Pergamon

Cement and Concrete Research 32 (2002) 1077–1085

CEMENT AND CONCRETE RESEARCH

Initial hydration of tricalcium silicate as studied by secondary neutrals mass spectrometry
II. Results and discussion

Ivan Odler*, Stephan Cordes

Institute of Nonmetallic Materials, Technical University Clausthal, 38678 Clausthal-Zellerfeld, Germany

Received 10 October 2001; accepted 16 January 2002

Abstract

The hydration of tricalcium silicate (C_3S) was studied by secondary neutrals mass spectrometry (SNMS), a method that enables determination of the Ca/Si ratio of the formed calcium silicate hydrate (C-S-H) phase with an extremely low information depth. It was found that the magnitude of this parameter within the hydrate layer formed at the surface of the nonhydrated C_3S is not constant and increases with increasing distance from the liquid–solid interface. It was also found that, at a constant distance from the surface, the Ca/Si ratio declines with hydration time. The kinetics of the hydration process is characterized by a very fast initial reaction, followed by a dormant period and a subsequent period of renewed hydration. The rate of hydration becomes distinctly accelerated by elevated temperature and retarded by the presence of sucrose, while NaCl affects the initial hydration kinetics only to a small degree. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Calcium silicate hydrate (C-S-H); Characterization; SNMS

1. Introduction

In the first paper of this series [1] the principle of secondary neutrals mass spectrometry (SNMS) and the possibilities of the use of this method in cement research were discussed. Also reported was the preparation of the target to be studied in the analysis and the calibration, which had to precede the actual measurements. In this second paper, data that were obtained in measurements aimed at determining the CaO/SiO_2 ratio of the C-S-H phase formed in the initial stages of hydration of tricalcium silicate (abbreviated C_3S), as well as the kinetics of this process are reported.

The hydration of C_3S is a complex process characterized by the formation of a nearly amorphous calcium silicate hydrate phase (called commonly C-S-H phase) of variable stoichiometry and calcium hydroxide. In the initial stage of hydration, the C-S-H phase is formed at the surface of the original anhydrous C_3S, whereas calcium hydroxide dissolves, to precipitate later from the liquid phase.

In the study of the hydration of C_3S the two main questions asked concern the kinetics of the process and the stoichiometry of the formed C-S-H phase. The answering of these questions in the initial stage of hydration is, however, associated with particular experimental difficulties, caused by the limited thickness of the hydrate layer present.

In earlier work on the subject efforts were made to estimate the stoichiometry of the C-S-H phase formed in the initial stage of hydration from the composition of the liquid phase being in contact with the hydrating C_3S. The obtained results varied greatly depending on the experimental conditions employed, but generally indicated the formation of a C-S-H phase having a molar CaO/SiO_2 ratio less than 3.0 (Refs. [2–5] and others). In other studies, in which the CaO/SiO_2 ratio of the C-S-H phase was calculated from the degree of hydration as determined by X-ray diffraction and the free $Ca(OH)_2$ content, values both identical with those of the original C_3S [6] as well as distinctly reduced [7,8] were found.

---

* Corresponding author. 16 Olde Village Drive, Winchester, MA 01890, USA. Tel./fax: +1-781-721-7773.

E-mail address: ivanodler@aol.com (I. Odler).

PII: S0008-8846(02)00739-1

The CaO/SiO_2 ratio, or more exactly the Ca/Si ratio in the hydrate layer formed at the C_3S surface, has been analyzed also directly, applying X-ray photoelectron spectroscopy (XPS), called also electron spectroscopy for chemical analysis (ESCA). To do so, Menetier et al. [9] and Jawed et al. [10] allowed tablets made from powdered C_3S to hydrate in excessive amounts of water at ambient temperature for different periods of time and analyzed the Ca/Si ratio of the hydrate formed at the surface. They found already after 5 s a reduction of this ratio to Ca/Si = 2.2–2.5, followed by a maximum with Ca/Si = 2.8–2.9 after 20 s and subsequently a decline of this value to Ca/Si = 1.5 within 30 min. From the obtained results, the authors postulated the formation of a “first” hydrate with CaO/SiO_2 ratio distinctly lower than 3.0 right after first contact with water. The development of the subsequent Ca/Si ratio maximum was tentatively attributed to a chemisorption of Ca^{2+} ions on the initially formed surface and the renewed decline of the ratio to the continuation of the formation of a hydrate with reduced Ca^{2+} content. At a hydration temperature of 4 °C the Ca/Si ratio decreased initially fast and subsequently moderately, without developing a maximum; it stayed consistently below that found at ambient temperature. Similarly, in the hydration of dicalcium silicate the authors found analogous fluctuations in the Ca/Si ratio as seen in the hydration of C_3S, though they were less pronounced [11]. Results not too different were also reported by Trettin et al. [12].

In similar experiments on a cement paste Thomassin et al. [13] and Regourd et al. [14] observed between 5-s and 1-min fluctuations of the Ca/Si ratio between about 2.0 and 2.4. At the end of 1 min this ratio increased to 2.7, to decline subsequently to 1.9 within half an hour. The authors postulated four steps in the hydration process: (1) an initial congruent dissolution of C_3S, (2) the formation of an initial hydrate with $CaO/SiO_2 = 3$, (3) the formation of a secondary hydrate having a CaO/SiO_2 ratio higher than the primary hydrate ($Ca/Si \approx 2.0$) and (4) the formation of a tertiary C-S-H type I hydrate after the end of the dormant period.

Stadelmann et al. [15] found in C_3S pellets hydrated between 5 s and 480 min in a 10-fold amount of water Ca/Si values varying between about 1.6 and 3.5. In samples hydrated with water–solid ratio (w/s) = 333 the Ca/Si ratio declined between 0 and 120 min from 3.0 to 1.3.

In assessing the above ESCA results the information depth of this method must be taken into consideration. This depth has been estimated to be somewhere between 2 and 10 nm [9,10,14–16], which is probably greater than the thickness of the hydrate layer formed in the initial stages of hydration. Thus it must be assumed that the actual CaO/SiO_2 ratio of the C-S-H phase was lower than that found experimentally, until the contribution of the underlying nonhydrated C_3S became negligible due to a gradually increasing thickness of the hydrate layer.

As to the amount of C_3S undergoing hydration in the preinduction period, data published in the literature vary greatly. Based on their ESCA analysis results Regourd et al. [14] estimated the thickness of the primary layer to be 0.8 nm and that of the secondary layer after 15 min of hydration to be 6 nm. In related work Jawed et al. [10] and Menetrier et al. [11] measured the depth of the hydrate layer formed in the hydration of β-C_2S by progressively sputtering the surface with an argon ion beam. They found a value of 5 nm after 15 s and a value of 15 nm after 6 h of hydration.

In studies on large single crystals of C_3S Ings et al. [17] estimated the thickness of the formed hydrate layer from SEM micrographs and found average values of approximately 0.5 and 5 μm after 5 and 30 min, respectively.

Brown et al. [3] estimated the progress of hydration from the concentrations of Ca^{2+} in the liquid phase and found for suspensions with water–solid ratios between 0.7 and 20 after 5-min degrees of hydration between about 0.2% and 1.0%, which corresponds to hydrate layers about 1- to 5-nm thick. Based on similar experiments Trettin and Wiecker [5] estimated the thickness of the hydrate layer at the end of the preinduction period to be a few monolayers.

In our own work [8] we estimated the degree of hydration by X-ray diffraction and found for the beginning of the dormant period a value of about 1–2%, which corresponds to a depth of attack of about 10 to 20 nm.

In experiments whose results are presented within the present paper, the studied C_3S samples were allowed to hydrate in diluted water suspensions to prevent an oversaturation of the liquid phase with respect to $Ca(OH)_2$ and a possible simultaneous precipitation of this compound on the studied surface, which may have distorted the obtained results. The hydration of C_3S was performed both at ambient ($T = 20$ °C) and elevated ($T = 60$ °C) temperatures. To study the effect of accelerating and retarding additives on the hydration process, C_3S was allowed to hydrate also in NaCl and sucrose solutions, in addition to plain water.

2. Experimental

Pure C_3S (300 ± 1 mg), fraction 63–90 μm, was suspended in 3 g (w/s = 10), 30 g (w/s = 100), 100 g (w/s = 333) and 200 g (w/s = 666) of deionized water, or in a 3% solution of NaCl, or in a 0.7% solution of sucrose ($C_{12}H_{22}O_{11}$). Suspensions to be hydrated at ambient temperature were placed into polyethylene bottles that were kept rotating during the whole time of hydration. In a parallel series, identical suspensions were kept in a water bath at 60 °C and were stirred magnetically. At the end of the hydration time the suspensions were filtered rapidly through a glass filter and washed at the filter first with acetone and then with diethyl ether. Finally, the material was placed into an electric oven kept at 50 °C to remove residual traces of the solvent. Samples produced this way were submitted to SNMS studies in a way as described in part I of this paper. In supplementary measurements, DTA analyses were made to be sure that no free calcium hydroxide was present in the studied samples.

3. Results

Figs. 1–8 and 10) show the Ca/Si ratio depth profiles of C_3S samples that were allowed to hydrate at different water–solid ratios and at different temperatures for different periods of time. In all instances, the individual lines indicate the Ca/Si atomic ratio within the material as function of the distance from the water–solid interface.

3.1. Hydration in plain water at 20 °C

The Ca/Si ratio depth profiles found in samples that hydrated at 20 °C are shown in Figs. 1–4. In samples that hydrated with water–solid ratios between 100 and 666 a distinct lowering of the Ca/Si ratio in the surface region of the material was observed starting already at very short hydration times. The drop in the Ca/Si ratio became smaller with increasing distance from the surface and a value corresponding to that of the nonhydrated C_3S was found in a depth of about 80 nm. The overall extent of the reduction of the Ca/Si ratio tended to be increased with increasing water–solid ratio. Changes that developed during the first minute after contact with water persisted virtually unaltered for the next 20–30 min of hydration. Later on the Ca/Si ratio in the immediate vicinity to the surface continued to decline even further and attained eventually a value close to, or only moderately above 1.0. The increase of the Ca/Si ratio with the distance from the surface became gradually more and more moderate and the region in which this ratio stayed below 3.0 became extended. Within less than 90 min the Ca/Si ratio stayed below 3.0 in the whole region under study, i.e., 550 nm.

In samples that were allowed to hydrate at w/s = 10 the changes taking place at shorter hydration time were inconclusive. A distinct reduction of the Ca/Si ratio even within the region close to the surface became obvious only after about 90 min of hydration. The overall thickness of the region with Ca/Si below 3 did not exceed in these samples 200–300 nm even after 240 min of hydration.

3.2. Hydration in plain water at 60 °C

The Ca/Si ratio depth profiles of samples hydrated at elevated temperature are shown in Figs. 5–7. Just as at 20 °C, the hydration process started with a rapid development of a surface region having a reduced Ca/Si ratio. A ratio corresponding to that of nonhydrated C_3S was reached in a depth of about 100–150 nm. The subsequent dormant period became shortened to less than 10 min and was followed by a period in which the rate of hydration was accelerated, as compared to that taking place at ambient temperature. Also here, the ultimate Ca/Si ratio within the formed hydrate layer was close to, or only slightly above 1.0.

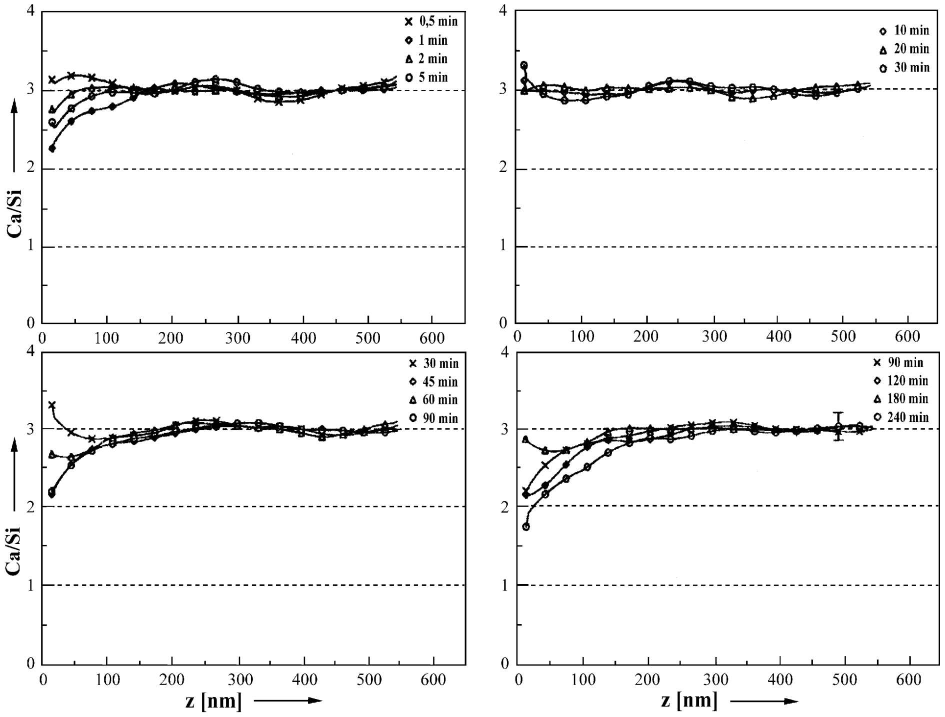

Fig. 1. Ca/Si ratio depth profiles in hydrated C_3S after different hydration times. Hydration temperature 20 °C, w/s = 10.

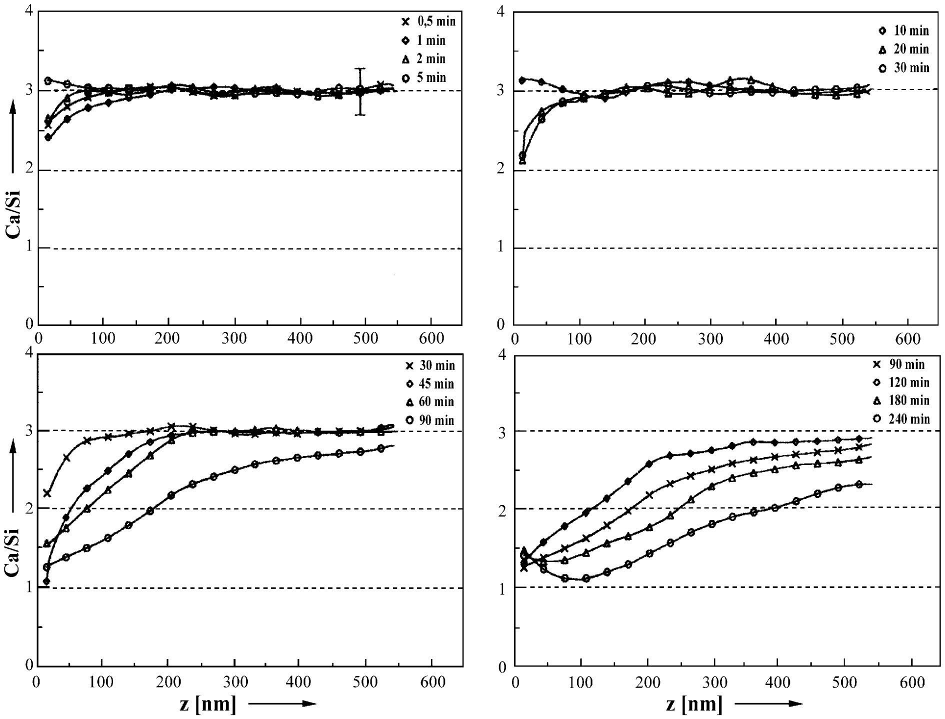

Fig. 2. Ca/Si ratio depth profiles in hydrated C_3S after different hydration times. Hydration temperature 20 °C, w/s = 100.

3.3. Hydration in the presence of NaCl

Fig. 8 shows the Ca/Si ratio depth profiles of C_3S samples that were allowed to hydrate at 20 °C in a 3% NaCl solution, rather than in plain water, at a water–solid ratio of 333. It appears that within the first 240 min the overall characteristics of the hydration process, as well as its kinetics, were not altered significantly by the presence of

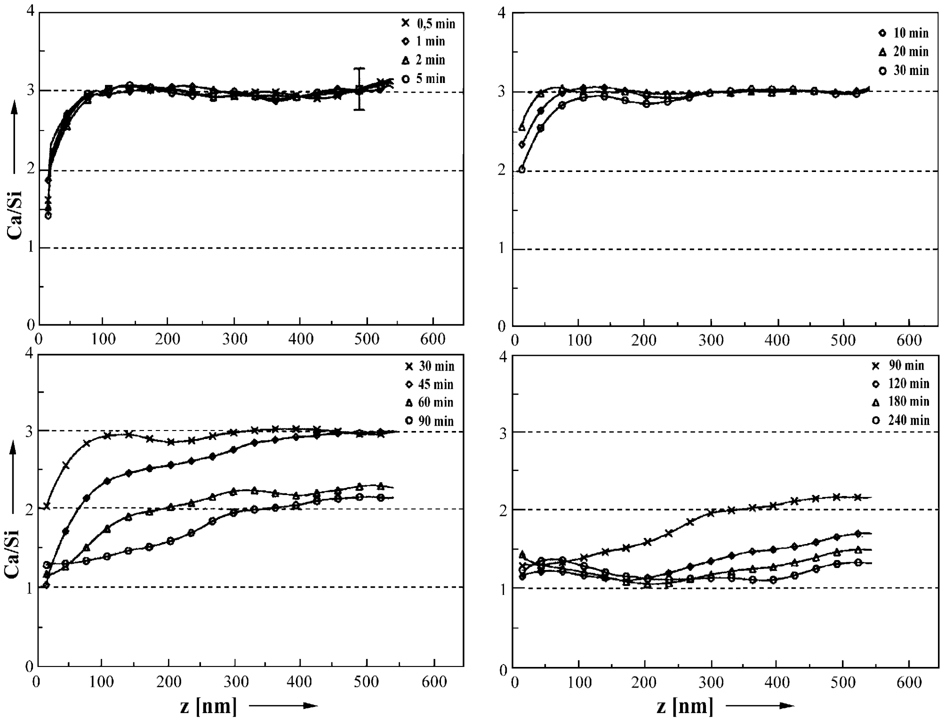

Fig. 3. Ca/Si ratio depth profiles in hydrated C_3S after different hydration times. Hydration temperature 20 °C, w/s = 333.

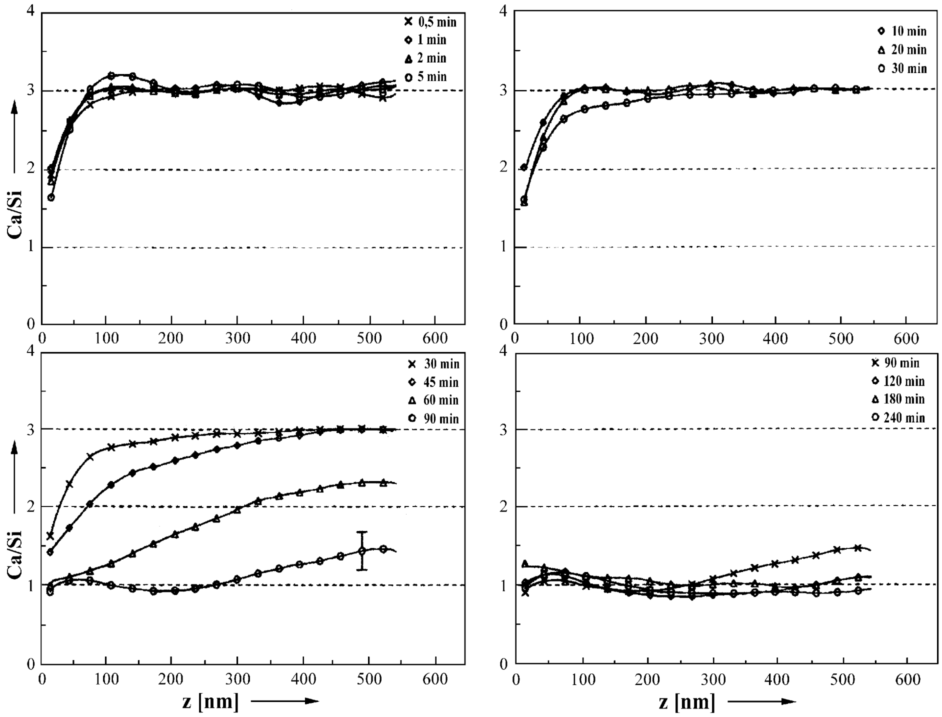

Fig. 4. Ca/Si ratio depth profiles in hydrated C_3S after different hydration times. Hydration temperature 20 °C, w/s = 666.

NaCl in the solution. Analogous results were also obtained in the study of samples hydrated at water–solid ratios of 100 and 666.

Fig. 9 shows the intensity ratio I_{Na}/I_{Ca} as a function of the distance from the surface for samples that hydrated for different lengths of time in a 3% NaCl solution at a water/

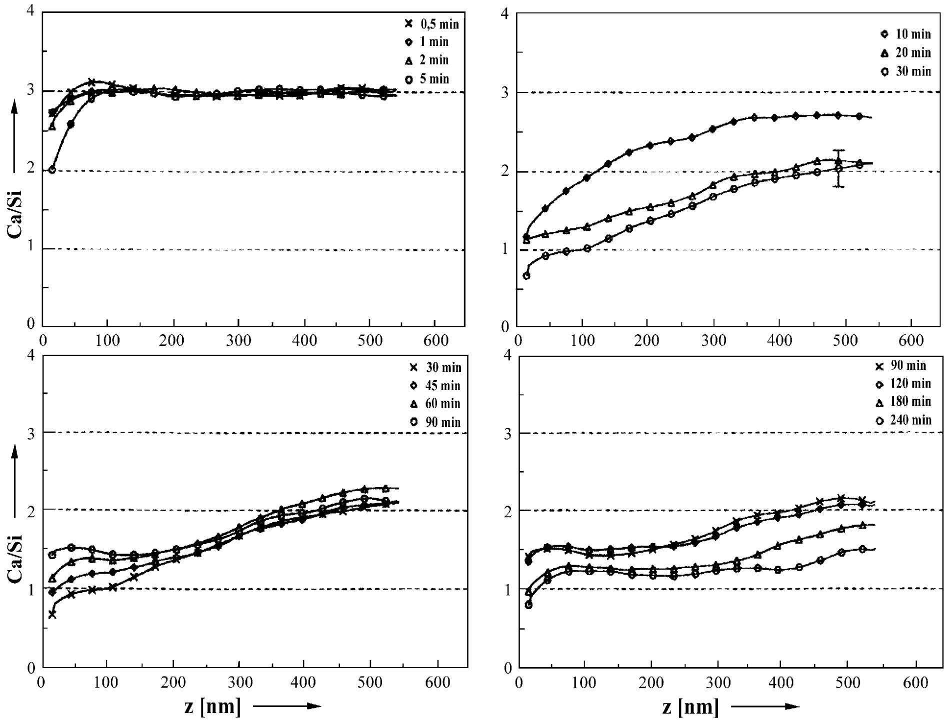

Fig. 5. Ca/Si ratio depth profiles in hydrated C_3S after different hydration times. Hydration temperature 60 °C, w/s = 100.

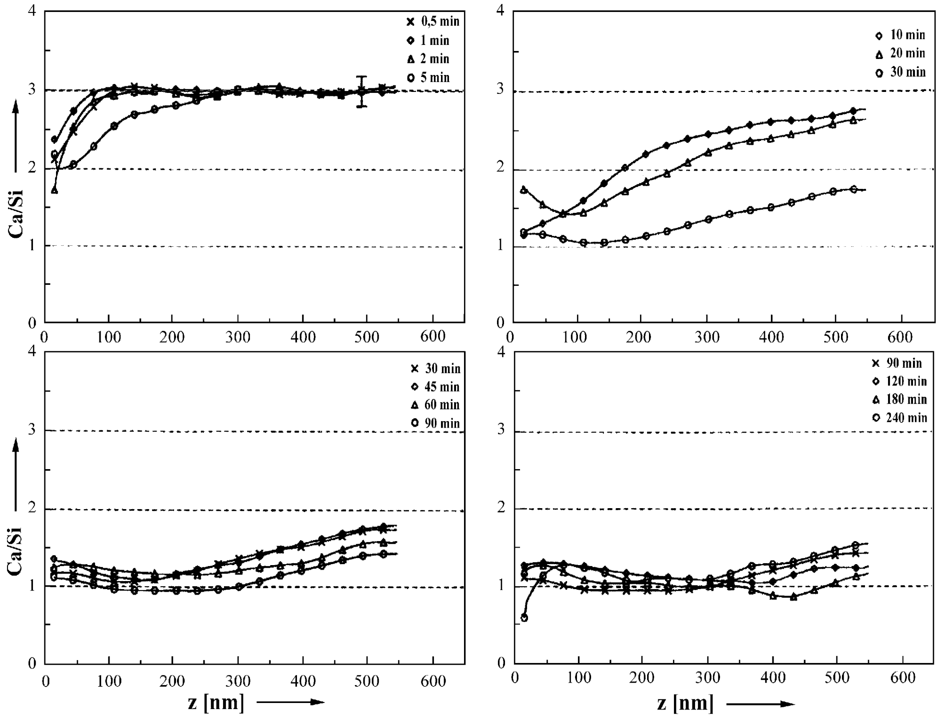

Fig. 6. Ca/Si ratio depth profiles in hydrated C_3S after different hydration times. Hydration temperature 60 °C, w/s = 333.

solid ratio of 333. It may be seen that this ratio generally declined with increasing distance from the surface, indicating the presence of declining amounts of Na^+ in the hydrated material. A comparison of depth profile curves obtained in samples that hydrated for different lengths of time indicates that at equal depths the Na^+ content initially declined moderately, to increase at longer hydration times. A similar trend was observed also in samples that were

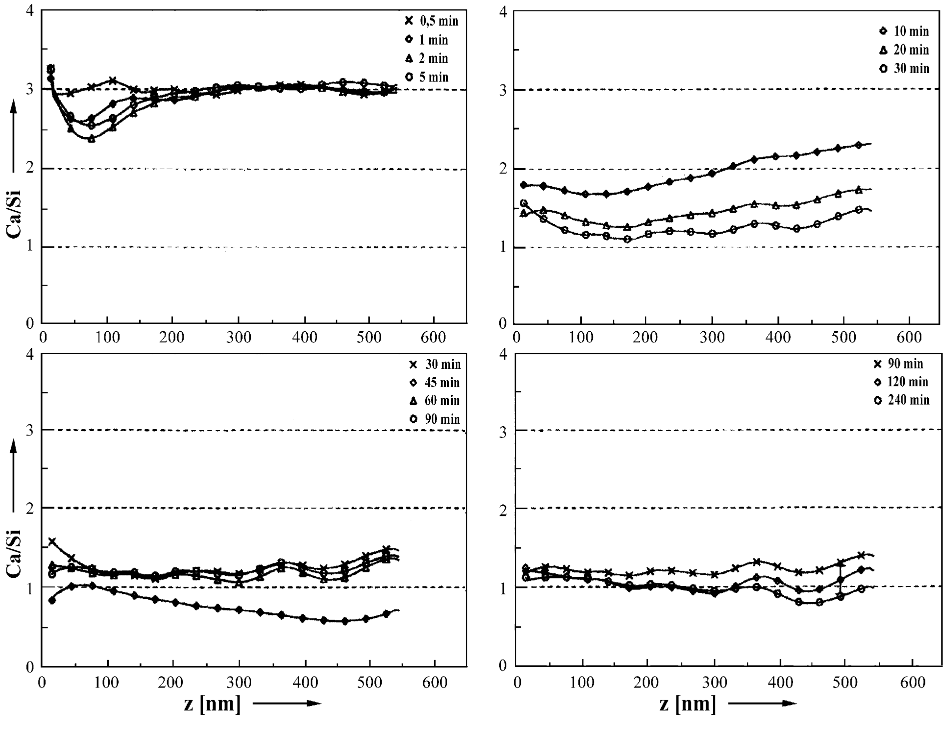

Fig. 7. Ca/Si ratio depth profiles in hydrated C_3S after different hydration times. Hydration temperature 60 °C, w/s = 666.

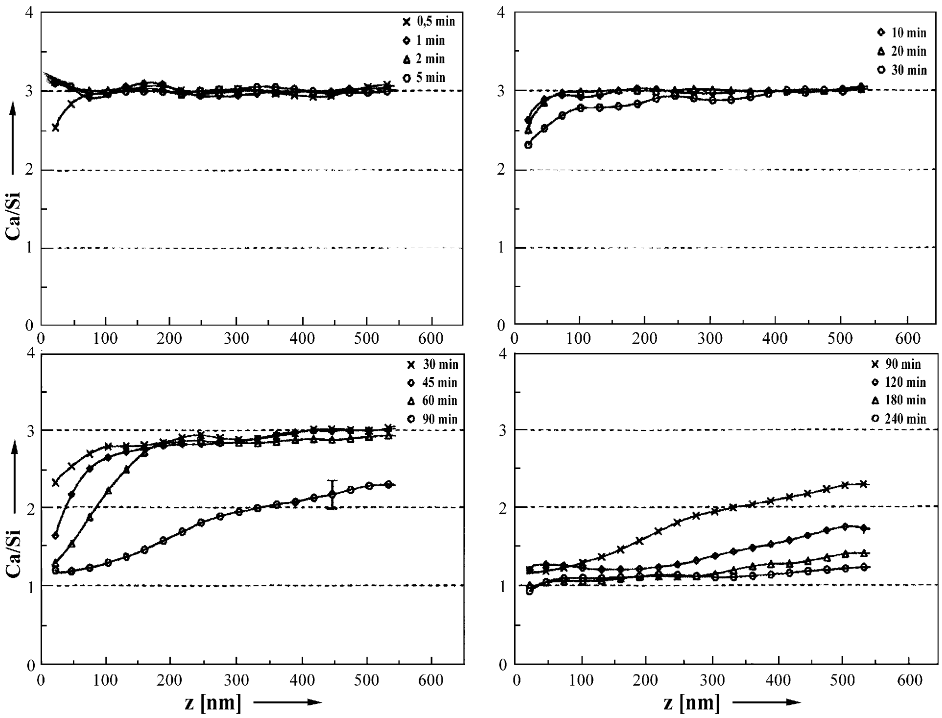

Fig. 8. Ca/Si ratio depth profiles in C_3S samples that were allowed to hydrate in a 3% NaCl solution for different hydration times. Hydration temperature 20 °C, w/s = 333.

allowed to hydrate at w/s = 100 and 666. The presence of Cl in the hydrated material was also observed, but the intensity of the pertinent SNMS signal was too weak and fluctuated too much to be suitable for a quantitative evaluation.

3.4. Hydration in the presence of sucrose

Fig. 10 show the Ca/Si ratio depth profiles of C_3S samples that were allowed to hydrate at 20 °C in a 0.7%

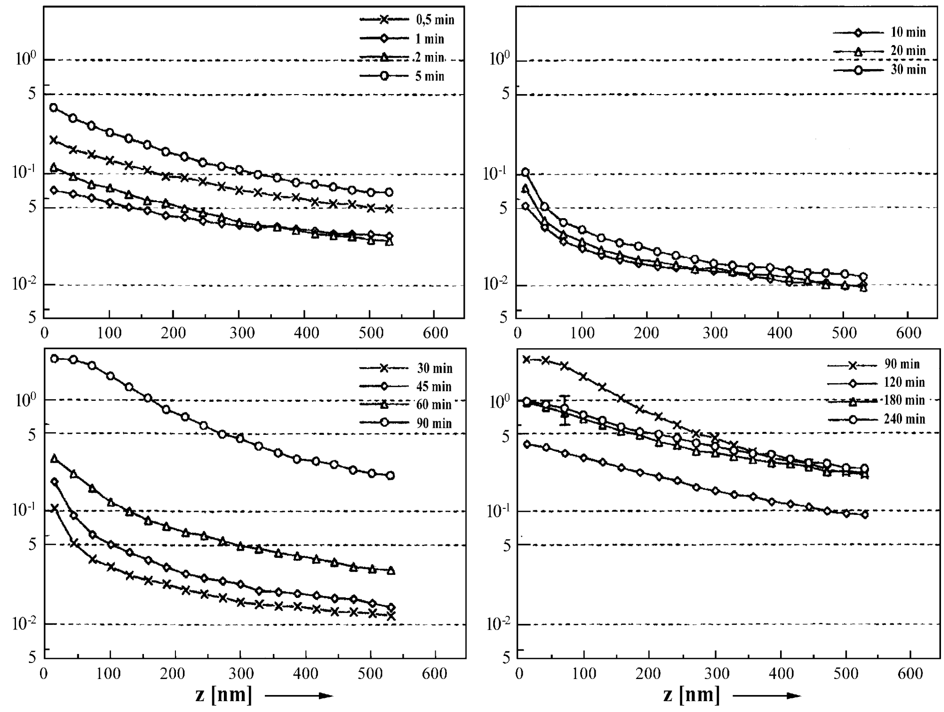

Fig. 9. I_{Na}/I_{Ca} ratio depth profiles in C_3S samples that were allowed to hydrate in a 3% NaCl solution for different hydration times. Hydration temperature 20 °C, w/s = 333.

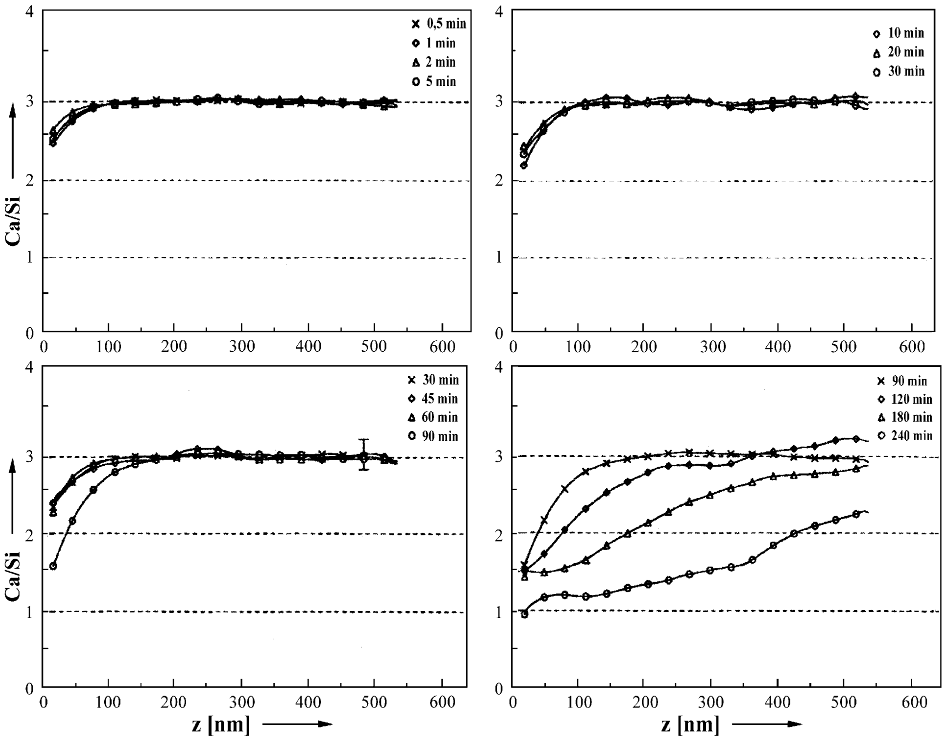

Fig. 10. Ca/Si ratio depth profile in C_3S samples that were allowed to hydrate in a 0.7% solution of sucrose for different lengths of time, Hydration temperature 20 °C, w/s = 333.

solution of sucrose at a water–solid ratio of 333. Also here, the overall characteristics of the hydration process did not differ significantly from that seen in the hydration in plain water; however, the hydration reaction became significantly slowed down.

4. Discussion

The obtained results confirmed earlier observations of a very fast initial hydration of C_3S right after contact with water (preinduction period), followed by an "induction" period (called also "dormant period") in which the hydration process virtually stopped for a certain length of time, to continue afterwards with a relatively high speed.

As to the stoichiometry of the formed C-S-H phase, the obtained data in essence confirmed previous results, according to which the CaO/SiO_2 ratio within the C-S-H phase formed in the hydration process is less than 3.0. However, as the employed method has an information depth of less than 1 nm, it was also possible to study the distribution of the CaO/SiO_2 ratio within the existing hydrated material, in addition to determining only the average CaO/SiO_2 value. The obtained data indicate that—at least transitionally—the hydrate layer formed at the surface of a C_3S particle does not possess a constant CaO/SiO_2 ratio within its whole volume. In all our measurements, it was observed that this value increased with increasing distance from the water–solid interface, until a Ca/Si ratio corresponding to the original nonhydrated C_3S was reached. It was also found that at a given distance from the liquid–solid interface the existing CaO/SiO_2 does not stay constant, but decreases as the hydration progresses. Such finding indicates the existence of a Ca^{2+} ion leaching process taking place in the material.

The CaO/SiO_2 ratio of the C-S-H phase found in our experiments after long enough hydration times was significantly lower than reported by other investigators, i.e., only a little above 1.0. The development of a C-S-H phase with such a low bound CaO content may have been due to the very high water–solid ratios employed in our experiments, at which the $Ca(OH)_2$ concentration in the liquid phase did not reach even its saturation level. It remains also uncertain whether, after a complete hydration, this extremely low Ca/Si ratio does exist in the whole volume of the original C_3S particle or just in a region adjacent to the surface.

Increased temperature and additions of calcium chloride or sucrose to the liquid phase did affect the overall characteristics of the hydration process and the CaO/SiO_2 ratio of the formed C-S-H phase only insignificantly, but the kinetics of the reaction was affected markedly in the case of increased temperature and sucrose addition. As the CaO/SiO_2 ratio of the C-S-H phase is known to be always below 3.0 the region in which hydration already had taken place may be distinguished from that of the nonhydrated C_3S on the basis of this ratio. In Table 1, the thickness of the hydrate layer formed after different hydration times is summarized. It is apparent that the hydration reaction became accelerated to a significant degree in samples hydrated at elevated

Table 1
Thickness of hydrate layer formed after different hydration times (nanometers)

	w/s						
Hydration time (min)	10	100	333	666	333, NaCl	333, sucrose	333, 60 °C
< 5	75	70	70	70	55	70	235
10	–	75	75	70	55	75	> 500
20	–	–	–	75	60	75	
30	–	90	100	200	215	75	
45	100	170	390	375	215	75	
60	100	205	>500	>500	230	75	
90	140	>500			>500	140	
240	290					>500	

temperature and was noticeably retarded by the addition of sucrose, whereas calcium chloride had only little effect on the progress of hydration.

In assessing data shown in Table 1 one has to take into consideration that the measurements were performed on nearly spherical C_3S particles, rather than on flat surfaces, and the rate of abrasion caused by sputtering was determined using nonhydrated C_3S, rather than a hydrated material, in which this rate may not be fully identical. Under these conditions, the data shown on the thickness of the hydrate layer must be considered to be only approximate.

Our measurements also indicated an incorporation of Na^+ and Cl^- ions into the C-S-H phase if NaCl had been dissolved in the mixing water. It is remarkable that—just as in the case of the CaO/SiO_2 ratio—the concentration of both the Na^+ and Cl^- ions did not stay constant within the whole hydrate layer but varied depending on the distance from the existing water–solid interface.

As already stated in part I of this paper, the SNMS method is not suitable for determining directly the amount of water bound within the formed C-S-H phase. It is remarkable, however, that in our tests on hydrated samples we observed consistently a gradual increase of the intensity of the signals belonging to Ca and Si in the course of measurement. In our view, such increase may indicate a gradually declining content of bound water in the formed C-S-H phase with increasing distance from the surface. It is also possible, however, that a certain reduction of the bound water content in the C-S-H phase may occur in the course of measurement due to a warming of the material.

5. Conclusions

The hydration of C_3S is initiated by a rapid but short-lasting formation of a thin hydrate layer at the surface of the nonhydrated substrate; this initial period of fast hydration is followed by a dormant period in which the hydration progresses very slowly and a period of a renewed accelerated hydration.

The stoichiometry of the C-S-H phase constituting the hydrate layer formed at the surface of C_3S is not uniform; its CaO/SiO_2 ratio increases with increasing distance from the water/hydrate interface and—at a constant distance—declines as the hydration progresses.

An increase of temperature accelerates the hydration of C_3S, but alters only insignificantly the overall characteristics of this process.

The presence of NaCl alters barely the kinetics of C_3S hydration. At the same time both Na^+ and Cl^- become incorporated into the formed C-S-H phase in amounts declining with the distance from the water/hydrate interface.

The presence of sucrose in the liquid phase retards the hydration of C_3S significantly, without altering noticeably the overall characteristics of the process.

References

[1] S. Cordes, I. Odler, Initial hydration of tricalcium, silicate as studied by secondary neutrals mass spectrometry (SNMS): I. Sample preparation and calibration, Cem. Concr. Res. 32 (2002) 1071–1075.

[2] I. Jawed, J. Skalny, Surface phenomena during tricalcium silicate hydration, J. Colloid Interface Sci. 85 (1982) 235–243.

[3] P.W. Brown, E. Franz, G. Frohnsdorff, H.F.W. Taylor, Analysis of the aqueous phase during early C_3S hydration, Cem. Concr. Res. 14 (1984) 257–262.

[4] H.F.W. Taylor, Proposed structure of calcium silicate hydrate gel, J. Am. Ceram. Soc. 69 (1986) 464–467.

[5] R. Trettin, W. Wieker, Zur Hydratation von Trikalziumsilikat: I. Ursachen der Induktionsperiode, Silikattechnik 37 (1986) 75–78.

[6] S. Brunauer, D.L. Kantro, The hydration of tricalcium silicate and β-dicalcium silicate from 5 °C to 50 °C, in: H.F.W. Taylor (Ed.), The Chemistry of Cement, Academic Press, New York, 1964, pp. 287–309 (Chap. 7).

[7] N. Kawada, A. Nemoto, Calciumsilikate im fruhen Verlauf der Hydratation, Zement–Kalk–Gips 20 (1967) 65–71.

[8] I. Odler, H. Dorr, Early hydration of tricalcium silicate: I. Kinetics of the hydration process and the stoichiometry of the hydration products, Cem. Concr. Res. 9 (1979) 239–248.

[9] D. Menetrier, I. Jawed, T.S. Sun, J. Skalny, ESCA and SEM studies on early C_3S hydration, Cem. Concr. Res. 9 (1979) 472–482.

[10] I. Jawed, D. Menetrier, J. Skalny, E.E. Lachowski, K. Mohan, H.F.W. Taylor, Hydration studies on cement and silicates, World Cem. Technol., (1981) 124–137.

[11] D. Menetrier, I. Jawed, T.S. Sun, J. Skalny, Surface studies on hydrated β-C_2S, Cem. Concr. Res. 10 (1980) 425–432.

[12] R. Trettin, G. Oliew, C. Stadelmann, W. Wieker, Very early hydration of dicalcium silicate-polymorphs, Cem. Concr. Res. 21 (1991) 757–764.

[13] J.-H. Thomassin, M. Regourd, P. Baillif, J.-C. Touray, Etude de l'hydratation initiale du silicate tricalcique par spectrometrie de photoselectrons, C. R. Acad. Sci., Paris, Ser. C 288 (3) (1979) 93–95.

[14] M. Regourd, J.-H. Thomassin, P. Balliff, J.-C. Touray, Study on the early hydration of Ca_3SiO_5 by X-ray photoelectron spectroscopy, Cem. Concr. Res. 10 (1980) 223–230.

[15] C. Stadelmann, R. Trettin, W. Wieker, M. Ramm, Studies on the hydration of Ca_3SiO_5 by ESCA and krypton adsorption measurements, Cem. Concr. Res. 15 (1985) 145–150.

[16] F.U. Hillebrecht, E. Kisker, Festkűrper, Bergmann, E. Schaefer (Eds.), Lehrbuch der Experimentalphysik Band 6, W. Raith + Walter de Gruyter, Berlin, 1992, p. 259.

[17] J.B. Ings, P.W. Brown, G. Frohnsdorff, Early hydration of large single crystals of tricalcium silicate, Cem. Concr. Res. 13 (1983) 843–848.