

Hydration Kinetics of Tri-calcium Silicate in the Presence of Superplasticizers

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Received: October 30, 2002

A recently developed method based on Differential Scanning Calorimetry (DSC) has been used to study the hydration kinetics of tri-calcium silicate (C_3S) in the presence of superplasticizers. We studied some of the most common additives employed in the cement industry, i.e., a sulfonated naphthalene–formaldehyde polycondensate, a polycarboxylate and a polyacrylate. The overall hydration kinetics of the superplasticized pastes have been obtained and compared to that of C_3S cured in pure water. Superplasticizers do not change the kinetic laws involved in the hydration processes, the first according to an Avrami–Erofeev nucleation and growth law, and the second a three-dimensional diffusion equation. However, the induction times of the tri-calcium silicate paste are affected by the presence of additives. The polycarboxylate and the polyacrylate additives reduce the temperature dependence of the so-called “dormant period”. The activation energy of the nucleation and growth stage is about doubled in the presence of superplasticizers, and is the largest for the polyacrylate additive, that is the most effective additive. DSC analysis shows that a larger amount of water reacts with C_3S during the acceleration period in the presence of polycarboxylic and the polyacrylic additives, meaning that the water is more available, i.e., the paste is more fluid. SEM images show that the acrylic additive produces a change in the morphology of the formed hydrated calcium silicate gel, from a fiber-like structure to a sheet-like structure. The quantitative determination on how additives affect the curing process of cement is reported for the first time, allowing a determination of a scale of additives efficacy based on activation energies of the nucleation process.

Introduction

In modern cement technology superplasticizers (SP) have greatly contributed to the improvement of “high-performance concretes” (HPC). These polymeric compounds confer to concrete pastes high flowability, keeping low the water content, improving the workability, and ensuring high mechanical strength, shrinkage, and durability of the hardened composite.^{1–3} Before the introduction of these additives, paste workability during mixing and casting processes was gained using a high water excess. However, at the end of the hydration process of cement, the un-reacted water remains trapped inside the cement matrix and, as it evaporates, an undesired increase of porosity is developed that compromises the composite performances, such as mechanical strength and resistance to “external-agents”. With superplasticizers, pastes can be produced with a sufficient amount of water to perform the hydration reaction. As a result, the structure of the composite is more compact and presents higher durability and resistance.

From a chemical point of view, superplasticizers can be classified according to their different chemical structures and performances. Nowadays, among the most used additives are sodium salts of sulfonated melamine–formaldehyde copolymers (MSF) or sulfonated naphthalene–formaldehyde copolymers (NSF). Both compounds permit a reduction of the water excess of about 30%, producing only a limited retardation of the setting

and hardening processes. Unfortunately, with these additives a loss of fluidity in time (“slump loss”) is observed that is an undesired effect. The “last generation” of SP (namely polyacrylic and polycarboxylic polymers) overcomes the previous limit with a much lower dosage. These compounds affect the hydration of Portland cement,^{4–6} and in particular, they produce a retardation in setting time. Despite the large efforts, the comprehension of the setting process and of the mechanism of action of superplasticizers is at the infant stage.

A correct characterization of additive effects on the hydration kinetics would be the comparison of the overall hydration kinetics of cement, with and without additives. Recently, the application of quasi-elastic neutron scattering to the investigation of the cement setting process^{7–13} has been reported. In these studies the amount of un-reacted water (Free Water Index, FWI) versus time has been obtained. This index shows a typical trend that can be divided into three major periods. During the first 2 h of the cement hydration, the reaction proceeds slowly and FWI values are very close to unity. Several theories attempt an explanation of the presence of such a “dormant” period. Some theories invoke the formation of a “barrier layer”, due to precipitation of the first products of the reaction that inhibit the diffusion of H_2O , Ca^{2+} , and OH^- .¹⁴ Some other theories assume the formation of an electrical double-layer inhibiting diffusion of water molecules and calcium ions.¹⁴ This induction period suddenly stops at time t_i , probably because of the breakdown of the previous conditions; at this point the hydration shows a dramatic acceleration, with a rapid decrease of FWI with time (nucleation period). This second acceleration period stops at time t_d at which begins a deceleration period that is

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the final stage of the hydration process. During this last period the reaction kinetics is controlled by the diffusion rate of species through the mass of the hardened paste.

In previous studies we investigated the hydration process of C_3S , the major constituent of cement, by using quasi elastic neutron scattering^{9,10} and by a novel approach based on Differential Scanning Calorimetry (DSC).¹⁵ We determined the FWI parameter from the amount of water that can solidify and melt, the so-called freezable water. The fraction of reacted C_3S , α , can be calculated from the DSC curves of freezable water melting, α being inversely proportional to the experimental enthalpy of fusion of freezable water present in the C_3S /water paste. From the FWI parameter the kinetic mechanism of the cement hydration process has been obtained. In this work we study the hydration kinetics of Ca_3SiO_5 in the presence of superplasticizers, determining the amount of free water by means of the DSC method recently developed.¹⁵ The effect of added superplasticizers is correlated to the kinetic parameters obtained for the nucleation and diffusion periods of the hydration process. A scanning electron investigation has been performed to point out possible morphological changes of the C_3S phase upon additive addition.

Experimental Section

Synthetic tri-calcium silicate (C_3S), supplied by CTG, Italcementi Group, with BET specific surface area 0.44 ± 0.05 m²/g and particle median radius 6.0 μ m, has been used.

Three different superplasticizers have been studied, i.e., the sodium salt of sulfonated naphthalene-formaldehyde polycondensate (NSF), a polycarboxylate (HSP114), and a polyacrylate (HSP111), all obtained from CTG-Italcementi. Superplasticizers water solutions (10 g/L) have been prepared. Water was purified by a Millipore Organex system ($R \geq 18$ M Ω cm).

Approximately 50 mg of C_3S has been weighed and manually mixed with 20 mg of pure water or additive solution for one minute. In this way a paste with a 0.4 water/ C_3S ratio by mass and with 0.4% of additive on C_3S weight has been produced. The paste (roughly 40 mg) was transferred in a steel pan (diameter 7.4 mm, capacity 60 μ L, from Perkin-Elmer) and sealed with the appropriate cover equipped with a neoprene O-ring to avoid water leaking. Each sample was maintained in a thermostatic bath at constant temperature (10, 20, 30, and 40 °C). DSC measurements were performed using a Perkin-Elmer calorimeter DSC7, connected with a personal computer; data were elaborated with Pyris software for Windows, version 3.52. Measurements were repeated until about 20 days after mixing.

Each measurement was carried out with the following temperature program: from room temperature down to -30 °C at 40 °C/min, isothermal regime at -30 °C for four minutes from -30 °C to -12 °C, at 20 °C/min, and from -12 °C to $+14$ °C at 4 °C/min.

The isothermal step at -30 °C was performed to ensure free water to freeze despite possible supercooling effects.

Each DSC curve showed a peak relative to water freezing and a peak due to its melting. From the enthalpy variation of the water melting we calculate the Free Water Index (FWI) according to the procedure reported in a previous work.¹⁵

To observe the effect of additives on C_3S single grain, Scanning Electron Microscopy has been used to analyze very diluted samples, with the same additive concentration used for the C_3S paste. To this purpose, 100 mg of C_3S in 5 mL of a 10 g/L solution of additive has been incubated at 25 °C for 24 h. A drop of this water suspension was dissolved in 2 mL of ethanol, to stop the hydration and to avoid particle agglomera-

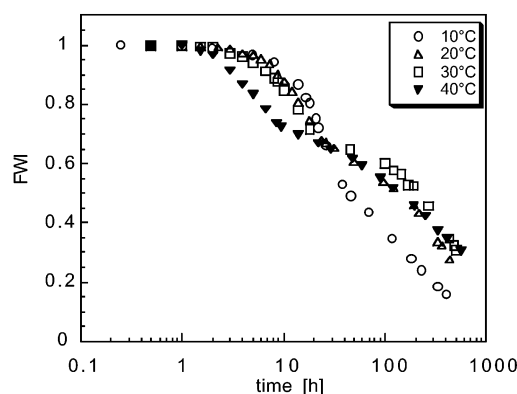


Figure 1. FWI versus time for a C_3S paste cured in pure water ($w/c = 0.4$) at 10, 20, 30, and 40 °C.

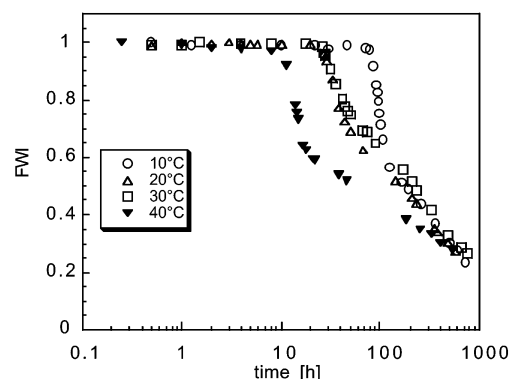


Figure 2. FWI versus time for a C_3S paste cured in water ($w/c = 0.4$) with NSF at 10, 20, 30, and 40 °C.

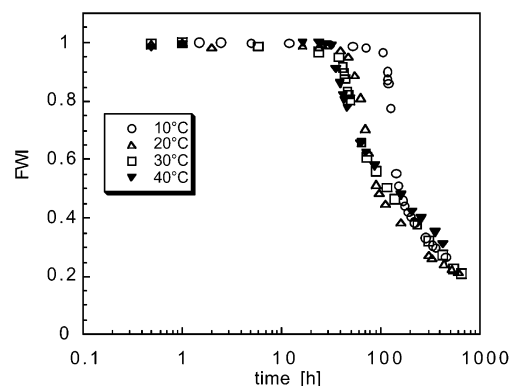


Figure 3. FWI versus time for a C_3S paste cured in water ($w/c = 0.4$) with HSP111 at 10, 20, 30, and 40 °C.

tion. A few microliters of this latter suspension were deposited onto microscopy stubs and dried. The instrument used was a Low-Vacuum SEM LEO 1450VP, equipped with a VPSE detector (Variable Pressure Secondary Electron), with an accelerating voltage interval of 200 V–30 kV. We operated in low vacuum condition, with a pressure variable between 35 and 60 Pa inside the sample chamber.

Results and Discussion

Figures 1–4 report the log-linear plots of FWI vs time obtained for samples cured at 10, 20, 30, and 40 °C with and without additives. Curves show the typical shape, composed of three different periods. FWI slowly decreases until time t_i , then a sharp fall corresponding to the onset of the nucleation and growth process is observed. A change of slope can be clearly seen, indicating the beginning of the diffusional regime, t_d . The

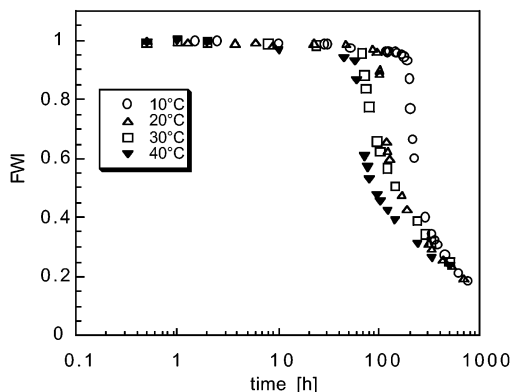


Figure 4. FWI versus time for a C₃S paste cured in water ($w/c = 0.4$) with HSP114 at 10, 20, 30, and 40 °C.

TABLE 1: Parameters of the Nucleation-and-Growth Process and of the Diffusional Period, for C₃S Hydration in Water with and without Superplasticizers

	T (°C)	nucleation and growth			diffusion-limited	
		t_i (h)	k (h ⁻¹)	M	t_d (h)	$K_d \times 10^{15}$ (m ² /h)
water	10	8	0.0084	1.3	38	4.42
water	20	6	0.0163	1.1	32	2.72
water	30	5	0.0192	1.0	18	2.42
water	40	1.5	0.0388	1.1	9.5	1.91
NSF	10	78.5	0.0041	1.3	126	1.84
NSF	20	27	0.0072	1.3	49.5	2.38
NSF	30	26	0.0165	0.9	47.5	2.18
NSF	40	11.5	0.0542	1.1	18	1.50
Hsp111	10	107	0.0015	1.6	168	1.31
Hsp111	20	48	0.0058	1.2	96	1.53
Hsp111	30	41.5	0.0161	0.9	89.5	2.14
Hsp111	40	32	0.0402	0.8	87	1.81
Hsp114	10	192	0.0034	1.4	288.5	1.40
Hsp114	20	96.5	0.0100	1.1	167.25	1.63
Hsp114	30	68	0.0272	0.8	144.5	2.14
Hsp114	40	60	0.0696	0.7	96.75	1.84

influence of the storage temperature on the duration of the induction (or “dormant”) period is evident from the t_i values reported in Table 1.

FWI was calculated from each measurement according to the following relationship:¹⁵

$$\text{FWI} = \{\Delta H_{\text{exp}}\} / \{0.286\Delta H_{\text{init}}\} \quad (1)$$

where ΔH_{exp} is the value measured from the area of the peak of water melting, 0.286 is the average weight fraction of water in the pastes, and ΔH_{theor} is the theoretical value of fusion enthalpy of water in the C₃S/water paste. In the previous work,¹⁵ ΔH_{init} immediately after mixing, was found to be approximately 85% of the value of pure water (333 J/g), in agreement with the influence of the sample heterogeneity on the enthalpy changes as determined by DSC.¹⁶ For this reason, extracted FWI values were corrected by this factor and, as a result, each curve starts from unity at the beginning of the hydration reaction.

As previously described,¹⁵ the Avrami–Erofeev (A-E) model accounts for the nucleation process.^{17–19} According to the A-E law, the variation of α (degree of reaction) in time is

$$\alpha = 1 + \alpha_i - e^{-k(t-t_i)^M} \quad (2)$$

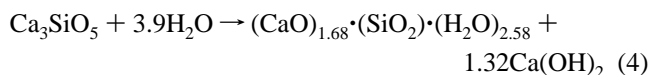
where t_i is the initial time of the acceleration period, k is the rate constant, and M is a parameter dependent on dimensionality of the system and on the type of particle growth.

The previous equation can be linearized and written in the form

$$\ln \left[\ln \left(\frac{1}{1 + \alpha_i - \alpha} \right) \right] = \ln k + M \ln(t - t_i) \quad (3)$$

In this way, given t_i both k and M can be obtained from a linear plot.

The stoichiometric coefficients involved in the hydration reaction of C₃S are known to vary in time, and these variations should be taken into account to obtain a relation between FWI and the degree of reaction. However, according to Fuji and Kondo²⁰ the hydration reaction can be simplified in the following form:



In this way the relation between FWI and degree of reaction can be simply written^{7,20}

$$(1 - \text{FWI}) = \frac{3.9\alpha}{12.7(w/c)} \quad (5)$$

where 12.7 is the ratio between molecular weights of C₃S and H₂O. At our w/c ratio, the relation can be further simplified in

$$\alpha = (1 - \text{FWI}) \quad (6)$$

Each experimental curve has been fitted (an example is reported in Figure 5 for C₃S cured with HSP111) according to the Avrami–Erofeev law, and the rate constants deduced from the fitting are listed in Table 1. The addition of additives to C₃S produces two main effects. The first effect is the strong delay in the setting of C₃S paste. The maximum increment of t_i and of t_d (and therefore the delay in the setting) is induced by HSP114, followed by HSP111 and NSF. The second is that in the presence of superplasticizers the end of the nucleation and growth period corresponds to a lower value of FWI. We found that these additives enhance the availability of water inside the paste, so that the hydration of C₃S is more effective. The explanation for this effect is not clear, even if SEM images suggest some morphological changes in the products of hydration, with a probably consistent change in the particle size distribution.

Analysis of Table 1 indicates that rate constants, k , are temperature dependent and, in particular, increase with temperature. Activation energies can be easily obtained from the Arrhenius equation

$$k(T) = A \exp(-E_a/RT) \quad (7)$$

by plotting $\ln(k)$ versus $1000/T$, as reported in Figure 6. Table 2 reports the activation energies for the C₃S hydration in water with and without additives.

As previously noted,^{8,15} t_i values follow an Arrhenius-type behavior and the activation energies for the induction process are reported in Table 2. The activation energy values are comparable (38 and 43 kJ/mol) for pure water or NSF additive samples. Lower values have been found in the case of HSP additive class (28 and 29 kJ/mol for HSP111 and HSP114, respectively). Polycarboxylic additives reduce the temperature dependence of the induction time at which the cement hydration reaction starts.

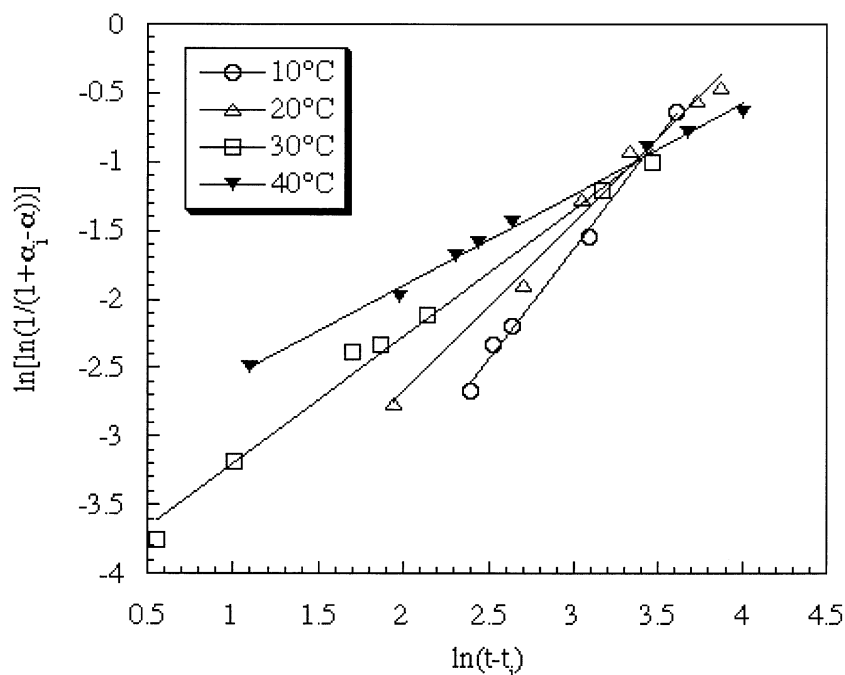


Figure 5. Avrami–Erofeev fitting for samples of C_3S cured in water in the presence of HSP111.

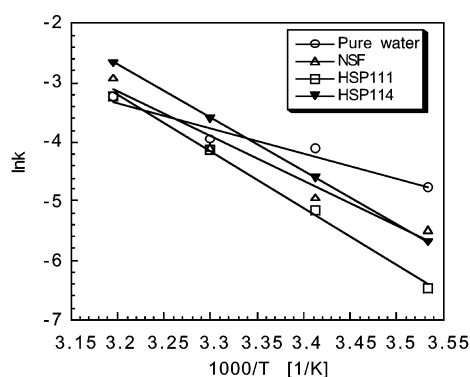


Figure 6. Arrhenius fitting for the acceleration stage of samples cured with and without superplasticizers.

TABLE 2: Activation Energies for the Three Stages of the Hydration of C_3S in Presence of Pure Water and Different Superplasticizer Solutions

	E_i (kJ/mol)	E_a (kJ/mol)
water	38	35
NSF	43	63
HSP111	28	75
HSP114	29	74

The possible explanation of this effect has to be ascribed to the different mechanism of adsorption of the additives on the C_3S grain surface.^{1,2}

The activation energy for the nucleation and growth period obtained for C_3S hydration in pure water is 35 kJ/mol. This value is in good agreement with the literature, where an activation energy interval from 30 to 40 kJ/mol, depending on the particle size distribution, is reported.^{8,21}

In the presence of superplasticizers the activation energies for the hydration are significantly higher than in pure water. The polycarboxylate and the polyacrylate give similar results (74–75 kJ/mol), suggesting a similar mechanism, while the naphthalene–sulfonic additive has smaller activation energy (63 kJ/mol). To the best of our knowledge, there are no works reporting estimation of activation energies for the hydration

process in the presence of superplasticizers; for this reason, it is impossible to make a comparison with previous data. However, even if the number of additives studied so far is limited, the increment in the activation energies provides evidence for a change in the mechanism of the C_3S hydration when superplasticizers are present in solution.

A deeper analysis of the effect of superplasticizers can be obtained examining the M value. This parameter is related to the morphological characteristics of the growing crystals through the following relation:^{7,15}

$$M = (P/S) + Q$$

where P can be equal to 1, 2, or 3 corresponding to the growth of fibers, sheets, or polygonal forms, respectively; S can be equal to 1 or 2 corresponding to phase boundary growth or to diffusion of the reacting species through a liquid phase; and finally Q equal to 0 means no nucleation, whereas Q equal to 1 indicates a constant nucleation.

Table 1 shows that in our case, with and without superplasticizer addition, the average value of M is around unity and confirms previous results.^{22,23} This value of M is consistent with two possibilities: (i) fibers–phase boundary–no nucleation, ($P = 1$, $S = 1$, $Q = 0$; also reported in the literature as (1,1,0)), and (ii) sheets–diffusion–no nucleation, ($P = 2$, $S = 2$, $Q = 0$; (2,2,0)).

To discern the effective morphology of hydrated phases a SEM investigation was performed on diluted suspensions of C_3S in pure water and in superplasticizer solutions. Figure 7a shows the SEM image of C_3S in pure water: the grain surface is covered by a fiberlike hydrated phase. This kind of morphology has already been observed in the previous work¹⁵ and attributed to the reported (1,1,0) type of growth. In the case of samples cured with SP (Figure 7b–d), the fibrillar structures are not present, also after long incubation periods, while the formation of some other regular structures around the main grains is enhanced. This is consistent with a different type of growth that seems to correspond to the (2,2,0) mechanism, i.e., a growth of sheets with diffusion and no nucleation. Other experiments are in progress in order to verify the real nature of this

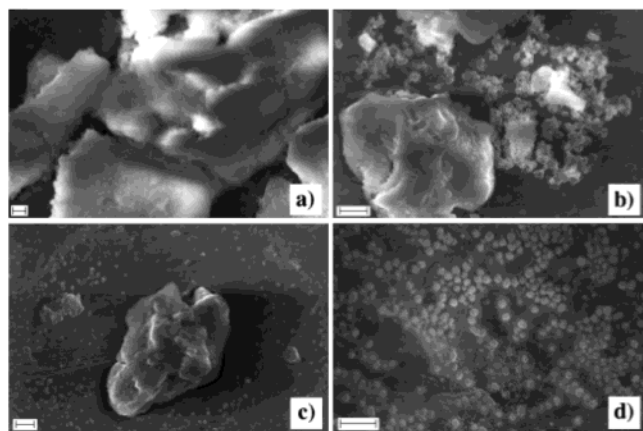


Figure 7. SEM micrographs of C_3S suspensions ($w/c = 50$), cured at 25 °C for 24 h: (a) C_3S in pure water, bar = 1 μm , WD = 9 mm, EHT = 20.00 kV, Chamber = 35 Pa; (b) C_3S in water with NSF, bar = 3 μm , WD = 11 mm, EHT = 18.00 kV, Chamber = 45 Pa; (c) C_3S in water with HSP111, bar = 2 μm , WD = 10 mm, EHT = 18.00 kV, Chamber = 50 Pa; (d) C_3S in water with HSP114, bar = 1 μm , WD = 8 mm, EHT = 28.00 kV, Chamber = 37 Pa.

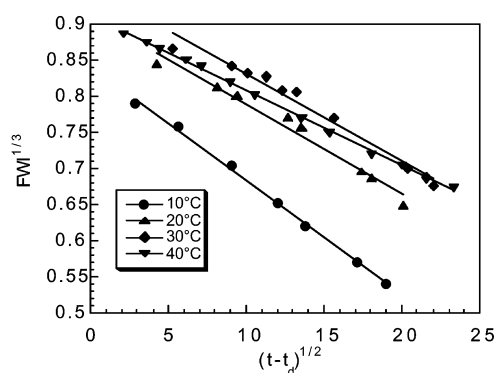


Figure 8. Fitting for samples of C_3S cured in pure water according to the diffusional law.

morphological change in the hydrated phase and, in particular, in the case of cement pastes.

When all the external part of C_3S particles has reacted and CSH can no longer be formed on the surface, the hydration continues toward the interior of the grains. In these conditions the reaction rate is controlled by the diffusion of species across the gel phase. The relation between degree of reaction (expressed in terms of FWI) and time is the following:^{7,8,20}

$$FWI^{1/3} = -(2K_d)^{1/2}(t - t_d)^{1/2}/R + (FWI_d)^{1/3} \quad (8)$$

where K_d is the diffusional constant, t_d the initial time of diffusional period, FWI_d is the FWI relative to t_d , and R is particle radius.

For each curve, data with time greater than t_d (reported in Table 1) were considered to follow the previous law. Only the fits obtained for pastes with pure water are reported in Figure 8. From eq 8 it is evident that the diffusional constant K_d (listed in Table 1) can be calculated from the slope $(2K_d)^{1/2}/R$. The values obtained for pastes of C_3S in pure water are very similar to those reported in a previous work with neutron scattering, with the same w/c ratio and with similar surface area of the powder,⁸ further confirming the validity of our method. Several studies present in the literature showed K_d values to be independent of temperature.^{8,15} This is attributed to the competition between two different contributions, the thermal activation of the diffusional process and the higher density of the gel phase

at higher temperatures.^{8,15,24,25} The diffusional constants would tend to increase as the temperature because of the first contribution, but the higher the temperature, the more impervious the “walk” of molecules across the medium, with a consequent decrease of diffusional constants. The decreasing trend of the K_d observed for C_3S hydration in pure water, as the temperature increases, should indicate that in this case the second contribution is predominant. When C_3S is hydrated in the presence of a superplasticizer, any clear trend for diffusional constants is found as a function of temperature probably due to the fact that the two previous contributions to the diffusion process offset each other.

Conclusions

In the present work we have applied Differential Scanning Calorimetry (DSC) for the “in situ” analysis of the hydration kinetics of Ca_3SiO_5 (C_3S) in the presence of superplasticizers. We investigated the effect of the most used cement additives, i.e., naphthalene-sulfonic, polyacrylate and polycarboxylate. The method enabled us to follow the overall hydration kinetics, and to deduce the Free Water Index (FWI) versus the time of the curing process. The C_3S hydration proceeds according to three steps: induction, acceleration, and deceleration period. The Avrami–Erofeev law describes the acceleration period, while the final part of the FWI curve follows a three-dimensional diffusion equation.

The kinetic analysis enables us to obtain the activation energies for the induction period and for the nucleation-and-growth process of the hydrated phase, the M parameter (related to the morphological characteristics of the growing crystals), and the diffusional constants for pastes cured with and without superplasticizers. The values obtained for pure water are in good agreement with those reported in the literature. The presence of additives gives rise to a dramatic increment of activation energy value for the acceleration period, while the M parameter remains roughly constant. These results indicate modifications in the hydration mechanism, probably related to the morphology of the hydrated phase, as evidenced by SEM micrographs. To the best of our knowledge, there are no works reporting estimation of activation energies for the hydration process of C_3S in the presence of superplasticizers. Since the activation energies are directly related to the nucleation process and, therefore, to the setting process, their knowledge permits the realization of a scale of additive efficacy, providing for the first time a quantitative approach to the field.

In conclusion, the analysis of the additive performance through the activation energies of the nucleation period provides for the first time a tool for rationalizing the very complex process of cement setting in the presence of additives. This is extremely important for the very large number of applications of the most used material in the human activity.

Acknowledgment. The authors thank Dr. L. Cassar and M. Biagini (CTG-Italcementi Group) for invaluable comments and discussions. Financial support from CTG-Italcementi Group, Ministero dell’Istruzione, Università e della Ricerca Scientifica (MIUR, grant PRIN-2001), and Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, CSGI, is gratefully acknowledged.

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