fig. 2. Hydration rate/age.

2.3. XRD studies

Rigaku Rad Max/III C model (Rigaku International Co., Tokyo, Japan) was used. The unreacted C_3S was quantitatively determined. The percentage of reacted C_3S was calculated and is shown in Fig. 1. Rate of hydration (α) with various percentages of TiO_2 was calculated using Eq. (1) [5]:

$$\alpha = \frac{\text{Reacted moles } C_3S \cdot 100}{\text{starting moles } C_3S \cdot h} \qquad (1)$$

This is reported in Fig. 2.

2.4. Chemical analysis

Free lime Ca $(OH)_2$ was estimated using ethanol glycerol method [6] in samples hydrated from 1 h to 28 days at different intervals. Data is presented in Fig. 3.

2.5. Weight loss

Mettler Thermal Analyser (TA-1; Mettler Instruments, Zurich, Switzerland) was used for the study. The weight of sample was 50 mg and heating rate was 6°C/min in air (static) atmosphere. Weight loss at 1000°C was obtained from the thermogravimetric (TG) curve after making corrections for weight loss at 110°C, and was considered as combined water. Results are reported in Fig. 4.

3. Results and discussions

The results of hydration study (Fig. 1) revealed that the percentage of tricalcium silicate that reacted with water was much lower during the first hour and was maximum between 1 and 4 h for the pure C_3S and doped samples. Up to a period of 1 day the C_3S reacted and the rate of hydration for the sample doped with 1% TiO_2 remained at a minimum in comparison to pure C_3S 2, 4, and 6% TiO_2-doped samples (Figs. 1 and 2). The specimen doped with 2% TiO_2 also reacted at a slower rate but was faster than 1% TiO_2 during the same period. At 2 days the percent of C_3S that reacted is almost the same for the specimens doped with up to 2% TiO_2 as that of undoped specimen (Fig. 1). Between 2 and 3 days, the 1%-doped sample overtook the hydration as compared to the pure C_3S and thereafter it remained high (up to 28 days) (Fig. 1). At 3 days and longer, the reactivity proceeded in the increasing order of the percent of TiO_2 added in C_3S.

The specimen with 4% TiO_2 showed a higher degree of hydration in comparison to pure C_3S and 1 and 2% TiO_2-doped specimens from 1 h to 28 days (Fig. 1). The specimen with 6% TiO_2 displayed a much higher percent of C_3S reacted and hydration rate than the 4% TiO_2 specimen did at all ages studied (Figs. 1 and 2). These results are supported by the results of free lime estimation (Fig. 3) and also from

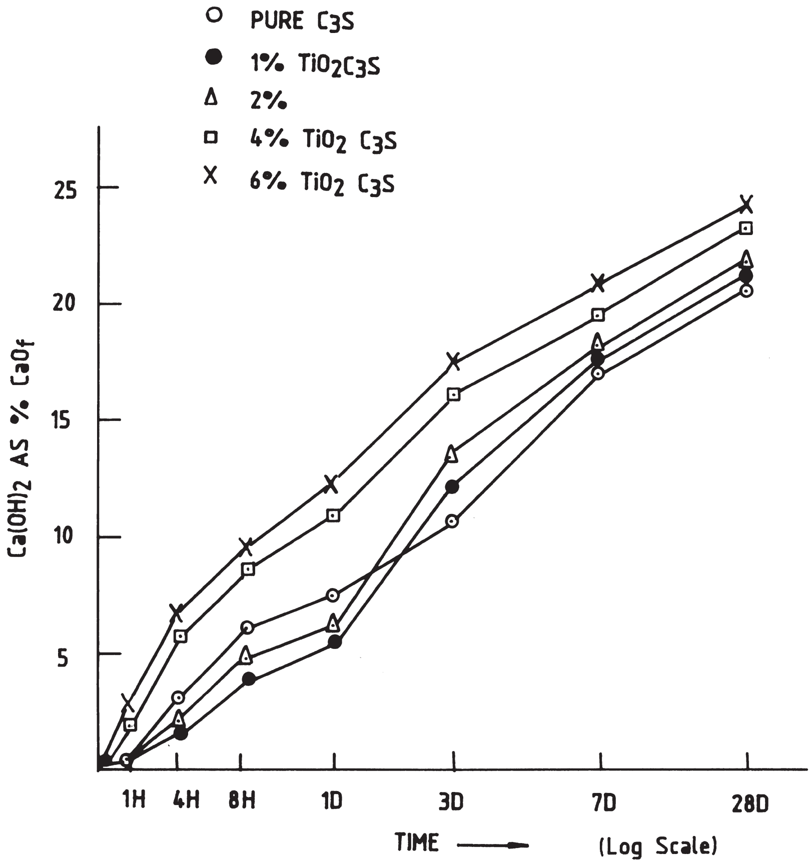

Fig. 3. Free lime/age of hydration.

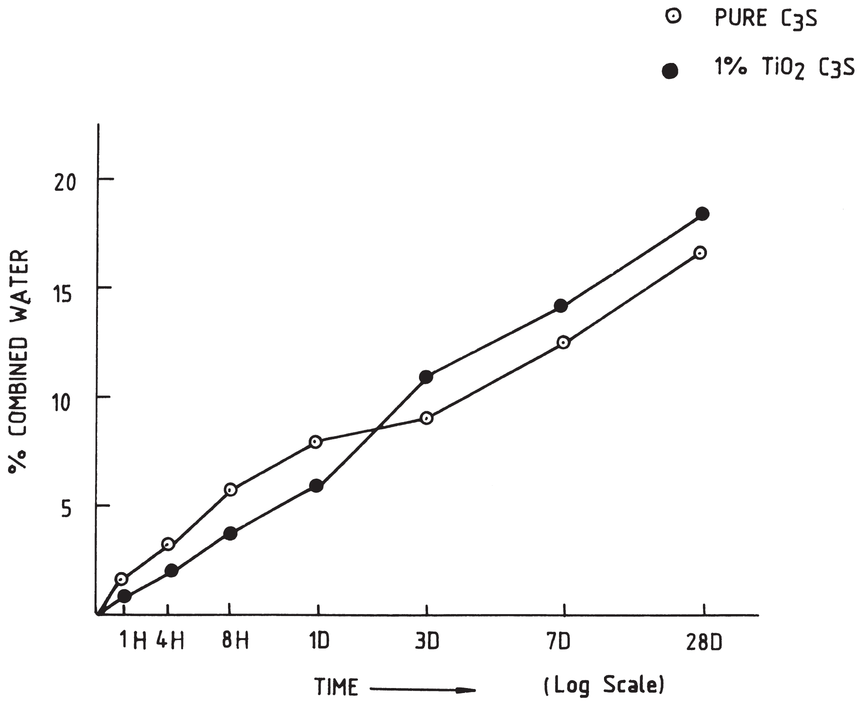

Fig. 4. Combined water/age.

the combined water as estimated by DTA-TGA (Fig. 4). The percent free lime in the 1% TiO_2-doped specimen was the least among all the specimens studied up to 1 day (Fig. 3). Percent combined water in the same specimen was less than that of the pure C_3S up to 1 day. At approximately 2 days the combined water was the same for the 1%-doped specimen as that of the pure C_3S (Fig. 4). Between 2 and 3 days the combined water in the 1% specimen overtook that of the pure C_3S, then it remained high up to 28 days. The specimen containing 0.5% TiO_2 behaved almost the same as pure C_3S.

It was reported earlier from XRD studies [4] that TiO_2 retained the triclinic polymorphic form of pure C_3S up to 2%. Introduction of 4% TiO_2 alters this to the monoclinic form, which is reported to have a higher tendency of hydration than the triclinic form [7]. For this reason the specimen having 4% TiO_2 shows the higher percent of hydration as compared to the specimens containing TiO_2 up to 2%.

XRD results showed [4] that $CaOTiO_2$ compound was present in the specimen having 6% TiO_2. It also adopted the rhombohedral form. A number of studies have revealed that this modification, when hydrated, is more reactive and develops higher strength than either monoclinic or triclinic forms [8].

In our study the same trend has been observed (Figs. 1, 2, and 3) as percent reacted C_3S, rate of hydration, and free lime are more in the case of 6% TiO_2 C_3S than with 0 to 4% TiO_2-doped C_3S for the ages of 1 h to 28 days. It may be attributed to the rhombohedral form of C_3S and the hydraulic behaviour of $CaOTiO_2$ formed in the 6% TiO_2 specimen.

Kondo and Yoshida [9] studied the hydration behaviour of tricalcium silicate containing 0.07 mole TiO_2 (2.43% by wt) using a water cement ratio of 0.5 at 20 ± 1°C. To compare the rate of hydration, the thickness of the reacted layer was calculated from the data of the particle size distribution and the data of the degree of hydration. It was reported that in the early period, the rates of hydration of C_3S and its solid solution is considered to be a kind of autocatalytic reaction. In the case of Ti-bearing C_3S the initial hydration period is prolonged, but the degree of hydration at 1 to 3 days is high because of the rapid autocatalytic hydration. Kondo and Yoshida also studied the hydration by monitoring the setting of mortar and its strength at various intervals. It was observed that the setting of mortar made with C_3S occurs within a few hours after mixing, whereas the setting of C_3S with titania occurred after approximately 10 h. The mortar strength (compressive strength) of pure C_3S (cement:sand:water = 1:3:0.5 at 20°C) at 1 day was much higher than that of the Ti-doped specimen. The strength of the Ti-bearing specimen at 3 days was almost double that of pure C_3S. Higher strengths were noticed at 7 and 28 days for the Ti-bearing specimen than the pure C_3S.

It was also reported that when alite or C_3S contains TiO_2 [1] the reaction within 1 day is retarded, but the subsequent reaction is remarkably accelerated. It is regarded that the reactivity is increased because of the substitution of Ti for Si in the structure of C_3S, but the retardation of the initial period in the C_3S and alite-containing Ti may be attributed to the difficulty of the growth of nuclei of more stable hydrate formed in the impermeable coating [10].

In this study also it was observed that in the C_3S-bearing titanium up to 2% the hydration reaction is initially retarded but is fast between 1 and 3 days. After 3 days this hydration reaction proceeds at a comparatively slower rate.

4. Conclusions

1. Introduction of TiO_2 into C_3S affects the hydration behaviour of tricalcium silicate by (a) modifying the polymorphism of C_3S and (b) forming a $CaOTiO_2$ compound that affects the hydraulicity of C_3S.
2. TiO_2 has an inhibiting effect on the early hydration reaction of C_3S but only up to 2%. With 1% TiO_2 in C_3S, the extent of hydration becomes least, up to 1 day. The concentration of up to 2% TiO_2 slows down the hydration process for approximately 2 days and thereafter picks up to exceed the degree of hydration of undoped C_3S. Concentrations of more than 2% TiO_2 have an accelerating effect on the hydration process from the initial period to the decay period.

Acknowledgment

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