Rate and Mechanism of Hydration of Tricalcium Silicate in an Early Stage

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1. Introduction

The hydration of tricalcium silicate (C_3S) is not only an important reaction but a fascinating one, as well. The situation, however, has seemed for less satisfactory in our understanding the rate and mechanism of the early hydration of C_3S . Reviewing the works of many researchers which had been done, Copeland and Kantro¹⁾ proposed a sequence of reactions during the first few hours as follows: The first reaction upon contact of C_3S with water is hydrolysis of C_3S . The solid product of the hydrolysis is a reaction intermediate left as a coating remaining on C_3S surfaces, which retards the reaction. The intermediate product has a CaO/SiO_2 ratio somewhat below 3 and has little, if any, bound water. The hydrolysis proceeds to form a solution that is supersaturated with respect to calcium hydroxide and also with respect to the C-S-H gel finally formed. The increase in rate of heat liberation at about 2 hours indicates that cleaning of surfaces by dissolution of the intermediate product to form C-S-H gel has started. Maximum lime concentration in solution is reached at about this time. The increase in rate of hydration is accompanied by a decrease in CaO/SiO_2 ratio of the reaction product and the first appearance of extractable lime (between 2 and 4 hours). At 4 hours the C/S of the C-S-H gel has fallen to about 1.6. The lime concentration has decreased somewhat. Crystalline $Ca(OH)_2$ is nucleated in the period between 4 and 6 hours at which time the rate of hydration reaches its maximum. The rate of hydration then decrease as surfaces become covered and space becomes filled with C-S-H gel.

One important point of their interpretations will be the postulation of reaction intermediate whose CaO/SiO_2 ratio will be variable from 3 to 1.6 in the course of time. Nothing is known, however, of its structure²⁾. We have pointed out the presence of a considerable amount of adsorbed water on C_3S surfaces and described that upon contact of C_3S with water at water/ C_3S weight ratio of 0.7, about one molecular layer of outer-

most C_3S surfaces dissolved into water congruently, followed by an immediate adsorption of 3 to 4 mole layers of water molecules on them³⁾. These adsorbed water molecules seemed to metastabilize the surfaces for a while. During a dormant period, however, these water molecules were supposed to react gradually with the substrate to form an "intermediate product" on the C_3S surfaces, the postulation of the intermediate product being set forth from such a preconceived idea that hydration reaction will proceed uniformly all over the C_3S surfaces.

In order to obtain a more refined concept with regard to the rate and mechanism of the early hydration of C_3S , we have continued to study the hydration of C_3S in paste form by four major means, that is, calorimetry, determinations of combined water and solute concentration of solution, and electron microscopies. The hydration temperatures were between 10°C and 40°C and water/ C_3S weight ratios varied from 0.7 to 10. In carrying out the present work, emphasis was laid on the following items,

1) to follow the way how two kinds of tobermorites different in morphology, very thin crinkled foils and needle-like cigar-shaped agglomerates, are formed, and the change in their quantities with hydration time.

2) to know whether C_3S surfaces covered by water molecules are durable or not, and in this connection to estimate the heat of wetting of C_3S by water.

3) to confirm the roles of supersaturated solution playing on the initiation of hardening stage.

4) to set up kinetic equations representing the overall reaction in an early stage by use of the three kinds of kinetic data which should be equivalent in terms of the percentage hydration of C_3S , though some corrections are necessary for each datum owing to its inherent requirements.

2. Experimental

2.1 Materials

Tricalcium silicates, sample No. 1 and 2, were

Table 1. Some properties of 3 CaO·SiO₂ used.

Sample No.	CaO/SiO ₂ mol ratio	Free CaO (wt%)*	Surface area** (m ² /g)	Density
1	2.98	<0.02	0.38	3.14
2	2.99	<0.02	0.43	3.12
3	3.00	0.10	0.44	—

* The values described in the previous paper were corrected after reexamination.

** by BET method

the same as described previously³⁾, and No. 3 which contained 0.10% of free lime was prepared in the same procedure as that for No. 1. Some properties of these samples were shown in Table 1.

2.2 Analysis of the solution in the paste

To determine the concentrations of calcium and silicate ion in the aqueous solution of the C₃S paste, the solution was squeezed out of the paste by hand loading through a plunger and absorbed into the filter paper, then subjected to chemical analysis³⁾.

2.3 Determination of combined water

The combined water was determined for the hydrated sample which was processed first by mixing the C₃S paste with iso-propyl alcohol to arrest the hydration, then by replacing the alcohol with petroleum ether centrifugally. The sample was placed as wetted with petroleum ether on a combustion boat made of silica glass, and the combined water was released by heating to 850°C in a tube furnace while a slow stream of nitrogen was passed through, absorbed in a methanol-glycol solution and titrated with Karl-Fisher's reagent^{3),4)}. Thus, the combined water described in this paper must be defined as the one combined to the solid phase tightly enough not to be released by the dissolving effect of absolute iso-propyl alcohol.

2.4 Calorimetries

Three kinds of calorimetric measurements were conducted for a) continuous heat evolution accompanying the hydration of C₃S, b) heat of immersion of C₃S in water, and c) heat of solution of completely hydrated C₃S.

a) the continuous calorimetry This was done with the twin-type conduction calorimeter which was prepared by Ōyōdenki Kenkyujo as CM-502 Model, the construction having been described previously^{3),5),6)}. At each run of experiment 1 to 8 g of C₃S was taken in the sample holder of Dropping Type Attachment and dropped down in water of reaction cell after thermal equilibrium was attained. In the case of a high water to C₃S mixing-ratio over 2, fused alumina powder was blended as a filler in an amount necessary for preventing segregation of water from the paste. By use of the calorimeter the rate of

heat evolution was directly followed, and in conversion of the ratecurve to the cumulative or integralone, the heat conserved in the reaction cell must of course be taken into account at any hydration time³⁾.

b) Heat of immersion The same calorimeter was used. In practice, however, Break-Ampoule Type Attachment was employed, which was capable of holding and breaking an ampoule and agitating the content rushed out of it in the twin type reaction cell. The samples weighed about 3 g were taken in the thin wall ampoules 12 mm in diameter and 45 mm in length. Pretreatment consisted of outgassing the sample at 450°C for one hour under a pressure less than 10⁻⁴ mmHg. Heat of ampoule breaking was in general cancelled out between sample calorimeter and reference one, and the deflection caused by ampoule breakings in both calorimeters didn't exceed ±3 μV, which corresponded to about ±0.02 cal.

The heat of immersion of C₃S in water was estimated by two methods. The first method consisted of the determinations of the heat evolved by contact of de-moistured C₃S with saturated lime solution during a predetermined period after breaking the ampoule and the increment in Ca²⁺ ion concentration of the solution during the same period. Free lime which was liberated from C₃S according to the following reaction⁷⁾, was assumed to be soluble in the saturated lime solution.

Then the heat of immersion can be estimated by the following,

$$q_1 = Q - \left(\frac{q_0}{3-n} + h_{ca} \right) PC'_{ca} \times 10^{-3} \quad \dots\dots (2)$$

wherein,

q_1 : heat of immersion, cal/g C₃S

Q : observed heat evolution cal/g C₃S

q_0 : heat of hydration of C₃S, both reaction products being in solid, cal/m mol C₃S

h_{ca} : heat of solution of Ca(OH)₂ (solid) in saturated lime solution, cal/m mol

P : mixing weight ratio of saturated lime solution to C₃S

C'_{ca} : increment in Ca²⁺ ion concentration of the solution, m mol/l

Alternatively, one can roughly estimate q_1 as a difference between the heat evolved in the mixture of completely de-moistured C₃S with saturated lime solution and that for an aerated C₃S. The validities of these methods will be mentioned later.

c) Heat of solution of the completely hydrated C₃S The heat evolved on complete hydration of C₃S was estimated by use of the solution calorimeter written in JIS R 5203-1962, where the

sample with a fineness less than 3 microns was used to facilitate the hydration of C_3S to an ultimate state at a water to C_3S ratio of 1.0, at 20°C.

2.5 Electron microscopies

Electron micrographs and diffraction patterns of selected-area (SED) were taken with a JEOL, JEM-T8 electron microscope for C-S-H samples which were sprinkled over a microgrid of collo-dion supported by copper mesh. EM-ASID Scanning Image Observation Device attached to JEM-100B electron microscope was used to explore the change of C_3S surface with hydration time. Evaporation of carbon layer (ca. 100 Å) followed by gold layer (ca. 300 Å) on the sample was effected prior to scanning.

3. Results

3.1 Dissolution of C_3S in water and in saturated lime solution

The aqueous solutions of the C_3S pastes which

※ denote the hydration in saturated lime solution

Fig. 1. Ca^{2+} ion concentrations of the solutions in the mixtures of C_3S with water and with saturated lime solution.

Fig. 2. Silicate ion concentrations of the solutions in the mixtures of C_3S with water, and K values of Eq. (3) (keys are the same with Fig. 1).

can be separated by use of the squeeze method were analyzed for lime and silica. The hydrations were effected both in water and in saturated lime solution at water to C_3S ratios between 0.7 and 10, and at temperatures between 10°C and 40°C. The results were shown in Fig. 1 and 2.

There were seen different aspects in Ca^{2+} ion concentration curves between the sample No. 1 or 2 and No. 3. For No. 1 and 2, it has already been mentioned that on mixture with water at a water to C_3S ratio of 0.7, C_3S dissolved instantaneously in water at a stoichiometric mole ratio of $CaO/SiO_2=3$ or congruently⁹⁾. The fact was found also true for the cases with water to C_3S ratios of 3 and 10.

Except for the case of C_3S No. 3 where the concentration of Ca^{2+} ion attained instantaneously to a saturation with almost no dissolution of silicate ion, the Ca^{2+} ion concentrations at this immediate stage were only around 5 mmol/l irrespective of the water to C_3S ratio and of temperature. Though in unsaturated state with respect to $Ca(OH)_2$, the concentration of 5 mmol/l itself must be under the restriction of some solubility products which are a function of both Ca^{2+} ion and silicate ion concentrations. One solubility product may be written as,

$$K = [Ca(OH)_2]^{1.63} [SiO_2] \dots\dots\dots (3)$$

where $[Ca(OH)_2]$ and $[SiO_2]$ are the concentrations, mmol/l of each constituent, and K value is 0.625 at 30°C when the Roller and Ervin's data in the system $CaO-SiO_2-H_2O$ are used⁸⁾. This sort of expression was also given by Halsstead and Lawrence⁹⁾ whose formula was $K = [Ca(OH)_2]^{1.9} [SiO_2]$, K being 3.4 at 25~40°C. From the data in Fig. 1 and 2, K values of Eq. 3 can be obtained in the course of hydration as shown in Fig. 2, this suggesting that both ions were in such a supersaturated state that K values were 15 to 20 times higher than that in equilibrium*.

As expected from the supersaturations and rapid decreases in SiO_2 ion concentrations, a hydrous silicate precipitated out of the solution, which was C-S-H(I) having an analytical composition of $CaO/SiO_2=1.4$ as mentioned in later 3.4.

After the instantaneous reactions ceased, Ca^{2+} ion concentrations increased with a low but rising velocity as if a new reaction would start, until the maximums were attained which were

* In an extreme case where there exists a solution saturated towards C_3S and the following equilibrium is established at the solid/electrolyte solution interface without any intermediate product on the solid surface, $C_3S + H_2O \rightleftharpoons 3 Ca^{2+}(aq) + SiO_4^{4-} + 2 OH^-(aq)$, the activities of the ions in the solution are of the order of 1 molal according to Stein's estimation²²⁾.

about twice as high as the solubility of $\text{Ca}(\text{OH})_2$ at 20°C . The maximum supersaturations were also revealed even when the hydrations of C_3S were effected in saturated lime solution as seen in Fig. 1. The reason why the new and second type of supersaturation with respect to $\text{Ca}(\text{OH})_2$ appeared, and the role of this supersaturation playing on the initiation of hardening stage will be discussed later.

3.2 Combined water bound in the immediate stage

In the previous paper³⁾, it was reported that upon contact of C_3S with water at a water to C_3S ratio of 0.7, the combined water amounted instantly to a constant value of $0.045 \pm 0.005 \text{ wt}\%$ irrespective of the hydration temperature. This was true for the case with a water to C_3S ratio of 10 and also for the case where the hydration was effected in saturated lime solution.

Now, it is of interest to break down the combined water of $0.045 \text{ wt}\%$ to allot to the respective hydrous matters that form in the immediate stage. In this stage, the dissolution of C_3S No. 1 or 2 occurred congruently to give Ca^{2+} ion concentration of 5 m mol/l , then the precipitation took place out of the solution according to the formula (1) with a n value of 1.4. Hence, the amount of C_3S dissolved in water of the paste with a water to C_3S ratio of 0.7 will be,

$$5 \times \frac{1}{1.6} \times 0.7 \times 10^{-3} = 2.2 \times 10^{-3} \text{ m mol/g } \text{C}_3\text{S}$$

Total combined water

$$\frac{0.045}{1.8} = 25 \times 10^{-3} \text{ m mol/g } \text{C}_3\text{S}$$

Water of C-S-H(I)^*

$$2.2 \times 10^{-3} \times 2 \times 0.7 \times 0.7 \\ = 2.16 \times 10^{-3} \text{ m mol/g } \text{C}_3\text{S}$$

Water of $\text{Ca}(\text{OH})_2^*$

$$2.2 \times 10^{-3} \times 1.6 \times 0.7 \times 0.7 \\ = 1.72 \times 10^{-3} \text{ m mol/g } \text{C}_3\text{S}$$

Otherwise fixed water

$$(25 - 2.16 - 1.72) \times 10^{-3} \\ = 21.1 \times 10^{-3} \text{ m mol/g } \text{C}_3\text{S}$$

Therefore, most of the combined waters consist of "otherwise fixed water" and can be considered as an adsorbed water on the surface of C_3S . It will be no doubt that the adsorption of water should take place after the dissolution of some of the outermost layers of C_3S grains has ceased, the number of the layers dissolved being nearly proportional to the water to C_3S ratio employed as shown in Fig. 1 and 2. At the ratio of 0.7, the dissolution of $2.2 \times 10^{-3} \text{ m mol } \text{C}_3\text{S/g}$ nearly

corresponds to about one mol layer on the outmost surface³⁾. Using the cross sectional area of $11.4 \text{ \AA}$ for one water molecule, the adsorbed water of $21 \times 10^{-3} \text{ m mol/g } \text{C}_3\text{S}$ will correspond to 3.8 and 3.4 molecular layers of water molecules on the surface of C_3S No. 1 and No. 2 respectively.

3.3 Heat evolution in the course of hydration and heat of immersion of C_3S in water

The heat evolution rates of C_3S No. 1, 2 and 3 in water and No. 1 and 2 in saturated lime solution were followed at a water to C_3S ratio of 0.7 at 20°C . The results were shown in Fig. 3.

*denote the hydration in saturated lime solution

Fig. 3. The rates of heat evolution accompanying the hydrations of C_3S in water and in saturated lime solution.

The evolutions of heat in the first 20 minutes were estimated for three C_3S samples to 0.13, 0.12 and 0.48 cal/g C_3S respectively. The high heat evolution of 0.48 cal for C_3S No. 3 will be due to its free lime content of 0.10%, which must generate a heat of hydration of $1.0 \times 10^{-3} \times (278 + 48) \text{ cal} = 0.326 \text{ cal}$. In saturated lime solution, the heat evaluations of C_3S No. 1 and 2 were considerably less than in water at an immediate stage, which were corresponding to the very low changes in Ca^{2+} ion concentration of the solution.

Here, we must note that the C_3S samples could not be entirely free from moisture in practice, but contained about $0.03 \pm 0.01 \text{ wt}\%$ of adsorbed moisture just before it was dropped into water or saturated lime solution in the reaction cell of calorimeter. This will imply that the originally adsorbed moisture on the C_3S sample should suffer almost no substantial change at the moment of mixture with saturated lime solution. In the case with water, however, C_3S should immediately dissolve from the outermost surface layer having some adsorbed moisture until a concentration of $5 \text{ m mol } \text{Ca}^{2+}/\text{l}$ was attained, followed by re-coverage by almost the same amount of water mole-

* About 30% by weight of the total amount of the solution in the paste was squeezed out for the analysis of the solution and about 30% of the solutes was not precipitated by addition of iso-propyl alcohol.

cules as that of the original.

As a water to C_3S ratio of 0.7 is just necessary for one molecular layer of the outermost surface of C_3S grains to dissolve in water⁹⁾, the hydration of C_3S No. 1 and 2 in water will proceed at an immediate stage following such a consecutive order as $III \rightarrow II \rightarrow I \rightarrow IV$ at a water to C_3S ratio above 0.7 and $III \rightarrow I \rightarrow IV$ below 0.7 in the following diagram (Fig. 4), which shows the hydration routes of C_3S . In Fig. 4, $C_3S_{H_2O ad.}$ denotes the C_3S covered by (or "skinned" with) adsorbed water molecules, and q_0 , q_1 etc. are the heat of reactions per g C_3S of the respective systems.

Fig. 4. Schematic view showing the routes of hydration-reaction of C_3S in an early stage through which C-S-H (I) and C-S-H (II) can be formed (q_0 , q_1 , q_3 ,... are the heat of reaction, cal/g. C_3S of respective systems, and (I) and (S) denote the liquid and solid phases respectively).

Hence, for the mixture of C_3S No. 1 or No. 2 with water the net heat evolved in the immediate stage will be $(q_0 + q_2)$ irrespective of water to C_3S ratio, provided that the concentration of silicate ion drops down to nil.

The heat of hydration of C_3S , q_0 was re-determined by the solution calorimetry, resulting in 110 ± 2 cal/g C_3S . The values hitherto known are 120 ± 3 cal/g¹⁰⁾ at room temperature and 96.5 ± 1.5 cal/g at $23^\circ C$ ¹¹⁾, and the latter does not take into account the heat of adsorption of water on hydrous products.

We have tried to find q_1 , heat of immersion of C_3S in water at $20^\circ C$. As the hydration of the completely de-moistured C_3S in saturated lime solution will proceed along route $I \rightarrow V$ in Fig. 4, q_1 may be estimated by use of equation (2). In practice, at a saturated lime solution to C_3S ratio of 20, Q and C'_{Ca} were determined in the first 1.5 hours at $20^\circ C$. With $P=20$, $q_0=110 \times 228 \times 10^{-3} = 25.1$ cal/mol, $h_{Ca} = 2.7$ cal/mol, $n=1.6$, we find $q_1=0.052$ and 0.050 cal/g for C_3S No. 1 and 2 respectively, as shown in Table 2.

Table 2. Determination of heat of immersion of C_3S in water at $20^\circ C$.

	Q cal/g C_3S in 1.5 hrs	Concentration of Ca^{++} ion (m mol/l)		$C'_{Ca^{++}}$ (m mol/l)	q_1 (cal/g C_3S)	
		initial	after 1.5 hrs		by Eq. 2	alternative method
C_3S (No. 1)	0.136	21.43	21.63	0.20	0.052	0.055
C_3S (No. 2)	0.162	21.50	21.77	0.27	0.050	0.057

These values are equivalent to 530 ± 40 erg/cm², the change in energy per unit of surface area of C_3S . The alternative procedure was applied, in which q_1 was roughly estimated from the difference between heat evolved in the mixture of completely de-moistured C_3S with saturated lime solution and that for the aerated C_3S . The aerated C_3S contained moisture of 0.03%, and hydrations were effected for 1.5 hours with $P=20$, at $20^\circ C$. As a result, mean q_1 was 0.056 cal/g which differs a little from that obtained by the former procedure as shown in Table 2.

3.4 Electron microscopic observations on C_3S paste

In the followings will be mentioned the circumstances in which two kinds of C-S-H different in morphology come to appear, together with the results obtained with a scanning electron microscope for the hydrated C_3S .

3.4.1 Observations on the two kinds of C-S-H in the C_3S paste It is well known that two rather distinct habits of particles, thin foil and laths (or cigar-shaped agglomerates), are observed for C-S-H phase produced by the paste hydration of C_3S at room temperature^{12), 13)} and this was the case for our C_3S paste after a hydration time of 1.5 hours at a water to C_3S ratio of 0.7, at $20^\circ C$, as shown in Fig. 5. In view of the fact that paste hydrations can take place following the two different routes, I-V and II (III)-IV in Fig. 4, the habits of particles should depend on the route through which the particles were developed.

The C-S-H phase which produced through the route II (III)-IV or through solution can readily be prepared as an isolated matter when C_3S was stirred in several fold of water for only one minute or less at room temperature, then filtered rapidly to obtain a filtrate. When the filtrate was allowed to stand in a vessel free from carbon dioxide, precipitation occurred in time, because of the supersaturation of the filtrate with regard to C-S-H as mentioned in 3.1. The electron micrograph of the precipitate obtained revealed clearly very thin crumpled foils as seen in Fig. 6. SED patterns taken for the precipitate corresponded to d -spacing of 5.1 Å (weak), 3.00 Å (strong), 2.72 Å (strong) and 1.79 Å (medium). From

Fig. 5. C_3S (No. 1)-water paste, $W/C=0.7$, after 1.5 hours at $20^\circ C$, showing thin foils of C-S-H(I) together with particles of C-S-H(II).

Fig. 6. Isolated foils of C-S-H(I), which precipitated out of the filtrate of C_3S (No. 1)-water suspension at $20^\circ C$.

Fig. 7. Isolated particles of C-S-H(II), which developed in 2.5 hours' paste hydration of C_3S (No. 1) using saturated lime solution, $W/C=0.7$ at $25^\circ C$.

these data, together with the analytical composition determined to be a CaO/SiO_2 ratio of 1.40, the precipitate could well be identified with C-S-H(I).

On the other hand, the C-S-H phase developed through the route I-V could be observed mostly as cigar-shaped or laths like particles as shown in Fig. 7, which was taken for the ultrasonated C_3S -ethyl alcohol mixture after a 2.5 hours paste hydration of C_3S in saturated lime solutions at a water to C_3S ratio of 0.7 and at $25^\circ C$. In saturated lime solution there must scarcely be any

Fig. 8. Pictures of C_3S (No. 2) surfaces after 5 seconds, 20 minutes, 2.5 hours, 4 hours and 7 hours hydration in saturated lime solution, $W/C=0.7$ at $25^\circ C$ respectively, showing topochemical nucleation and growth of C-S-H(II). At 4.0 hours the new nucleations are visible on the exposed surface.

Fig. 9. Pictures of C_3S (No. 2) surface after 1 hour, 2.5 hours and 4.5 hours hydration in water, $W/C=0.7$ at $25^\circ C$ respectively, showing the precipitated foils of $C-S-H(I)$ together with topochemically generated $C-S-H(II)$ particles.

chance to form $C-S-H(I)$ through the route II (III)-IV or through solution. Although the analytical composition was not examined, the $C-S-H$ phase thus obtained may be classified as $C-S-H(II)$ on the basis of morphology.

3.4.2 Scanning electron microscopies The detail of the surfaces of C_3S hydrated in saturated lime solution at $25^\circ C$ was explored using scanning electron microscope, typical figures being shown in Fig. 8. Although no visible change occurred on C_3S hydrated only for 5 seconds, needle- or rod-like particles came to appear here and there on the exposed and smooth surface after 20 minutes as if the hydration should start with topochemical nucleation of $C-S-H(II)$ as in the case of $\beta-C_2S$ in water⁽⁴⁾, and then grew up with sideways generation of secondary nuclei to form aciculated mass or parallel-oriented fibres in 2.5 hours, without considerable changes in both length and number of the particles. These particles of $C-S-H(II)$ seemed to fall off readily from the surface on which they grew when ultrasonation was effected on the C_3S -dispersing medium mixture as mentioned above. After 4 hours hydration, a large number of particles was generated newly on the exposed surface and grew up and increased in number along the hydration time. Fig. 9 and 10 show the pictures of C_3S hydrated in water at $25^\circ C$. On the exposed surface of C_3S hydrated for one hour at a water to C_3S ratio of 0.7, flaky particles are visible (Fig. 9 (a)) which must be the precipitated $C-S-H(I)$. After 2 hours, the particles of $C-S-H(II)$ were seen together with precipitated $C-S-H(I)$. The reason why $C-S-H(II)$ didn't be visible in Fig. 9 (a) will probably their minuteness in size enough to be hidden under gold-coatings by the process of vapor deposition (2.5). Since the amount of the precipitates should increase with increasing water to C_3S ratio as stated in 3.1, the surfaces of C_3S

Fig. 10. Picture of C_3S (No. 2) surface hydrated for 2.5 hours, $W/C=10$ at $25^\circ C$, showing that it was markedly disfigured by precipitated $C-S-H(I)$.

were expected to become markedly disfigured at a water to C_3S ratio of 10, the image being taken as seen in Fig. 10.

3.5 Rate of the hydration reaction in an early stage

The immediate reaction of C_3S upon contact with water involves 1) a congruent dissolution of C_3S , followed by precipitation of $C-S-H(I)$, 2) formation of "skinned" surface with adsorbed water molecules and 3) spontaneous generation of $C-S-H(II)$ thereon. Once the immediate reaction has ceased, it begins so called "dormant period", in which heat evolution is mild and the increase in combined water is sluggish. In order to obtain a closer view on the hydration kinetics during this period, it is necessary first of all to examine whether the above three kinds of data can be expressed consistently in terms of degree

of reaction or not. On the basis of calculation, the reaction formula (1) was used but n value was varied between the followings,

A type reaction : to form C-S-H(I) by route II(III)-IV, $n=1.4$

B type reaction : to form C-S-H(II) by route I-V, $n=1.6$

It is possible to calculate the amounts of C_3S reacted, W_I , W_{II} and W_{III} from the three kinds of data by use of the equations (5), (7) and (9) respectively, for which the interpretations are given in the appendix.

From the values of Ca^{2+} and silicate ion concentrations :

$$W_I = W_A + W_B \dots\dots\dots (4)$$

$$W_I = \frac{P}{1.6} C_0 \times 10^{-3} + \frac{P}{1.4} \times (C_{Ca^{2+}} - C_0 - 1.4 C_{SiO_2}) \times 10^{-3} \dots\dots (5)$$

$$C_0 = C_{Ca^{2+}}^0 - 1.4 C_{SiO_2}^0 \dots\dots\dots (6)$$

where

W_A , W_B : the amount of C_3S reacted after A and B type reactions, mmol/g C_3S

$C_{Ca^{2+}}^0$, $C_{SiO_2}^0$: the concentrations of Ca^{2+} ion and silicate ions in the solution instantaneously after mixing C_3S with water, mmol/l

$C_{Ca^{2+}}$, C_{SiO_2} : the concentrations of both ions at any time, mmol/l

P : a water to C_3S weight ratio

From the values of combined water contents :

$$W_{II} = \frac{1}{\mu} \{M + P(C_{Ca^{2+}} + 0.6 C_{SiO_2}) \cdot (1 - \alpha \cdot \beta) \times 10^{-3} - M_{AD}\} \dots\dots\dots (7)$$

$$\mu = \frac{1}{W_I} (3.6 W_A + 3.4 W_B) \dots\dots\dots (8)$$

where

M , M_{AD} : the observed combined water and adsorbed water contents, mmol/g C_3S

α : the fraction of the solution remaining in the paste after squeezing

β : the fraction of the solute precipitated out of the solution in the paste by treating with alcohol

From the calorimetry :

$$W_{III} = \frac{1}{25} (q - Ph_C C_{Ca^{2+}} \times 10^{-3}) \dots\dots\dots (9)$$

where

q : amount of heat evolved, cal/g C_3S

h_C : heat of solution of solid $Ca(OH)_2$, cal/m mol

Using the equations together with the data in Table 3, the degree of reaction W_I , W_{II} and W_{III} mmol/g C_3S were calculated. The results were given in Fig. 11, showing that these values were fairly comparable with each other and that in spite of the long dormant period durable for 2 to 3 hours, the amount of C_3S reacted was only 0.02 mmol/g C_3S , which corresponded to the degree of reaction of only 0.46%.

The curves of W_I branched off from those of W_{II} and W_{III} at a time t_0 because of attainments

Table 3. Data showing the change in the concentration of Ca^{2+} ion and silicate ion in the solution, combined water and heat evolved in the course of hydration of C_3S in water at a H_2O/C_3S weight ratio of 0.7 and at 20°C.

Hydration time (min)	Ca ²⁺ , SiO ₂ concentration in the solution (mmol/l)						Combined Water (mmol/g C ₃ S)		Heat of hydration (cal/g C ₃ S)		
	C ₃ S (No. 1)		C ₃ S (No. 2)		C ₃ S (No. 3)		C ₃ S (No. 1)	C ₃ S (No. 2)	C ₃ S (No. 1)	C ₃ S (No. 2)	C ₃ S (No. 3)*
	Ca ²⁺	SiO ₂	Ca ²⁺	SiO ₂	Ca ²⁺	SiO ₂					
1	5.4	0.75	5.1	0.80	19.0	0.10	—	—	—	—	—
5	6.5	0.45	6.3	0.50	22.0	0.06?	—	—	—	—	—
10	7.3	0.37	7.5	0.36	24.0	—	0.025	0.025	0.11	0.11	—
20	8.4	0.31	8.9	0.23	26.0	—	—	—	0.13	0.12	—
30	9.5	0.22	10.3	0.17	27.0	—	0.029	—	0.15	0.15	—
40	10.3	0.20	12.0	0.13	28.0	—	—	0.031	0.18	0.18	—
50	12.0	0.17	13.0	0.10	29.0	—	—	—	0.21	0.21	—
60	14.6	0.15	15.3	0.08	30.0	—	0.033	0.036	0.26	0.25	0.20
80	20.0	0.12	21.0	0.06?	31.5	—	—	—	0.33	0.33	0.22
90	23.8	0.10	25.4	—	32.5	—	0.042	—	—	—	—
100	26.3	0.09	28.5	—	33.5	—	—	0.056	0.43	0.43	0.25
120	32.4	0.07?	34.3	—	35.0	—	0.053	—	0.54	0.54	0.28
130	34.7	—	23.0	—	35.5	—	—	0.076	—	—	—
140	37.0	—	39.2	—	36.0	—	—	—	0.66	0.68	0.32
160	40.0	—	42.0	—	35.8	—	—	—	0.79	0.84	0.38
180	41.2	—	41.0	—	35.6	—	0.097	0.110	0.93	1.03	0.45
190	40.7	—	39.8	—	35.5	—	—	—	1.00	1.15	—
200	40.0	—	38.8	—	35.0	—	—	—	1.10	1.32	0.53
210	39.0	—	38.0	—	34.7	—	—	—	1.20	1.58	0.58
220	38.3	—	37.0	—	34.6	—	—	—	1.39	—	0.66
240	36.8	—	35.6	—	34.5	—	0.28	0.43	1.92	2.82	0.84
270	—	—	—	—	—	—	—	—	3.15	4.70	—
300	—	—	—	—	—	—	—	—	4.87	7.10	1.85

* Correction was made by subtracting heat of hydration and solution of free CaO (0.1%)

Fig. 11. The amounts of C_3S (No. 1 and 2) reacted at a water to C_3S ratio of 0.7 at $20^\circ C$ versus time, which were estimated from the data of Ca^{2+} ion concentration of the solution (W_I); combined water (W_{II}) and calorimetry (W_{III}). At t_0 the line W_{II} and W_{III} departed from the line W_I on which a maximum appeared at t_m .

Fig. 12. The relation between $\log(W - W_0)$ and $\log t$. Straight lines show the validity of Eq. (10) (keys are the same with Fig. 1).

Table 4. Constants, W_0 , k_1 , k_2 and t_0 in the Eqs. (11) and (15) evaluated for hydration of C_3S in an early stage.

Experiment No.	Conditions			Measure-ment**	Constants			
	C_3S Sample No.	Tempera-ture ($^\circ C$)	Water to C_3S ratio		W_0 m mol $\times 10^3$	k_1 m mol $hr^{-1.5} \times 10^{-3}$	k_2 m mol $hr^{-3} \times 10^{-3}$	t_0 hr
1	1	20	0.7	W	I, II	2.5	4.5	—
	1	20	1.0	W	III	3.1	5.4	2.5
2	2	20	0.7	W	I, II	2.4	5.6	—
	2	20	1.0	W	III	3.0	5.3	2.0
3	3	20	1.0	W	III	2.1	2.0	2.5
4	1	10	0.7	W	I, II	1.7	1.6	—
5	1	40	0.7	W	II	3.5	12.1	—
6	3	20	3.0	W	I	7.5	8.0	—
7	3	20	10.0	W	I	16.7	14.3	—
8	1	20	1.0	L	III	3.1	2.4	2.5
9	2	25	0.7	L	I	0.1	2.5	—
10	1	20	0.7	L	I	0.1	1.5	—

* W or L: hydration was effected in water (W) or in saturated lime solution (L)
** I, by Ca^{2+} ion concentration in the solution, II, by combined water and III, by calorimetry.

of Ca^{2+} ion concentrations to some critical super-saturations. When $(W - W_0)$ were plotted against time t on log-log paper, W_0 being obtained by extrapolating the curves to $t=0$, approximately parallel straight-lines were obtained with a mean slope of about 1.5, though the slope varied slightly between 1.46 and 1.68, as shown in Fig. 12. Hence, the dependence of W on t can be expressed as follows,

$W = W_0 + k_1 t^{1.5}$ (10)

The constants W_0 and k_1 were evaluated and

given in Table 4. W_0 is concerned with the immediate hydration of C_3S implying how much dissolution of C_3S occurs and how readily nuclei generate on it, while k_1 mainly with the later growth of the nucleated C-S-H (II). To say more precisely, k_1 may be expressed as $N_0 k / v_0$, where N_0 is a number of nuclei per g C_3S , $k t^{1.5}$ a mean volume of each C-S-H(II) particle aged for t hours and v_0 specific volume per m mol of C-S-H(II).

In Table 4, W_0 markedly depended on the

ratio of water to C_3S and was very small in the case of hydration in lime solution*. The constant k_1 became larger not only with increasing water to C_3S ratio but also with rising temperature. Therefore, the increasing water to C_3S ratio seemed to be in favour of nucleation of C-S-H(II), or larger N value**.

After the time t_0 , the expression of equation (10) was not valid and the observe curve deviated

Fig. 13. The amount of C_3S reacted in an early stage in comparison with those calculated by use of Eq. (10) and Eq. (15), the experiments No. 2 and No. 3 in Table 4 being exemplified.

* The reproducibility of the rates of reaction in an early stage was generally good in water even when the aged C_3S was used, whereas in saturated lime solution the effect of the aging of C_3S was often found significant. The experiments of 1967 (No. 9 and 10 of Table 4) in that solution showed W_0 of around zero, while those of 1970 (No. 8 of Table 4) W_0 of about 3. In all experiments the hydrations were effected for C_3S reheated at $1350^\circ C$. The effects of aging of C_3S preparation were already pointed out by Taplin¹⁵⁾ on the long term hydration.

** It is probable that C-S-H(I) precipitating or precipitated out of the solution may activate the skinned surface of C_3S to give rise to nucleation of C-S-H(II). The higher the water to C_3S ratio is, the more C-S-H(I) may precipitate. The addition of small amount of afwillite¹⁶⁾ or amorphous silica (Aerosil)¹⁷⁾ in C_3S paste was indicated effective to promote early hydration.

from the calculated one more and more with time as shown in Fig. 13. When the reactions were followed by calorimetry and $(W - W_0 - k_1 t^{1.5})$ were plotted against $(t - t_0)$ on log-log paper, almost straight lines were given with a slope of about 3 over $t = t_0$ to $t = 6$ hours. Accordingly, the empirical equation of (11) could be set up, which is applicable until the early stage of hardening of C_3S .

$$W = W_0 + k_1 t^{1.5} + k_2 (t - t_0)^3 \dots \dots \dots (11)$$

Some k_2 and t_0 were evaluated and given in Table 4.

4. Discussions

So called "the dormant periods" are durable for 2~3 hours in the paste-hydration of C_3S at room temperature. In the followings will be discussed the situations of surface of C_3S which permit "the dormant period", and the mechanism by which this is terminated.

4.1 Quasi-stable state of "skinned" C_3S

During the dormant period, the nucleation and growth of C-S-H(II) particles took place topographically on the surface of C_3S paste-hydrated in saturated lime solution, and besides C-S-H(II), were observed precipitated C-S-H(I) in the case of C_3S hydration in water. Permitting the presence of these particles, most area of the surface of C_3S remained smooth or exposed under the scanning electron microscope. The ratio of the surface area hidden under C-S-H(II) particles, without taking that under the precipitated C-S-H(I) into account, could be estimated to be few percents of the total surface area of C_3S after 2.5 hours' paste-hydration at $20^\circ C$.

It must be thought of that the exposed surface of hydrated C_3S is in reality being "skinned" by adsorbed water molecules and the thickness of "skin" was estimated 3~4 molecular layers of water molecules as described 3.2. The heat of wetting of C_3S by water was estimated about 0.051 cal/g C_3S or 530 erg/cm², which was nearly corresponding to that for such typical oxides as quartz, fluorite and titania.

One can roughly estimate the lowering of enthalpy level of the fresh surface of C_3S after adsorption of water by use of the following equation,

$$r = \frac{q_1}{\left(\frac{M_{AD}}{5-n}\right) M' q_0 \times 10^{-3}} \dots \dots \dots (12)$$

where, q_0 and q_1 are the same as those in Fig. 4

M_{AD} : mmol of adsorbed water, mmol/g C_3S

$5-n$: mmol of water to react with one mmol of C_3S (see Eq. (1))

M' : molecular weight of C_3S

With $q_1 = 0.051$ cal/g C_3S , $q_0 = 110$ cal/g C_3S , M_{AD}

$=0.021$ m mol/g C_3S , $n=1.6$ and $M=228$, we found $r=0.32$. This means that the adsorption of water molecules to form "skinned" C_3S stabilized the fresh surface of C_3S by 32% of the total enthalpy change of the hydration that would occur there for the adsorbed water molecules. Another thing in close relation to the quasi-stable state of the "skinned" C_3S is the appearance of the supersaturated solution with respect to calcium hydroxide, which can be interpreted in view of the fact that calcium ions situated on the outermost layer of the skinned C_3S must have higher chemical potentials than those of $Ca(OH)_2$ in solid state.[†]

These situation of the surfaces which are merely covered by adsorbed water molecules has often been explained to have "a hydrated skin on the unhydrated which has the same CaO/SiO_2 ratio as substrate or a high lime gel coating"^{11,18)}, or to be covered by "a hydrate (I) which can not be distinguished from the C_3S by an electron-microscope"¹⁹⁾.

4.2 Termination of dormant period induced by precipitation of $Ca(OH)_2$ out of the supersaturated lime solution

At the end of the dormant period, a large number of nuclei happened to appear as seen in Fig. 8(d), signifying that a new impetus is exerted on the exposed surfaces of the skinned C_3S . One possible impetus will be the precipitation of calcium hydroxide out of the supersaturated lime solution. When the terminations of the dormant periods were expressed by the times of rapid risings of heat evolution rates and combined water (t^*), these were virtually in a linear relation with the times it took for the concentrations of calcium ion in the solution of C_3S pastes to attain the maximum supersaturation (t_m), irrespective of water to C_3S ratio, temperature and as to whether paste-hydration in water or in saturated lime solution. The relation was shown in Fig. 14, wherein t_0 line lay below the 45° line from the origin.

Therefore, the precipitation of calcium hydroxide out of the supersaturated lime solution must exert an efficient seeding action for new births of C-S-H(II) nuclei on the exposed surface of skinned C_3S .

Although the term $k_2(t-t_0)^3$ involved in the empirical equation (11) was introduced to represent this effect of new nucleation and growth of C-S-H(II), one can express this in the other way as follows. The number of nuclei generated will

[†] By this reason the supersaturation was also found in the solution of the C_3S paste mixed with 15% $Ca(OH)_2$. The hydration of a C_3S sample mixed with crushed C_3S paste hydrated for along period was studied by Kondo and Daimon²⁰⁾.

Fig. 14. The times at which the dormant period terminated (t^*) and the precipitation of $Ca(OH)_2$ out of the solution began (t_0), with relation to the time it took for the concentration of Ca^{2+} ion in the solution of the C_3S paste to attain the maximum supersaturation (t_m).

be proportional to the amount of $Ca(OH)_2$ which was stoichiometrically splitted off from C_3S into the supersaturated lime solution though only to be soon precipitated, hence

$$\frac{dN}{d\theta} = m \frac{d(W_{II} \text{ or } W_{III} - W_I)}{d\theta} \dots\dots\dots (13)$$

where

N : number of new nuclei per gram C_3S

θ : time

W_I , W_{II} and W_{III} : amounts of C_3S reacted m mol/g C_3S which are calculated by use of the data of Ca^{2+} ion concentration, combined water and calorimetry respectively

m : a constant, m mol⁻¹

The precipitation of $Ca(OH)_2$ will start at the time of departure of the line W_I from the lime W_{II} or W_{III} in Fig. 11, the time being expressed as t_0 , and a C-S-H(II) particle nucleated at any time θ will grow up till the later time t to a volume of $k(t-\theta)^{1.5}$. Therefore, the total amount of C-S-H(II), m mol/g C_3S , formed between t_0 and t is

$$W' = \frac{1}{v_0} \int_{t_0}^t k(t-\theta)^{1.5} \left(\frac{dN}{d\theta} \right) \eta(\theta) d\theta \dots\dots\dots (14)$$

$\eta(\theta)$: an efficiency of seeding action of precipitating $Ca(OH)_2$, which is depending θ

v_0 : specific volume of C-S-H(II), ml/m mol

t_0 : the time at which the second nucleation of C-S-H(II) begins, hr

After the time t_0 , W_I can be approximated by a constant in comparison with the change of W_{II} or W_{III} with time, so that the overall amount of C_3S reacted till any early hardening stage t may

be expressed in place of equation (11) by the following,

$$W = W_0 + k_1 t^{1.5} + \frac{km}{v_0} \int_{t_0}^t (t-\theta)^{1.5} \left(\frac{dW}{d\theta} \right) \eta(\theta) d\theta \quad \dots\dots\dots (15)$$

The factor $\eta(\theta)$ may nearly be 1 in an early hardening stage, because that the almost surface area of skinned C_3S remains exposed to receive the seeding action of precipitating $Ca(OH)_2$ efficiently. Then, one can evaluate the integral equation (15) numerically by some conventional method²⁰⁾. For example, using the values of W_0 and k_1 for the experiments No. 2 and 3 in Table 4, one can obtain best representations by giving km/v_0 of $1.0 \text{ hr}^{-1.5}$ for both experiments at least in an early hardening stage as shown in Fig. 13. Since the later departures of calculated curves from observed ones were possibly caused by the assumption of $\eta(\theta)=1$, this must be expressed as a function of θ in order to interpret the overall hydration-kinetics, which was treated in the other paper²¹⁾.

5. Conclusion

The immediate reaction upon contact of C_3S with water involves i) the congruent dissolution of C_3S to form a supersaturated solution with respect to C-S-H, followed by precipitation of C-S-H(I), ii) the formation of "skinned" C_3S with about 3~4 molecular layers of adsorbed water molecules, the heat of immersion of C_3S in water being estimated to $530 \pm 40 \text{ erg/cm}^2$, and iii) the topochemical generation of nuclei of C-S-H(II) on the skinned C_3S . These reactions seemed to take place consecutively but almost simultaneously in water, but in saturated lime solution the reaction i) was negligible.

Once the immediate reaction has gone down, it enters into so-called dormant period, in which the growth of C-S-H(II) is predominant. During this period the degrees of reaction of C_3S were estimated from three kinds of data, calorimetry, increases in combined water and concentration of Ca^{2+} ion in the solution respectively, resulting in that they were consistently expressed by the equation (10). The dormant period terminated when the concentration of Ca^{2+} ion in the solution of C_3S paste attained to a critical supersaturation, the saturation ratio being about 2 with respect to calcium hydroxide, then the reaction proceed rapidly owing to the seeding action of precipitating $Ca(OH)_2$ for new and second nucleation of C-S-H(II) on the exposed area of C_3S -surface (see Fig. 8(d)). The overall amount of C_3S reacted in an early hardening stage could well be represented by the equation (15).

Appendix

[I] Calculation of the degree of reaction from Ca^{2+} ion and silicate ion concentration data.

The amount of C_3S reacted after A type reaction, W_A mmol/g C_3S , will be

$$W_A = \frac{P}{1.6} (C_{Ca^{2+}}^0 - 1.4 C_{SiO_2}^0) \times 10^{-3}$$

wherein P is a water to C_3S ratio, $C_{Ca^{2+}}^0$ and $C_{SiO_2}^0$ are the concentration (mmol/l) of Ca^{2+} ion and silicate ion in the solution instantaneously after mixing C_3S with water, whereas the amount of C_3S reacted after B type reaction W_B will be

$$W_B = \frac{P}{1.4} C'_{Ca^{2+}} \times 10^{-3}$$

wherein $C'_{Ca^{2+}}$ is the concentration of Ca^{2+} ion formed by this type of reaction. Hence, the total C_3S reacted, W_I mmol/g C_3S is

$$W_I = W_A + W_B = \frac{P}{1.6} (C_{Ca^{2+}}^0 - 1.4 C_{SiO_2}^0) \times 10^{-3} + \frac{P}{1.4} C'_{Ca^{2+}} \times 10^{-3}$$

When the observed concentration of both ions at any time are written as $C_{Ca^{2+}}$ and C_{SiO_2} , they are in relation of,

$$C_{Ca^{2+}} = C_{Ca^{2+}}^0 - 1.4 C_{SiO_2}^0 + 1.4 C_{SiO_2} + C'_{Ca^{2+}}$$

therefore,

$$W_I = \frac{P}{1.6} C_0 \times 10^{-3} + \frac{P}{1.4} \times (C_{Ca^{2+}} - C_0 - 1.4 C_{SiO_2}) \times 10^{-3} \dots\dots\dots (5)$$

$$C_0 = C_{Ca^{2+}}^0 - 1.4 C_{SiO_2}^0 \dots\dots\dots (6)$$

[II] Calculation of the degree of reaction from combined water data

In this calculation, the observed combined water, M mmol/g C_3S , must be corrected by subtracting the adsorbed water (M_{AD} , mmol/g C_3S), while by adding the loss of combined water arising from analytical procedure. Hence, the amount of C_3S reacted, W_{II} , mmol/g C_3S , can be represented by the following,

$$W_{II} = \frac{1}{\mu} \{ M + P(C_{Ca^{2+}} + 0.6 C_{SiO_2})(1 - \alpha \cdot \beta) \times 10^{-3} - M_{AD} \} \dots\dots\dots (7)$$

$$\mu = \frac{1}{W_I} (3.6 W_A + 3.4 W_B) \dots\dots\dots (8)$$

wherein μ is a mean combined water (mol) per one mol of C_3S reacted, α is the fraction of the solution remained in the paste after squeezing, and β is the fraction of the solution in the paste by treating with alcohol. Both α and β were approximately 0.7 and M_{AD} was 21.1×10^{-3} mmol/g in the case of $P=0.7$ as aforementioned.

[III] Calculation of the degree of reaction from calorimetry

In order to calculate the amount of C_3S reacted (W_{III}) from the data of heat evolution, the heat of hydration q_0 (Fig. 4) was assumed 110 cal/g C_3S or 25 cal/mmol C_3S irrespective of the species

of C-S-H. As heat of immersion q_i in water is not necessary to be taken into account, the heat evolved, q cal/g C_3S , will be expressed as follows,

$$q = 25 W_{\text{III}} + P \{ C_{\text{SiO}_2} h_S + (C_0 + C'_{\text{Ca}}) h_C \} \times 10^{-3}$$

wherein h_C and h_S are heat of solution of $\text{Ca}(\text{OH})_2$ and C-S-H, cal/m mol. Allowing the following approximation since h_S is unknown,

$$C_{\text{SiO}_2} h_S + (C_0 + C'_{\text{Ca}}) h_C \approx C_{\text{Ca}^{++}} h_C$$

then, W_{III} will be

$$W_{\text{III}} = \frac{1}{25} (q - PC_{\text{Ca}^{++}} h_C \times 10^{-3}) \dots\dots\dots (9)$$

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珪酸三石灰初期水和反応の機構と速度

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珪酸三石灰 (C_3S) と水との混合直後の反応は 3 つの内容をもち、i) 粒子表面から C_3S が水に congruent に溶解し、水溶液は C-S-H に関して過飽和となって C-S-H(I) を沈殿する、ii) 溶解後 C_3S 粒子表面に 3~4 分子層の水分子が吸着して表面を準安定化する。この時の吸着熱は 530 ± 40 erg/cm², iii) C_3S 粒子表面に局所的に C-S-H(II) の核を生成する。純水の代りに石灰飽和液を用いると i) の反応は無視できる。

その後の "Dormant Period" (誘導期間) 中は、C-S-H(II) の結晶成長が主反応で、この期間の反応率-時間関係は、水和熱測定、液相中の Ca^{2+} とシリケートイ

オン濃度の分析 および 固相の結合水定量結果 から、式 (10) で表わされた。誘導期間は、液相の Ca^{2+} イオン濃度が $\text{Ca}(\text{OH})_2$ に関する飽和比約 2 の最大過飽和に到達する時に終わり、水和反応は急速に進行するようになる。その引金は、C-S-H(II) の成長反応に伴って溶解する $\text{Ca}(\text{OH})_2$ が直ちに、 C_3S 粒子の露出された表面に析出し、新しい C-S-H(II) の核生成を誘発することになり、この C-S-H(II) の核生成-成長が増殖的に進むと見なすと、硬化初期段階までの反応量-時間関係は式 (15) によって表現される。

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