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Clinker mineral hydration at reduced relative humidities

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Abstract

Vapour phase hydration of pure cement clinker minerals at reduced relative humidities is described. This is relevant to modern high performance concrete that may self-desiccate during hydration and is also relevant to the quality of the cement during storage. Both theoretical considerations and experimental data are presented showing that C_3A can hydrate at lower humidities than either C_3S or C_2S. It is suggested that the initiation of hydration during exposure to water vapour is nucleation controlled. When C_3A hydrates at low humidity, the characteristic hydration product is C_3AH_6, hydrogarnet.

Keywords: Humidity; Hydration; Hydration products; SEM; Clinker

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1. Introduction

The pastes of modern high performance concrete normally have a low water-cement (w/c) ratio, 0.20–0.35, and contain mineral additions such as silica fume and admixtures such as superplasticizers. Such pastes do not contain enough water for the unrestricted hydration of the cement, and will therefore self-desiccate [1]; the internal relative humidity (RH) in the paste is lowered as loosely bound water is consumed by reaction. The cement hydration reactions are significantly hampered as the activity of the water decreases until at sufficiently low activities, as marked by low relative humidities, hydration activity ceases.

A related phenomenon of practical importance is the tendency for cement to hydrate during grinding, transport, and storage. During these processes cement is exposed to water vapour with which it reacts. This is known as prehydration and may affect subsequent setting and strength development of the concretes [2].

In order to understand and predict cement paste and concrete properties, knowledge of the mechanisms of cement hydration is essential. However, current knowledge of cement hydration at reduced relative humidities is inadequate for this purpose. Experiments are presented in this paper that elucidate this subject. This paper is based on a report [3] that gives a more detailed treatment.

2. Methods

2.1. Materials

Phase pure cement clinker minerals, C_3S (triclinic), β-C_2S (monoclinic), and C_3A (cubic), were produced by heating mixtures of constituent oxides or carbonates. The β-C_2S was stabilized by addition of 0.4 mol% H_3BO_3. After formation, the clinker minerals were ground in a ball mill to a specific surface area of approximately 370 m^2/kg (Rigden). According to quantitative X-ray powder diffraction (QXRD) and nuclear magnetic resonance (NMR) the phase purity of the clinker minerals was at least 99%; the detection limits for both NMR and QXRD are approximately 0.5 to 1%.

2.2. Water vapour exposure

The cement clinker minerals were exposed to different relative humidities for different times. Approximately 2 g of dry clinker mineral, C_3S, C_2S, or C_3A, was placed in a shallow layer on a Ø 43-mm dish and transferred to a humidstat with a controlled RH at a constant temperature. The exposure time ranged from 15 min to 1 year. Thereafter, physically held water was removed from the sample and the degree of hydration was calculated based on the measured weight changes.

The RH was maintained by saturated salt solutions placed in the base of the humidstats. The samples were ex-

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posed at four different temperatures. These were measured with a calibrated thermometer as: 9.4, 19.7, 31.5, and 39.9°C. In the remainder of this paper these exposure temperatures are referred to as 10, 20, 30, and 40°C. Before exposure to water vapour the samples were kept dry at the exposure temperature for 1 day. This ensured initial thermal equilibrium and prevented condensation of water vapour on the samples due to temperature differences.

Two different methods for water vapour exposure were used: (1) exposure at atmospheric pressure and (2) exposure in pure water vapour (i.e., the humidstat was evacuated at the start of the experiment and subsequently allowed to equilibrate). An adsorption equilibrium between the clinker minerals and the water vapour is attained faster when the humidstat is evacuated at the start of the experiment. At atmospheric pressure, measurements at exposure times shorter than a few days are partly disturbed due to lack of adsorption equilibrium.

After exposure to water vapour for a certain time cement clinker hydration was stopped, and physically held water was removed. Two different methods were used: (1) soaking in acetone for approximately 1 hour followed by heating at 105°C for 1 h, and (2) vacuum drying with a rotary pump for 1 h. During vacuum drying the final pressure was approximately 0.1 mbar (~0.5% RH). Heating for 1 h at 105°C after vacuum drying did lead to an additional water loss. However, the calculated degree of hydration was only changed typically by 1% upon heating at 105°C. This indicates that the amount of water removed by the vacuum drying technique is approximately equivalent to drying at 105°C.

2.3. X-ray diffraction

Selected samples of the clinker minerals hydrated in water vapour were examined by QXRD. In addition, several hydrated C_3S and C_2S pastes ($w/c = 0.5$) were examined. These are referred to as hydration at ~100% RH. After drying at 105°C the hydrated clinker mineral was spiked with CaF_2 and X-ray diffraction spectra were measured in the interval 10–60°. Distributions of the unhydrated clinker and crystalline hydration products obtained were determined based on multiphase Rietvelt quantification. No significant quantities of carbonated phases were detected.

2.4. Electron microscopy

Samples of C_3S, C_2S, and C_3A hydrated at different lengths of time at different relative humidities were examined by both transmission electron microscopy (TEM) and scanning electron microscopy (SEM) on a Jeol 2000EX Temscan electron (Jeol, Akishima, Japan) microscope equipped with a Link Systems AN10/85S EDX analyser (Link Systems, High Wycombe, England). Two hydrated C_3S and C_2S pastes ($w/c = 0.5$) were also examined. Specimens were prepared by dispersing samples of selected powders in 2-propanol and drying a drop of the resulting suspensions on copper grids that had carbon support films. TEM and SEM micrographs were obtained from the same particles. Because the specimens were uncoated in order to give good TEM images, there was some degradation of the SEM image quality.

3. Results and discussion

Table 1 shows the influence of the RH on the hydration of the investigated C_3S, C_2S, and C_3A clinker minerals. The degree of hydration (α) in Table 1 is calculated based on the measured amount of chemically bound water, as shown in Eq. (1):

$$\alpha = \frac{W_{chem.w.}}{W_{max.chem.w.}} = \frac{W_{hyd.cl.} - 1 - W_{phys.w.}}{W_{max.chem.w.}} \qquad (1)$$

All weights in this formula are relative to the ignited clinker weight: g/g ignited clinker. $W_{hyd.cl.}$ is the weight of hydrated clinker mineral, $W_{chem.w.}$ is the weight of chemically bound water, and $W_{phys.w}$ is the weight of physically bound water. Physically bound water is defined as water lost during drying to constant weight at 105°C, and chemically bound water is defined as water held above this temperature. $W_{max.chem.w.}$ is the amount of chemically bound water at complete hydration, $\alpha = 1$ [4], as seen in Eq. (2):

$$W_{max.chem.w.} = \begin{cases} C_3S = 0.24\ g/g \\ C_2S = 0.22\ g/g \\ C_3A = 0.40\ g/g \end{cases} \qquad (2)$$

The degrees of hydration presented in Table 1 are based on the above literature values for $W_{max.chem.w.}$. However, the

Table 1
Degrees of hydration (%) of C_3S, C_2S, and C_3A after exposure to different relative humidities at 20°C

	Time (days)	Exposure RH (%)						
		23	43	66	75	85	95	98
C_3S	1	0	0	0	0	0	0	0
	3	0	0	0	0	0	0	0
	7	0	0	0	0	0	0	1
	14	0	0	1	0	0	1	12
	30	0	0	1	1	1	4	29*
	90	0	0	2	1	2	33*	36
	365	0	1	3	1	4	72	67
C_2S	1	0	0	0	0	0	0	0
	3	0	0	0	0	0	−0	0
	7	0	−2	1	0	0	0	0
	14	0	0	0	0	0	0	1
	30	0	0	1	0	2	1	5
	90	0	0	1	0	0	1	15
	365	0	1	1	1	1	16	49
C_3A	1	0	0	0	0	2	6	8
	3	0	0	0	0	6	18	23*
	7	0	0	0	1	16	30*	36
	14	0	0	0	6	26	35	40
	30	0	0	1	18	28*	37	44
	90	0	0	3	24	33	41	48
	365	0	0	8	28*	45	52	61

*Studied by SEM.

literature values are determined for paste hydration. During gas phase hydration the RH is lower than 100% and hydration products formed under these conditions may differ from those formed during paste hydration. Consequently, the above literature values for the maximum amount of chemically bound water may not be applicable.

To examine this, 14 gas phase hydrated and three paste hydrated (w/c = 0.5) clinker mineral samples were examined by QXRD. From these measurements the amounts of $Ca(OH)_2$ produced and amounts of remaining clinker were determined. By comparison with the measured weight loss it was possible to calculate the amount of chemically bound water, $W_{max.chem.w.}$, of the gel solid. In addition, the molar C/S or C/A ratio of the gel solid was determined.

Crystalline C_3AH_6 was recognized as the major hydration product of C_3A. Some minor unidentified phases were observed by QXRD but none of the hydrated C_3A samples contained CH. The measurements did not indicate that RH influenced the hydration product of C_3A. A reaction equation for the gas phase hydration of C_3A is: $C_3A + 6H \rightarrow C_3AH_6$. In agreement with the required value for paste hydration, $W_{max.chem.w.}$, is 0.40.

On the other hand, the hydration products of C_3S and C_2S did change systematically with the exposure RH. For paste hydration (w/c = 0.5) or hydration close to 100% RH the measured molar C/S ratios of the C-S-H phase and $W_{max.chem.w.}$ values agreed with the literature values for normal paste hydration: approximately 1.7 and 0.23, respectively, are suggested as representative values in the literature [4]. However, when the exposure RH was lower the C/S ratio increased and the amount of chemically bound water decreased. For C_3S exposed for 3 months at 83% RH and 40°C, $W_{max.chem.w.}$ was measured as 0.12 and the C/S ratio was 3 [almost no $Ca(OH)_2$ was detected]. This unusual stoichiometry may be a natural consequence of hydration in water-deficient conditions.

Despite the indications from the QXRD examination, the above literature values for paste hydration were used for calculation of the degrees of hydration shown in Table 1. The values should not be taken as exact figures, but as indicators of the progress of hydration.

Some scatter is observed for the measurements in Table 1. From the experimental procedure, including weighing accuracy, it should be possible to measure the degree of hydration within ±1%, but some samples seem to deviate by at least 2% (c.f., C_2S, 7 days and 43% RH; also C_2S, 30 days and 85% RH). The reason for these deviations is not known.

Despite this, a number of conclusions are possible. The measurements presented in Table 1 show that the clinker minerals C_3S, C_2S, and C_3A have fundamentally different sensitivities to RH. C_2S hydration is hampered to a greater extent by decreased RH than C_3S hydration, which again is more sensitive than C_3A hydration. This observation agrees with thermodynamic calculations [5] and experimental results in the literature [2,6]. After 1 year of water vapour exposure at 20°C the limiting RH for hydration of the C_3S, C_2S, and C_3A seems to be approximately 85, 90, and 60%, respectively.

A slight hydration of both C_3S and C_2S is apparently observed at low relative humidities (e.g., 66% RH). However, this may be due to measuring inaccuracy or to a small amount of free CaO in the clinker mineral preparations: CaO is able to hydrate even at very low relative humidities.

In relation to Portland cement the results presented here should be interpreted with caution. The clinker minerals in a typical Portland cement contain foreign oxides incorporated in their structure [7]. Such impure clinker minerals may have somewhat different hydration properties than the "pure" clinker minerals examined in this project, containing ≤0.1 wt% total impurity in C_3S and C_3A. Even the type and amount of stabilizer used for forming β-C_2S is reported to affect the rate of hydration of the β-C_2S [8]. Furthermore, no interaction with other compounds normally present in Portland cement (e.g., gypsum) has been assessed.

Despite these reservations, the data are compared with those from cement by Powers [9] (Fig. 1). Powers stored portions of unhydrated cement at different relative humidities and measured the amount of chemically held water after 6 months of storage. From the figure it can be seen that the water take-up is significantly increased above 80% RH.

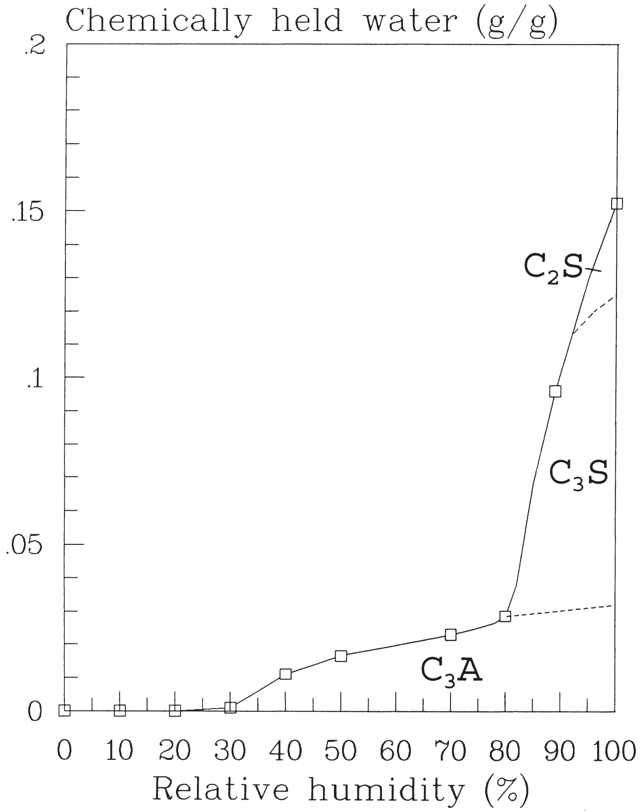

Fig. 1. Amounts of chemically bound water held by dry cement exposed to water vapor of different relative humidities for 6 months. Boxes are measurements by Powers [9]; dotted lines suggest results using data in the current paper.

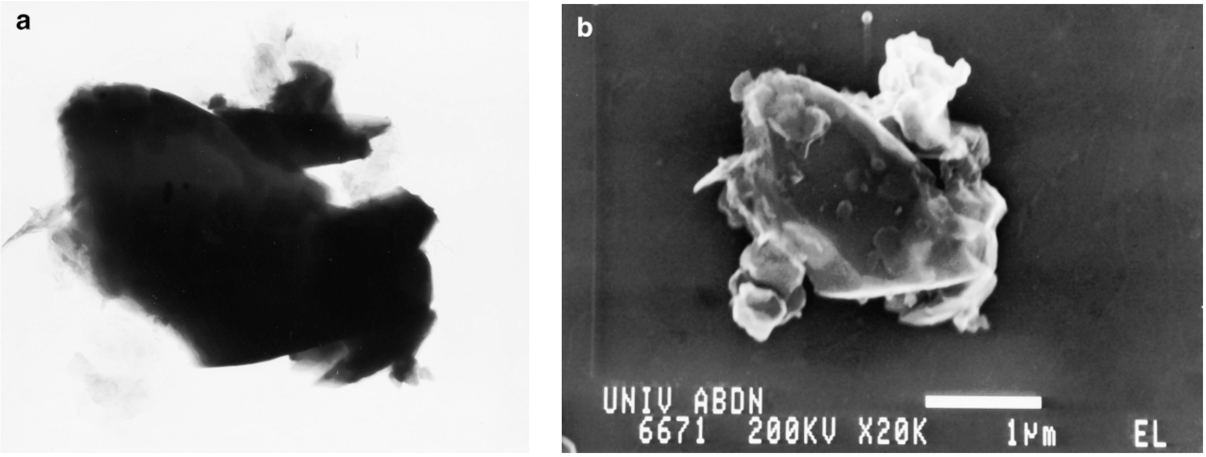

Fig. 2. TEM image (a) and SEM image (b) of C_3S hydrated 3 days at ~100% RH. This particle is completely unhydrated. Note some areas that are so thin they are almost invisible in the TEM micrograph are very prominent in the SEM image.

This may be due to hydration of the silicate clinker minerals, whereas the aluminate clinker minerals may be responsible for the hydration at lower relative humidities. In Fig. 1 the limiting RH for the hydration of the cement is lower than for the pure clinker minerals examined in this project. This may be a consequence of differences between pure clinker minerals and clinker phases in Portland cement, as well as the presence of gypsum, alkali sulfates, or other substances. Hydration of C_4AF, not included in the present study, may also play a role.

3.1. Electron microscopy

3.1.1. C_3S and C_2S

In all the samples studied here, both unhydrated and fully hydrated particles were present, as well as those with intermediate degrees of hydration. Fig. 2 shows a completely unhydrated particle from the sample aged 3 days at ~100% RH. Even the thin regions at the edges of the grain gave strong diffraction patterns corresponding to C_3S. Their identity was further confirmed by EDX analysis. Fig. 3 shows a particle from the same specimen that has a considerable degree of hydration. Thin foils of C-S-H adhere to a central core of C_3S. The SEM shows that the hydration products completely cover the underlying grain. These differences in hydration reactivity of single clinker grains may be caused by differences in, for example, crystal strain [10] or impurities. The loose packing and irregular shape of grains may play a role as well. This creates a mutiplicity of geometries, some of which are more favourable for condensation than others. In this view, grains at favourable sites may become fully hydrated while others, not at or close to a favourable site, remain unhydrated.

Although the spatial resolution of the EDX system is sufficient to analyse the C-S-H, the dimensions of the regions of hydration products are so small that the energy density required for a usable X-ray signal is such that severe dam-

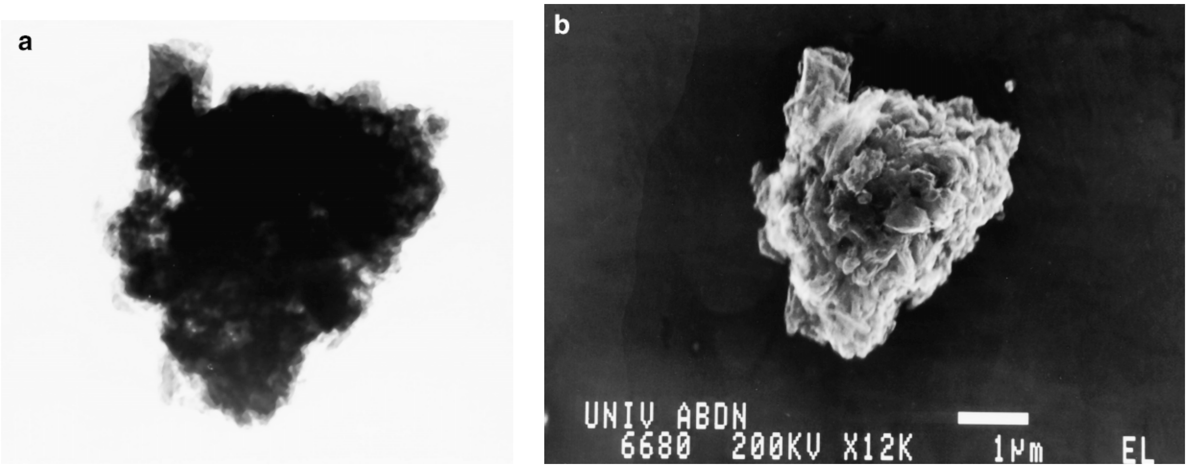

Fig. 3. TEM image (a) and SEM image (b) of C_3S particle hydrated 3 days at ~100% RH showing coating of hydration product.

age and compositional change occur during analysis. It was therefore not possible to obtain meaningful C/S ratios. The susceptibility to beam damage indicates the presence of much water in the hydration products [11]. At longer ages, there was no significant difference in the morphology of the hydration products. The hydration products of C_2S are morphologically similar to those of C_3S, although the degree of hydration was considerably lower.

3.1.2. C_3A

Four samples of C_3A hydrated for up to 1 year but with approximately the same degree of hydration were studied. As with the calcium silicates, the degree of hydration of individual particles varied from 0–100%. Fig. 4 shows micrographs of C_3A aged 7 days at 95% RH where clusters of C_3A crystals are bound together by hydration product. X-ray diffraction indicate that the hydration product is C_3AH_6, but the platelets observed here were much more susceptible to beam damage than normal C_3AH_6. In general crystallinity was lost as soon as observation began and, even under the mild conditions used, intumescence occurred, for example in the area circled in Fig. 4. For this reason EDX analysis was subject to severe calcium loss. This was the case at all ages studied.

3.2. Nucleation

In addition to the different sensitivities of the clinker minerals to the RH, Table 1 reveals another important feature; an induction period for the onset of hydration occurs. For example, 6% hydration is achieved after 14 days at 75% RH whereas 7 days exposure only leads to 1% hydration for C_3A.

This phenomenon may partly be caused by the exposure conditions. When a porous material is exposed to vapour an adsorption equilibrium is not established immediately. Different mechanisms will delay this process, such as diffusion of the vapour to reach the solid surface and dissipation of heat liberated by the adsorption process [12]. Typically, given the kinetic factors involved, diffusion is the dominating factor. The clinker minerals equilibrate much faster with the water vapour when the humidstat is evacuated at the start of the experiment; in pure water vapour transport is controlled by pressure differences whereas it takes place through molecular diffusion at atmospheric pressure. The sample load on the humidstats may cause a further delay of the water take-up as several samples were simultaneously exposed in the same humidstat for the measurements reported in Table 1. However, at long exposure times or low relative humidities the effects mentioned above diminish in significance.

The delayed hydration onset is probably an inherent feature of the hydration process; the presence of an induction period is a characteristic feature of reactions requiring nucleation. Experiments reported in the literature indicate that the onset of C_3S hydration in pastes is nucleation controlled [13,14]: addition of prehydrated C_3S or finely dispersed inert calcium carbonate may shorten the length of the induction period or increase the hydration rate. A further account of the mechanisms that may control the onset of hydration is given in a previous work [4].

Additional experiments were also performed in support of the above mechanism. From Table 1 it is seen that C_3A hydrates quite readily over a broad RH range, and for this reason C_3A was selected for these experiments. Whereas the experiments in Table 1 were performed at atmospheric pressure, the additional experiments were performed in pure water vapour (i.e., the humidstats were evacuated at the start of the experiment). Furthermore, each humidstat contained only one sample. This ensured that the onset of hydration was not significantly displaced due to a slow rate of adsorption.

The additional experiments with C_3A were also carried out at different relative humidities of 10, 20, 30, and 40°C. The results obtained at 20°C are plotted in Fig. 5. Each set of isothermal hydration curves has the same form with a well-defined dormant period followed by an acceleration of hydration.

Random fluctuations of the measurements can be observed. As an example, three different C_3A samples have

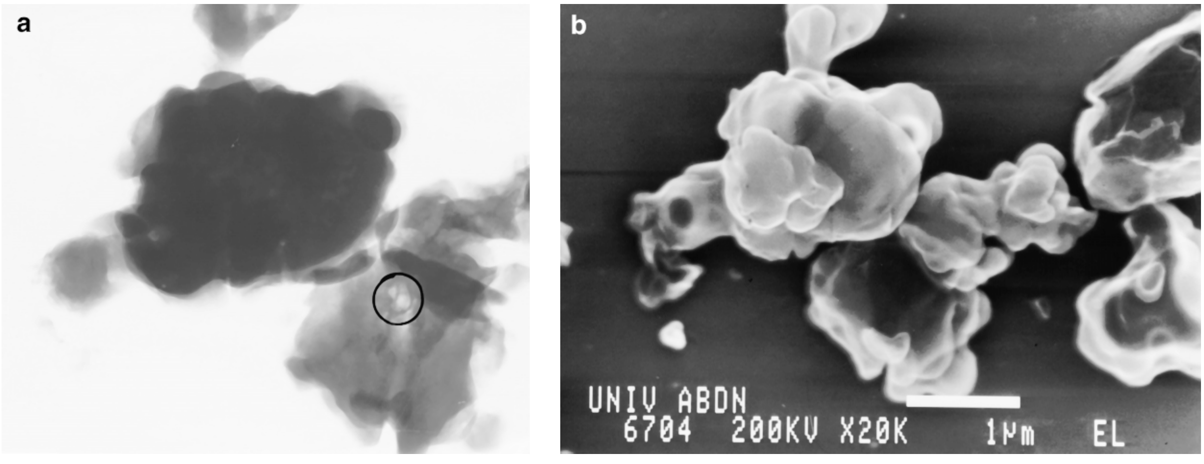

Fig. 4. TEM image (a) and SEM image (b) of C_3A hydrated 7 days at 95% RH. Note intumescence in circled area.

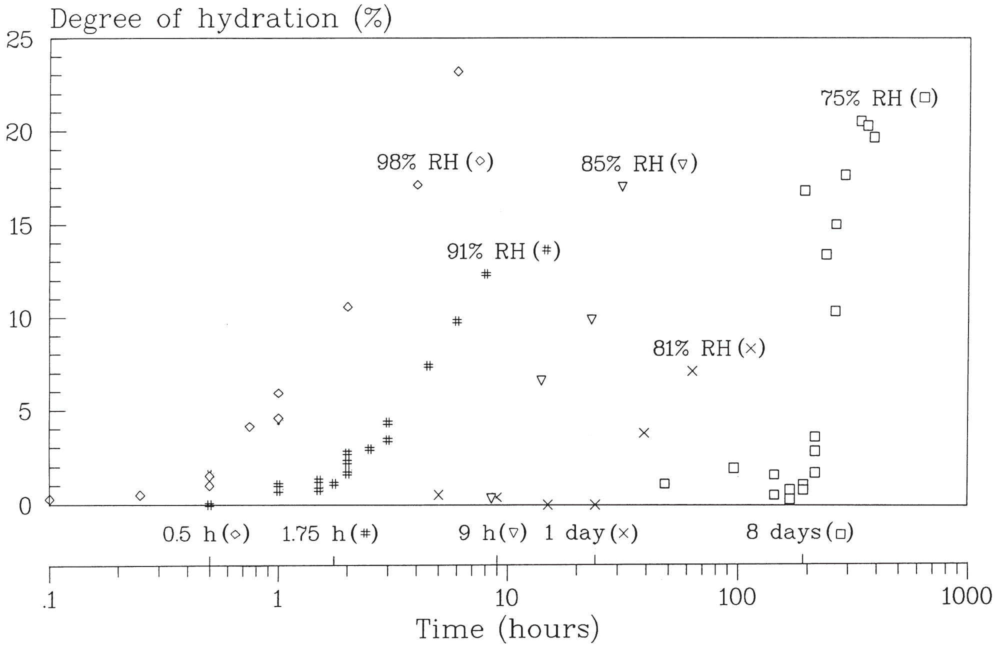

Fig. 5. Measured degrees of hydration (%) of C_3A after exposure to different relative humidities in pure water vapour. At each RH a well-defined dormant period occurs during which hydration is negligible. Suggested induction times are indicated on the time axis. Temperature: 20°C.

been measured after 8 days of exposure at 75% RH. For one of the samples 17% hydration is measured, whereas the two other samples were approximately 1% hydrated. After 11 days two different samples were 15 and 10% hydrated, respectively. The reason for this variability is not known. It may be due to experimental errors such as uncontrolled exposure conditions or the lack of thermal equilibrium at the onset of the experiments. However, it may also be the inherent feature of the hydration process at reduced relative humidities since nucleation is basically a statistically induced phenomenon caused by random fluctuations among the growing subcritical molecular clusters.

The observed induction times in Fig. 5 are not artefacts caused by the logarithmic time axis since they occur in equidistant time plots as well. The induction times found at the different temperatures and relative humidities are summarised in Fig. 6; a lower temperature or RH systematically increases the induction time.

To examine closer the above nucleation hypothesis, samples of C_3S, C_2S, or C_3A were slightly prehydrated at a high RH before they were transferred to lower relative humidities. Prehydrated clinker minerals will have plenty of existing growth sites (i.e., hydration will not have to pass through a nucleation stage). Unfortunately, these measurements were not conclusive. It was realized that the degree of accuracy for the measuring technique was insufficient to detect whether the hydration rate was increased by prehydration.

Another approach is to test whether the observed induction times presented in Fig. 6 are in agreement with nucleation theory. A thorough description of crystallization including nucleation is given by Mullin [15]. Based on nucleation rate and surface energy considerations, Mullin derives a formula to describe the duration of the nucleation controlled induction period, t_{ind}, of crystallization, as shown in Eq. (3):

$$\log[t_{\mathrm{ind}}] = k_1 + k_2 \cdot [\log(S)]^{-2} \qquad (3)$$

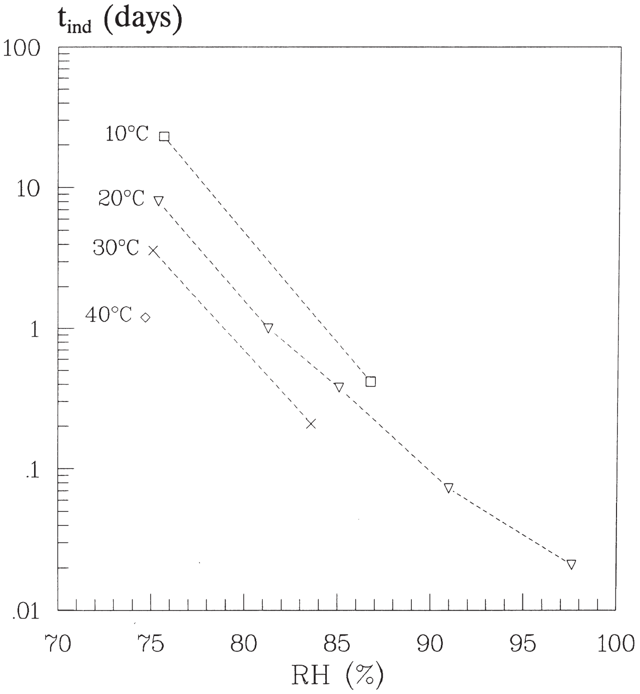

Fig. 6. Induction times for the hydration of C_3A when exposed to different relative humidities and temperatures.

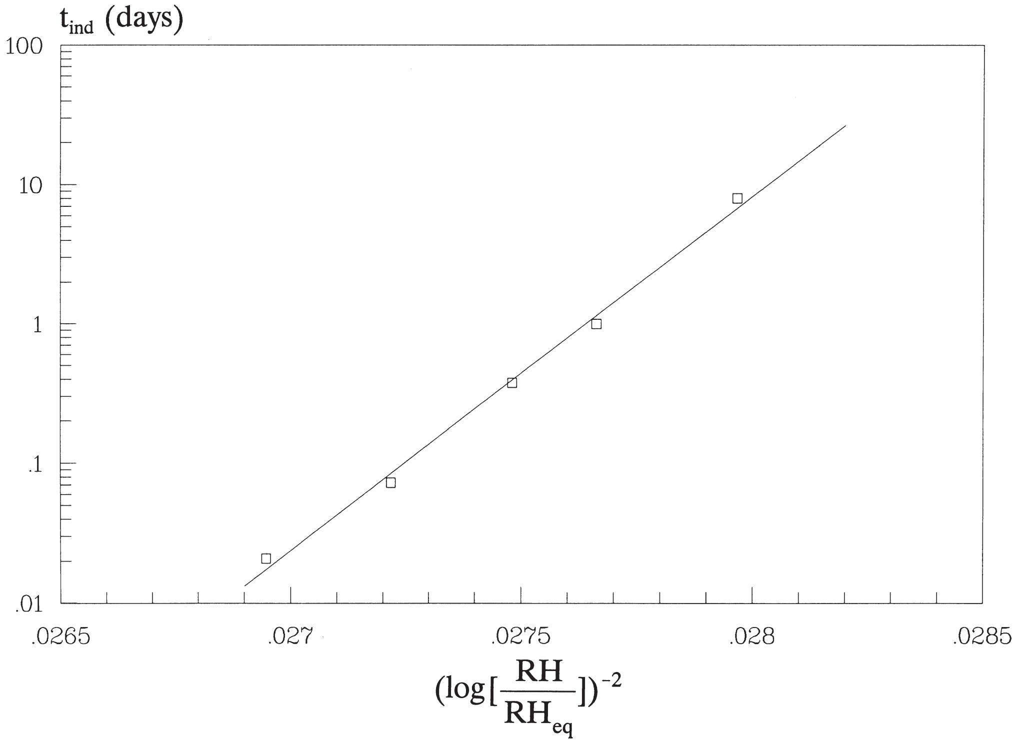

Fig. 7. Relation between induction time and RH for water vapour hydration of C_3A. Temperature: 20°C.

where S is the degree of supersaturation and k_1 and k_2 are experimentally derived parameters. If this equation is applied to water vapour hydration of clinker minerals the degree of supersaturation is: $S = RH/RH_{eq}$, where RH_{eq} is the thermodynamic equilibrium RH for the hydration process [3]. Based on X-ray diffraction evidence the gross reaction scheme for C_3A hydration was previously suggested to be C_3A (s) + 6H (g) $\rightarrow$ C_3AH_6 (s). For this reaction equation RH_{eq} is calculated [5] to be 0.000079% RH at 20°C.

Induction times from Fig. 6 are plotted in Fig. 7. The axes in the plot have been adapted to reproduce Eq. (3) as a straight line: according to the equation $\log(t_{ind})$ depends linearly on $[\log(S)]^{-2}$.

The measured points are reasonably well reproduced by a straight line. This is not proof that the onset of hydration is nucleation controlled, but at least it shows that Eq. (3) serves as a mathematical approximation of the process. The best-fit line in Fig. 7, calculated by linear regression, gives the regression parameters $k_1 = -70.2$ and $k_2 = 2540$, when induction time is days. Based on Eq. (3) the induction time at 43% RH, 20°C can be calculated as 30,000 years. Thus it is not surprising that hydration is not observed for C_3A at 43% RH (see Table 1).

4. Conclusions

The measurements presented in this paper show that the clinker minerals C_3S, C_2S, and C_3A have fundamentally different sensitivities to RH. C_2S hydration is more hampered by decreased RH than C_3S hydration, which again is more hampered than C_3A hydration. Within 1 year of exposure to water vapour at 20°C the limiting relative humidities for hydration of C_3S, C_2S, and C_3A are estimated to be 85, 90, and 60%, respectively. These are kinetic barriers because the equilibrium humidities above which hydration should commence are substantially lower.

The onset of hydration seems to be controlled by an induction period during which only little hydration occurs. The length of this period is increased when the exposure temperature or the RH, or both, are lowered. It has been suggested that this induction period could be controlled by nucleation. However, the measuring technique is not sufficiently accurate to prove this.

Measurements by QXRD indicate that the hydration products formed by the silicate clinker minerals depend on the hydration conditions. Low relative humidities favour formation of solid products with lower water contents. In addition, a low RH seems to increase the CaO/SiO_2 molar ratio of the C-S-H gel.

In water-rich regimes, C_3A hydration yields mixtures of AH_3 with highly hydrated calcium aluminates C_4AH_x ($x = 10$ to 19). In keeping with the principle stated above, in water-deficient regimes only a single hydrate is observed: the relatively low-water phase C_3AH_6. Its relatively high physical density suggests that it may be an undesirable product of postset hydration in low porosity pastes. These pastes require for their performance good space filling by the hydrates. If, however, high density phases form subsequent to set, internal porosity is likely to be enhanced, not reduced, by further hydration.

Acknowledgments

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