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Influence of temperature on autogenous deformation and relative humidity change in hardening cement paste

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Abstract

This paper deals with autogenous deformation and autogenous relative humidity change (RH change) in hardening cement paste. Theoretical considerations and experimental data are presented, which elucidate the influence of temperature on these properties. This is an important subject in the control of early age cracking of concrete. It is demonstrated that the traditional maturity concept generally is not applicable to autogenous deformation and autogenous RH change.

Keywords: Temperature; Kinetics; Humidity; Shrinkage; Autogenous

The pastes of modern high-performance concrete normally have a low water-to-cement (w/c) ratio, 0.20–0.35, and contain admixtures such as silica fume and superplasticizers. Such pastes do not contain enough water for the unrestricted hydration of the cement and, therefore, will self-desiccate. The internal relative humidity (RH) in the paste is lowered as loosely bound water is consumed by reaction. Self-desiccation gives rise to a bulk shrinkage, termed self-desiccation shrinkage, which may be so significant that the cement paste cracks if its deformation is restrained [1].

Self-desiccation and self-desiccation shrinkage are important examples of autogenous RH change and autogenous deformation, respectively, i.e., the change in RH and deformation of a sealed, unrestrained cement paste at a constant temperature. A number of other phenomena may lead to autogenous deformation and RH change, such as expansion due to salt crystallization and lowering of RH due to dissolution of salts in the pore water. Unfortunately, with the present incomplete understanding of the phenomena, there is no possibility of distinguishing measured autogenous RH changes due to self-desiccation from RH changes due to dissolved salts.

In this paper some theoretical considerations and experimental data are presented, which elucidate the influence of temperature on autogenous deformation and autogenous RH change. This is an important subject in the control of early age cracking of concrete. A further account of the autogenous phenomena in hardening Portland cement paste can be found in the literature [1–6]. This paper is based on a report [7] in which a more detailed treatment can be found.

1. Theoretical considerations

1.1. The maturity concept

The maturity concept within concrete technology is based on the idea that the influence of the temperature on the hydration rate is independent of the degree of hydration, α. The influence of temperature on hydration rate is given by so-called time-temperature functions (TTF), f(T).

To conform to the maturity concept the degree of hydration, $\alpha = \alpha(t,T)$, must satisfy Eq. (1) [8,9]:

$$\left.\frac{d\alpha}{dt}\right|_T = g_1(\alpha) \cdot f_1(T) \tag{1}$$

where t is time and T is the temperature.

According to Eq. (1), a certain temperature change will change the hydration rate by a certain factor, independent of the degree of reaction. Because the variables α and T in Eq. (1) are separable, a unique table of the influence of temperature on the hydration rate can be made: $f_1(T)$. In the literature several different functions have been suggested [8]:

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$$f_1(T) = \begin{cases} k \cdot T & \text{Nurse} \\ k \cdot (T + 10) & \text{Saul} \\ k \cdot 2^{(T/10)} & \text{Rastrup} \\ k \cdot \exp\left(-\frac{E_a}{RT}\right) & \text{Freiesleben Hansen} \end{cases}$$

Now, consider a property, $P = P(\alpha,T)$, which is a consequence of the hydration process, for example, heat of hydration, chemical shrinkage, autogenous deformation, etc. To apply the maturity concept to this property, it must satisfy Eq. (2):

$$\left.\frac{dP}{dt}\right|_T = g_2(P) \cdot f_2(T). \tag{2}$$

It can be shown [7] that the maturity concept will only be applicable to P when the property is independent of the temperature. This means P is determined solely by the degree of hydration. Suppose that a monotonous function, $P = h(\alpha)$, exists. In this case, we have as shown in Eq. (3):

$$\left.\frac{dP}{dt}\right|_T = \left.\frac{dP}{d\alpha}\right|_T \cdot \left.\frac{d\alpha}{dt}\right|_T = h'(\alpha) \cdot g_1(\alpha) \cdot f_1(T) = h'[h^{-1}(P)] \cdot g_1[h^{-1}(P)] \cdot f_1(T) = g_2(P) \cdot f_1(T). \tag{3}$$

Under these assumptions, it is seen that the maturity concept is valid for P, and the TTF for P is identical to the TTF for α.

1.2. Autogenous RH change, deformation, and the maturity concept

Self-desiccation shrinkage is an important type of autogenous deformation. Self-desiccation shrinkage is caused by chemical shrinkage, which is linked to the hydration process. Chemical shrinkage leads to a successive reduction in the meniscus radii. This increases the tensile stress in the pore water, increases the compressive stress in the solid phase, and consequently leads to an outer shrinkage [10]. In the following, a couple of examples of influence of temperature on self-desiccation shrinkage are considered.

1.2.1. Surface tension of pore water

The Kelvin equation describes the relation between compressive stress in the pore water, p_l, the meniscus radius, r, and the surface tension of the pore water, σ. If the contact angle of the pore water is assumed to be 0°, the Kelvin equation for the pore water pressure, p_l, in a circular cylindrical pore reads as given in Eq. (4):

$$p_l = \frac{-2 \cdot \sigma}{r}. \tag{4}$$

In this way, self-desiccation shrinkage is linked to the progress of hydration via the Kelvin equation. Eq. (4) shows that self-desiccation shrinkage depends on the surface tension of the pore water. However, σ is a temperature-dependent parameter; for pure water it is approximately 10% lower at 60°C than at 20°C. The pore water stress, therefore, is influenced by the temperature. Self-desiccation shrinkage thus will be temperature dependent as it is caused by the pore water stress: $\varepsilon = \varepsilon(\alpha,T)$. From a stringent mathematical point of view, a temperature-dependent surface tension precludes the maturity concept for self-desiccation shrinkage. However, the temperature dependence of σ is negligible in proportion to the thermal activation of the process; e.g., for an activation energy of 57 kJ/mol the hydration rate is increased by a factor of 17 when the temperature is changed from 20 to 60°C.

The RH in a cement paste is lowered due to dissolved salts and meniscus formation in the pore water. Based on the Kelvin equation and Raoult's law the RH, φ, can be calculated as:

$$\varphi = X_l \cdot \exp\left(-\frac{2 \cdot \sigma M}{r \rho R T}\right) \tag{5}$$

where X_l is the mole fraction of water in the pore fluid, σ is the surface tension of the pore water, M is the molar mass of water, r is the meniscus radius, ρ is the density of water, R is the gas constant and T is the Kelvin temperature.

The term $\sigma/(\rho \cdot T)$ is temperature dependent, whereas the meniscus radius is given by the hydration process, i.e., α. X_l may depend on both α and T, which indicates that Eq. (5) is of the form $\varphi = \varphi(\alpha,T)$. The maturity concept is, therefore, not applicable to autogenous RH change.

1.2.2. Multiple activation energies

Modern concretes typically contain pozzolans such as silica fume and fly ash. Parallel with the cement hydration, these additives hydrate and contribute to the strength development, chemical shrinkage, etc. Experiments have shown that the activation energy of the pozzolanic reactions generally is different from the cement hydration [11]. This indicates that the development of concrete properties probably is controlled by multiple activation energies. Theoretically, concrete properties that are a sum of processes with different activation energies cannot be described by a single activation energy [12].

Despite this, properties of pozzolan containing concrete are, in practice, modelled by a single activation energy. This may be acceptable as long as the property is dominated by the cement hydration. However, autogenous deformation and RH change are, in some cases, strongly influenced by silica fume addition [1]. This indicates that the hydration kinetics of both cement and silica fume may have significance. In that case, no single activation energy will describe the overall autogenous deformation satisfactorily.

Consequently, the maturity concept as defined by Eq. (2) will not be applicable.

2. Experimental details

2.1. Summary of experiments

The experiments performed include measurements of autogenous deformation and RH change in cement paste.

Eight different silica fume modified cement pastes were examined at four temperature levels. In addition, a single experiment of autogenous deformation during a stepped temperature course was performed. Table 1 shows a summary of the experiments performed.

2.2. Materials and mixing

The materials used consisted of two types of cement: (1) rapid-hardening Portland cement with a Blaine fineness of 410 m^2/kg and the following Bogue calculated phase composition (wt%): C_3S: 52.5, C_2S: 21.7, C_3A: 6.0, C_4AF: 10.3, $C\overline{S}$: 3.6, Free CaO: 1.57, Na_2O eq.: 0.55; and (2) white Portland cement with a Blaine fineness of 420 m^2/kg and the following Bogue calculated phase composition (wt%): C_3S: 66.1, C_2S: 21.2, C_3A: 4.3, C_4AF: 1.1, $C\overline{S}$: 3.5, Free CaO: 1.96, Na_2O eq.: 0.17.

Silica fume was used, with a specific surface of 20.5 m^2/g and the following chemical composition (wt%): SiO_2: 90.8, Fe_2O_3: 0.94, Al_2O_3: 0.54, MgO: 1.32, SO_3: 0.57. The silica fume was added as a dry powder.

Superplasticizer was added at a rate of 1.0% by weight of cement + silica fume. The superplasticizer is a napthalene-based dry powder.

Mixing was performed for 5 min in a 5-L epicyclic laboratory mixer. The water was added in two steps during mixing. This procedure ensures the homogeneity of the paste and the dispergation of the silica fume. The materials were approximately 20°C at mixing.

Table 1
Exposure temperature and approximate duration of measurements for the different cement pastes examined

Paste composition			Exposure temperature and duration				
Cement type	w/c	% sf	15°C (weeks)	20°C (weeks)	30°C (days)	40°C (days)	20–45°C (days)
White Portland cement	0.3	0	—	4	13	10	—
		5	—	4	13	10	—
		10	—	4	13	10	—
		20	4	4	13	10	12
Rapid-hardening Portland cement	0.3	0	—	4	13	10	—
		5	—	4	13	10	—
		10	—	4	13	10	—
		20	—	4	13	10	—

The water-cement ratio (w/c) is the pure weight ratio of water to cement. The silica fume percentage (% sf) is the weight ratio of silica fume to cement.

2.3. Measuring technique and equipment

Autogenous deformation is measured by a specially designed dilatometer, in which the cement paste is encapsulated in thin, corrugated PE molds. This ensured insignificant restraint of the hardening cement paste and permitted

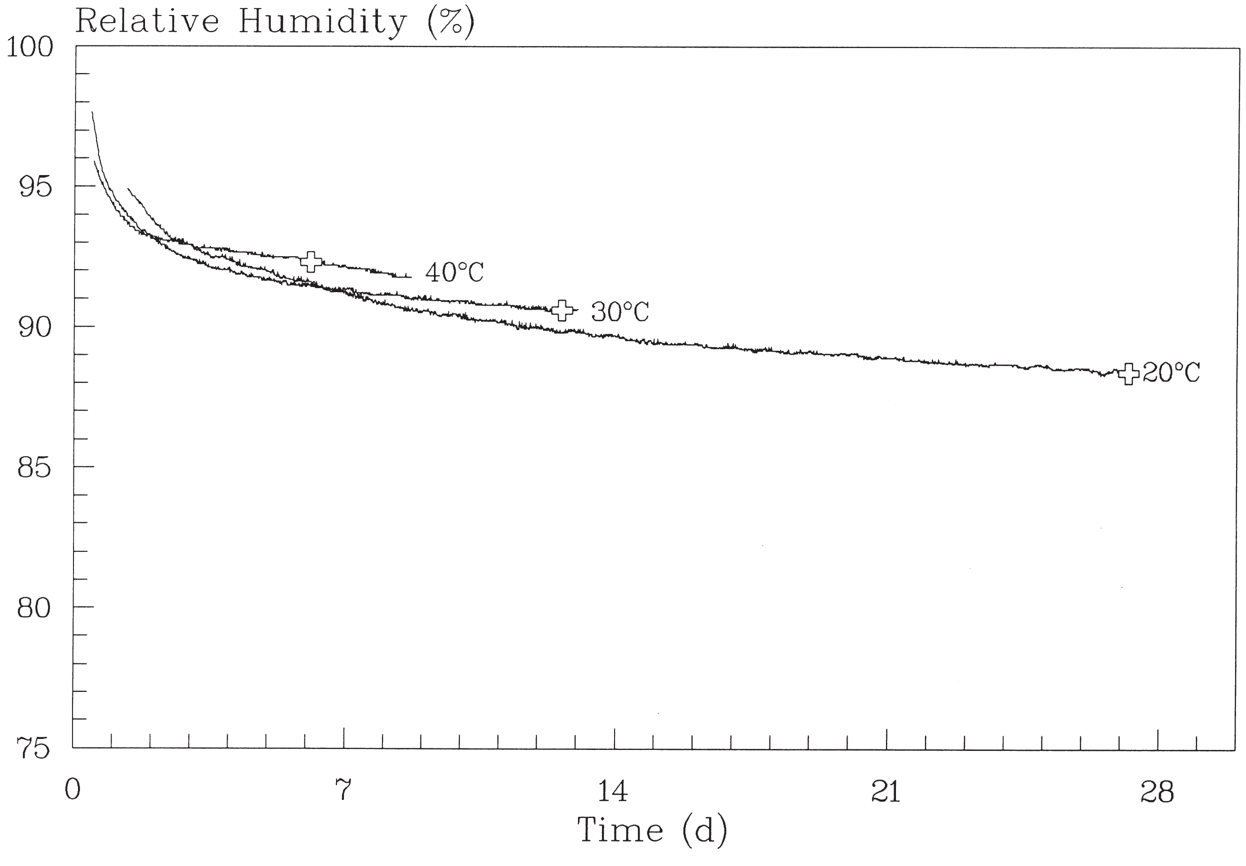

Fig. 1. Autogenous relative humidity change of cement paste of rapid-hardening Portland cement at w/c = 0.30 without silica fume addition. The exposure temperatures are marked on the curves. Time is measured from water addition. The very first data of the 20°C curve are missing due to a datalogger error. See text for explanation of markers.

measurements to commence shortly after casting, 30 min after water addition. During the tests the dilatometer bench with specimens is submerged into a thermostatically controlled glycol bath (±0.1°C). Autogenous deformation is measured simultaneously on two identical samples. A thorough description of the dilatometer and the sample preparation is published elsewhere [4,6].

Autogenous RH change is measured by a Rotronic Hygroscope DT (Rotronic ag, Bassersdorf, Switzerland) equipped with WA-14TH and WA-40TH measuring cells, which is built into a thermostatically controlled box (±0.1°C). Before and after every experiment the equipment is calibrated with saturated salt solutions in the range 75–100% RH. Autogenous RH change is measured simultaneously on four identical samples. A thorough description of the Rotronic Hygroscope and the sample preparation is published elsewhere [3,6].

3. Results and discussion

The discussion in this paper will be restricted to the influence of temperature on autogenous deformation and autogenous RH change. A discussion of the influence of cement type and silica fume addition can be found in the literature [1,3,6]. Only a part of the results will be shown. The full set of measurements can be found elsewhere [7].

3.1. Autogenous RH change

Two predominant features are observed when the temperature is increased: (1) the ultimate RH reached is increased, and (2) the development of autogenous RH change is accelerated. This is demonstrated in the following.

3.1.1. Influence of temperature on the RH level

Fig. 1 shows an example of the influence of temperature on the RH level. Hydration at an increased temperature leads ultimately to a higher RH level.

As shown in the following, the observed effect in Fig. 1 can be accounted for by the temperature dependence of the isotherm. It can be shown [13] that if the temperature is changed for a closed cement paste system it will result in RH change. The change in RH due to the temperature change is related to the heat of vaporization, ΔH_{vap}, of the physically held water in the cement paste as given in Eqs. (6) and (7):

$$\frac{d\ln(p)}{d(1/T)} = \frac{-\Delta H_{vap}}{R} \tag{6}$$

$$p = \varphi \cdot p_s \tag{7}$$

where p is the water vapour pressure, p_s is the pressure of saturated water vapour, T is the absolute temperature, φ is the relative humidity, and R is the gas constant.

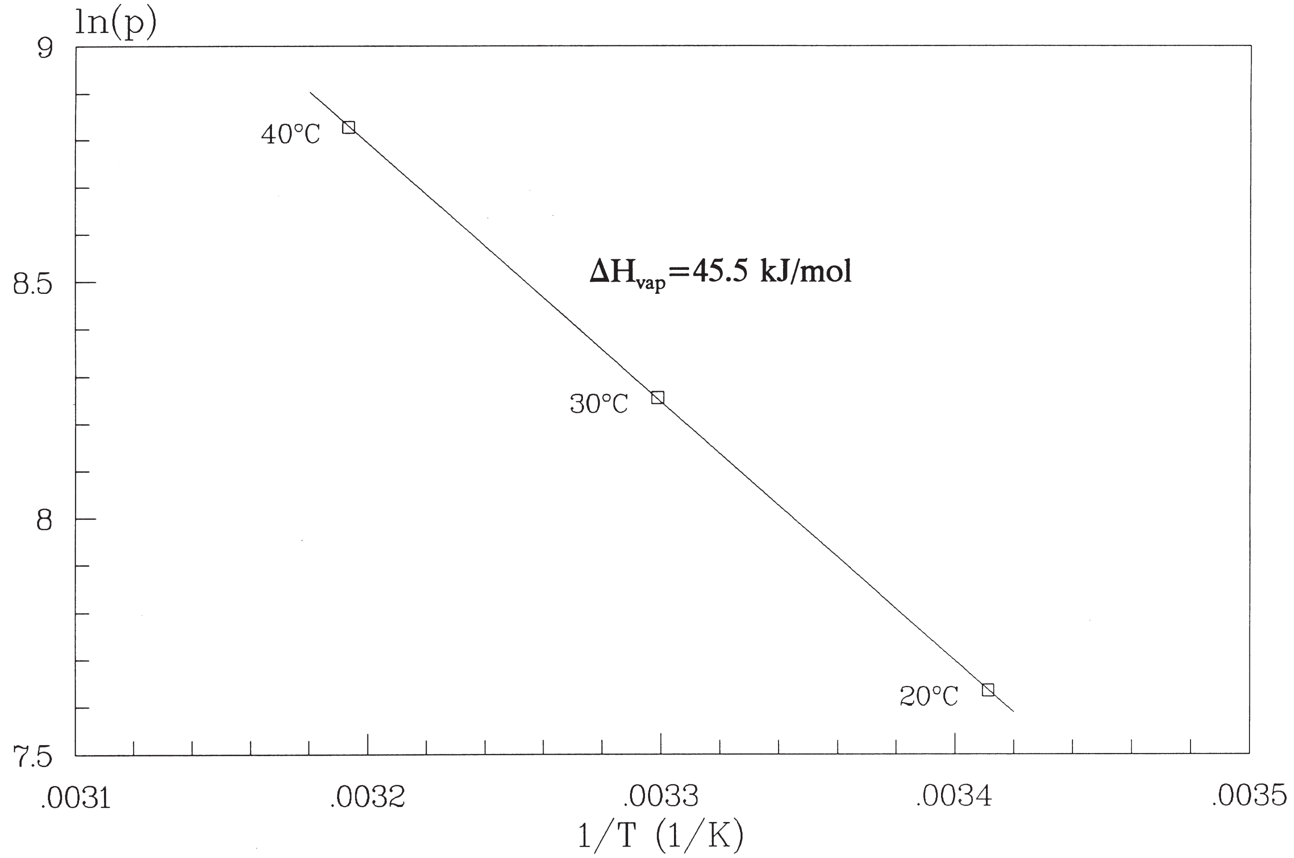

Fig. 2. Isosteric plot of the influence of temperature on water vapour pressure. The axes are transformed according to Eq. (6). The data are based on the markers shown in Fig. 1. Rapid-hardening Portland cement paste at w/c = 0.3 without silica fume addition.

To check this hypothesis, RH values from Fig. 1 can be used. The rapid-hardening Portland cement has an activation energy of 57 kJ/mol according to Geiker [14]. Based on this value, equivalent times at the different temperatures can be selected. The markers in Fig. 1 indicate this. Note that the paste in Fig. 1 does not contain silica fume, and its hydration rate will, therefore, be controlled only by the activation energy of the cement.

From the RHs measured at the time-temperature combinations marked in Fig. 1 water vapour pressures can be calculated, c.f. Eq. (7). Fig. 2 shows a plot in accordance with Eq. (6).

From the slope of the graph the enthalpy of vaporization can be calculated as 45.5 kJ/mol. This is close to the value reported in the literature [13] of approximately 47 kJ/mol at 90% RH. The deviation from this value may be caused by dissolved salts in the pore fluid.

3.1.2. Time-temperature influence on autogenous RH change

Fig. 3 shows an example of the influence of temperature on autogenous RH change. Increasing the temperature from 15 to 40°C markedly accelerates the autogenous RH change. Whereas the RH change at 40°C almost has leveled off within the first week of hardening, this takes more than 1 month at 15°C.

The equilibrium RH in Fig. 3 seems to be approximately 75%. This value may depend slightly on the temperature as discussed previously. If this temperature dependence is neglected it may be possible to model the influence of temperature as a pure time-temperature transformation.

A distinct break can be observed in the curves shown in Fig. 3. It is seen most clearly on the curves for 20°C and 30°C. However, numerical differentiation or changing the axis scaling reveals the break at 15°C and 40°C as well. The breaks are indicated with markers on the curves in Fig. 3. The plot shown in Fig. 4 indicates that the break time can be described as controlled by a thermally activated process.

Previous examinations [1,3,6] showed that the break is related to the initiation pozzolanic reaction of the silica fume. Based on measurements of chemical shrinkage [11] the activation energy of the pozzolanic reaction of the silica fume has been determined to approximately 80 kJ/mol. This is in agreement with the measurements presented in Fig. 4. The high activation energy indicates that the pozzolanic reaction is controlled by a chemical reaction [14].

A general maturity transformation of the curves in Fig. 3 based on the calculated activation energy for the break is not successful. For the RH change before the break it is realized that this activation energy is much too high. In contrast, if a low activation energy is applied the transformation at

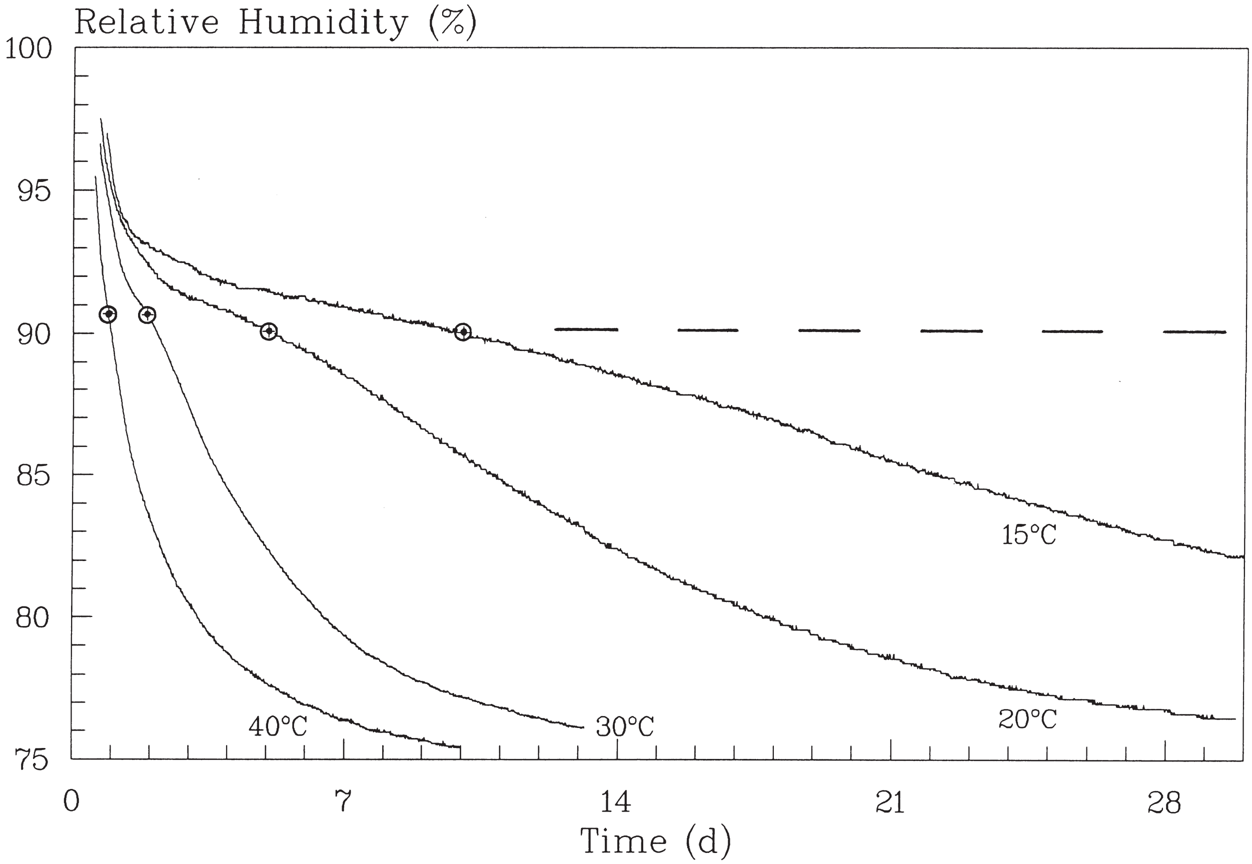

Fig. 3. Autogenous relative humidity change of cement paste of white Portland cement at w/c = 0.30 and 20% silica fume addition. The exposure temperatures are marked on the curves. Time is measured from water addition. See text for explanation of markers and dotted line.

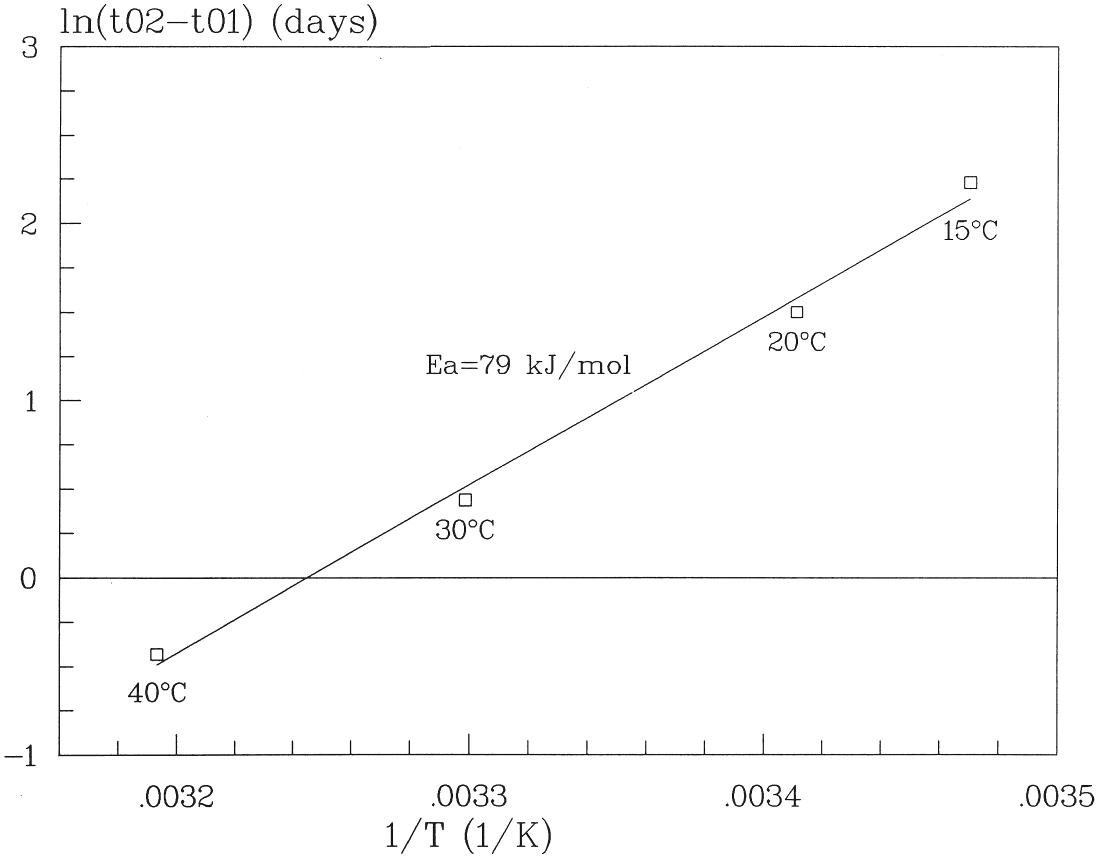

Fig. 4. Corrected break times from Fig. 3 plotted according to Arrhenius equation: d $\ln(t_{0.2} - t_{0.1}) = (E_a/R) \cdot d(1/T)$. The setting time, $t_{0.1}$, is subtracted from the break time, $t_{0.2}$, to eliminate the effect of an uncontrolled temperature during mixing and the first part of the hydration period. From the slope of the line the activation energy can be calculated as 79 kJ/mol.

early ages is good. But in that case the transformation is unacceptable at late ages. Conclusively, it does not seem possible to maturity transform the RH measurements in Fig. 3 based on a single activation energy.

It was shown previously [3] that the autogenous RH change of the silica fume modified cement pastes can be roughly described as consisting of two separate parts that superpose: (1) RH change due to the cement, and (2) RH change due to the silica fume. In Fig. 3 the dotted line illustrates the separation for the 15°C curve: The RH change below this line is supposed, mainly, to be due to the silica fume, whereas the part above the line is due to the cement. The courses at the different temperatures in Fig. 3 have been split up in this way.

Based on such separations into a cement part and a silica fume part, it is possible to maturity transform the two parts differently. Fig. 5 shows an example where the silica fume part is transformed with $E_a = 79$ kJ/mol and the cement part has been transformed with $E_a = 22$ kJ/mol. The hydration of the white Portland cement used in these pastes is known [14] to have an activation energy of 22 kJ/mol.

The transformed curves in Fig. 5 are reasonably similar, indicating that both activation energies, inherent in the paste, seem to influence the autogenous RH change.

3.2. Autogenous deformation

The features observed for autogenous RH change are observed for autogenous deformation as well. The ultimate amount of autogenous deformation developed after setting as well as the rate of autogenous deformation depend on the temperature. However, the autogenous deformation is more complex than the autogenous RH change. Several deformation mechanisms seem to be active, and they are not as clearly separable as for autogenous RH change.

On some of the deformation courses, especially at 20°C, expansion is observed. It may take place from setting until 1 day after water addition. The expansive mechanism may have a longer duration, but at least it is overridden by counteracting shrinkage at this time. Most likely, this expansion is due to ettringite formation in the cement paste. Ettringite formation is a well-known expansive process, and the point at which the expansion takes place is coincident with ettringite formation [15]. In addition, it was observed previously [16] that when synthetic C_3A and gypsum are added to cement paste, it may cause expansion after setting.

3.2.1. Time-temperature influence on autogenous deformation

Fig. 6 shows an example of the influence of temperature on autogenous deformation. Increasing the temperature

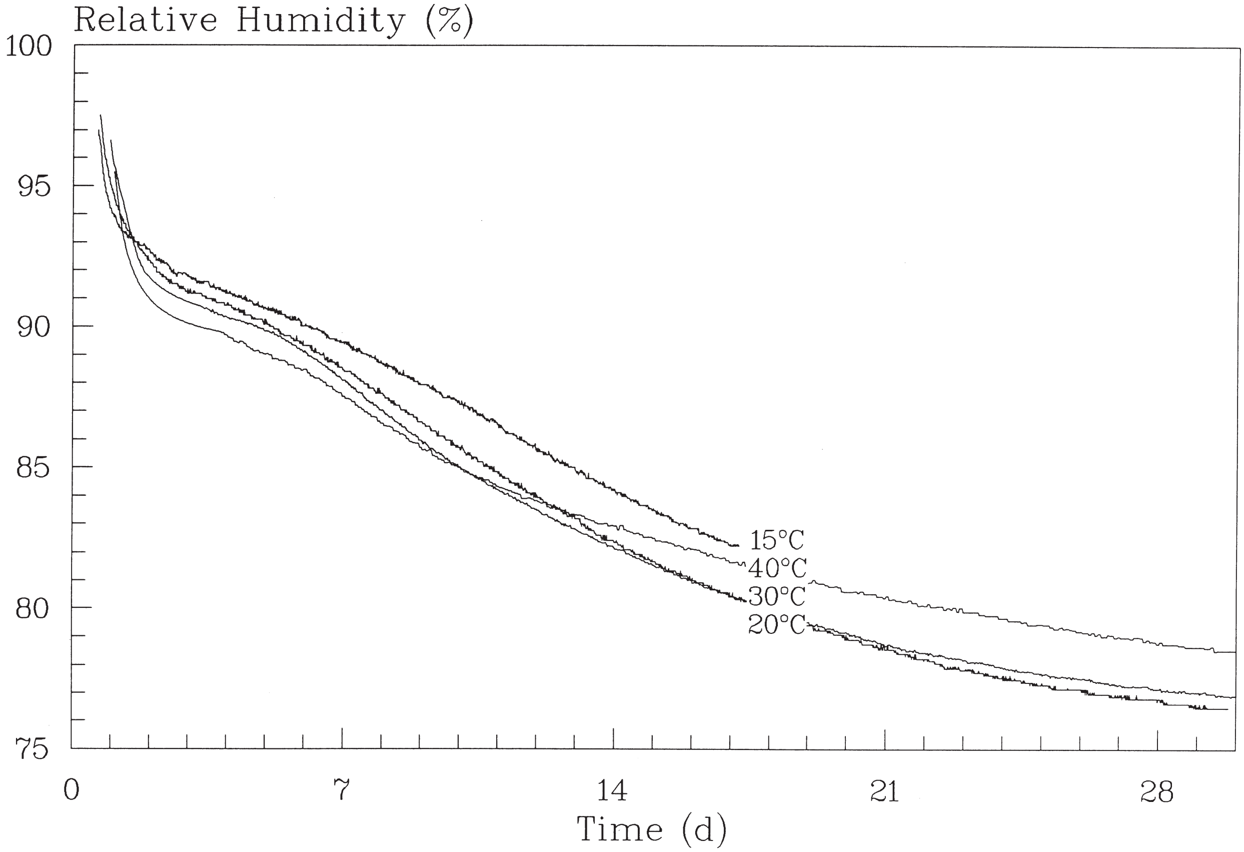

Fig. 5. Time-temperature transformation of the measurements shown in Fig. 3. The curves for the different temperatures have been transformed to 20°C based on two activation energies as described in the text.

from 15 to 40°C markedly accelerates the autogenous deformation. Whereas the deformation at 40°C has almost leveled off within the first week of hardening, this takes more than 1 month at 15°C.

An attempt to maturity transform the deformation curves in Fig. 6 reveals some similarities with the RH curves. A low activation energy has to be used to transform the early age deformation properly, whereas a high activation energy has to be used for the later ages. A maturity transformation based on a single activation energy is, therefore, not successful.

However, the deformation curves shown in Fig. 6 are more difficult to analyze than the corresponding RH curves shown in Fig. 3 for the following reasons:

A. The deformation is not an absolute measurement. The deformation has been arbitrarily fixed to 0 at time of setting. But the procedure is uncertain, ±100 μstrain, because the deformation rate is high at the time of setting.

B. The deformation curves do not display an observable break related to the silica fume reaction. Hence, it is not possible to divide the curves into a cement part and a silica fume part.

For this reason another approach has been attempted: a stepped change of the temperature during an experiment, see Fig. 7.

Increasing the temperature induces a thermal expansion and changes the deformation rate, as shown in Fig. 7. From the change in deformation rate the activation energy can be calculated by Eq. (8):

$$E_a(t_i) = \frac{R \cdot \ln\left[\left(\left.\frac{d\varepsilon}{dt}\right|_{t=t_i^-}\right) \Big/ \left(\left.\frac{d\varepsilon}{dt}\right|_{t=t_i^+}\right)\right]}{\dfrac{1}{T_{t_i^+}} - \dfrac{1}{T_{t_i^-}}} \tag{8}$$

where t_i is the time at the i'th temperature change, and t_i^- and t_i^+ refer to points just before and just after a temperature change, respectively.

At each temperature change it takes a few hours before the system stabilizes (see the dotted deformation rate curve in Fig. 7. This may be due to internal redistribution of water in the cement gel pore system. The observed longer time needed to stabilize the deformation rate at higher degrees of hydration may be related to this.

For the sake of calculation of activation energy the dotted deformation rate curve has been fitted by hand with second-degree polynomials. The calculated activation energy is given in Fig. 7 at each temperature change.

The time-temperature dependence of autogenous RH change was discussed previously. These measurements suggested that the activation energy for the pure cement

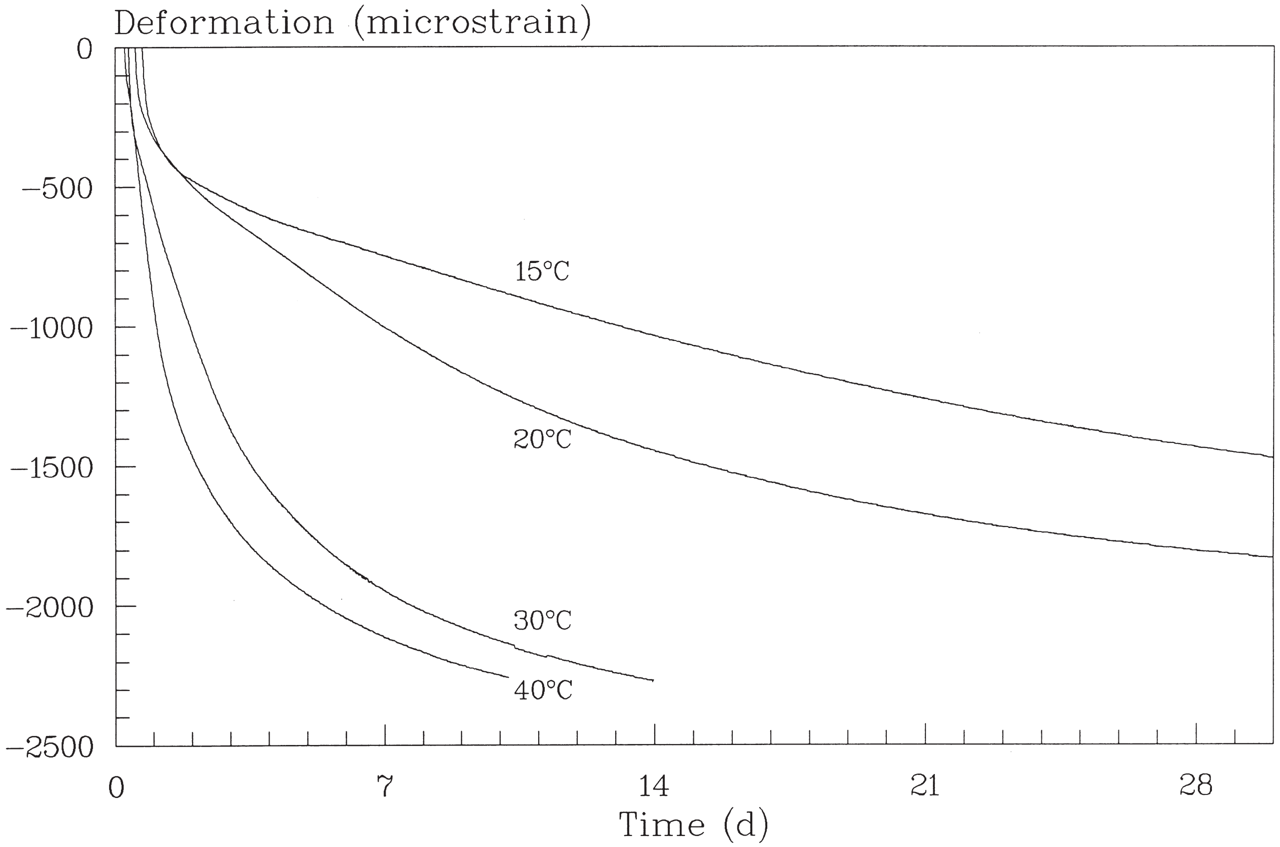

Fig. 6. Autogenous deformation of cement paste of white Portland cement at w/c = 0.30 and 20% silica fume addition. The exposure temperatures are marked on the curves. Time is measured from water addition. The deformation is fixed to 0 at time of setting.

hydration, 22 kJ/mol, dominates the first couple of days of hydration at 20°C. At later stages the activation energy for the silica fume hydration, approximately 80 kJ/mol, dominates.

No systematic changes of the activation energy as a function of the hydration time were observed in Fig. 7. The activation energy measured after 1 day at 20°C, 63 kJ/mol, is clearly higher than the activation energy for the pure cement hydration, 22 kJ/mol. The reason for this apparent discrepancy between autogenous RH change and autogenous deformation has not been accounted for. Possibly, the applied procedure of differential determination of activation energy as shown in Fig. 7 is too delicate to demonstrate such features.

An average activation energy based on all five temperature changes can be calculated as 87 kJ/mol. This is in reasonable accordance with the activation energy for silica fume hydration of approximately 80 kJ/mol.

4. Conclusion

According to the theoretical considerations and experimental evidence presented in this paper, the traditional maturity concept is not applicable to autogenous deformation and RH change. This is precluded due to a number of factors.

One example of this is the influence of temperature on the RH level. It was observed that the equilibrium RH generated by autogenous RH change depends on the temperature. From a mathematical point of view, such differences preclude the traditional maturity concept; however, in practice it is possible to predict the influence of temperature on the equilibrium RH and hence take it into account.

Another example is simultaneous reactions with different temperature sensitivities. Silica fume addition strongly affects autogenous deformation and RH change, and the reaction of the silica fume has a temperature sensitivity that is markedly different from the cement hydration. This specific effect will be present for other concrete properties, e.g., heat of hydration. However, it may have much less influence in that case.

The maturity concept can be extended to include simultaneous reactions with different temperature sensitivities. Based on this, time-temperature transformations of practical use can be performed in some cases.

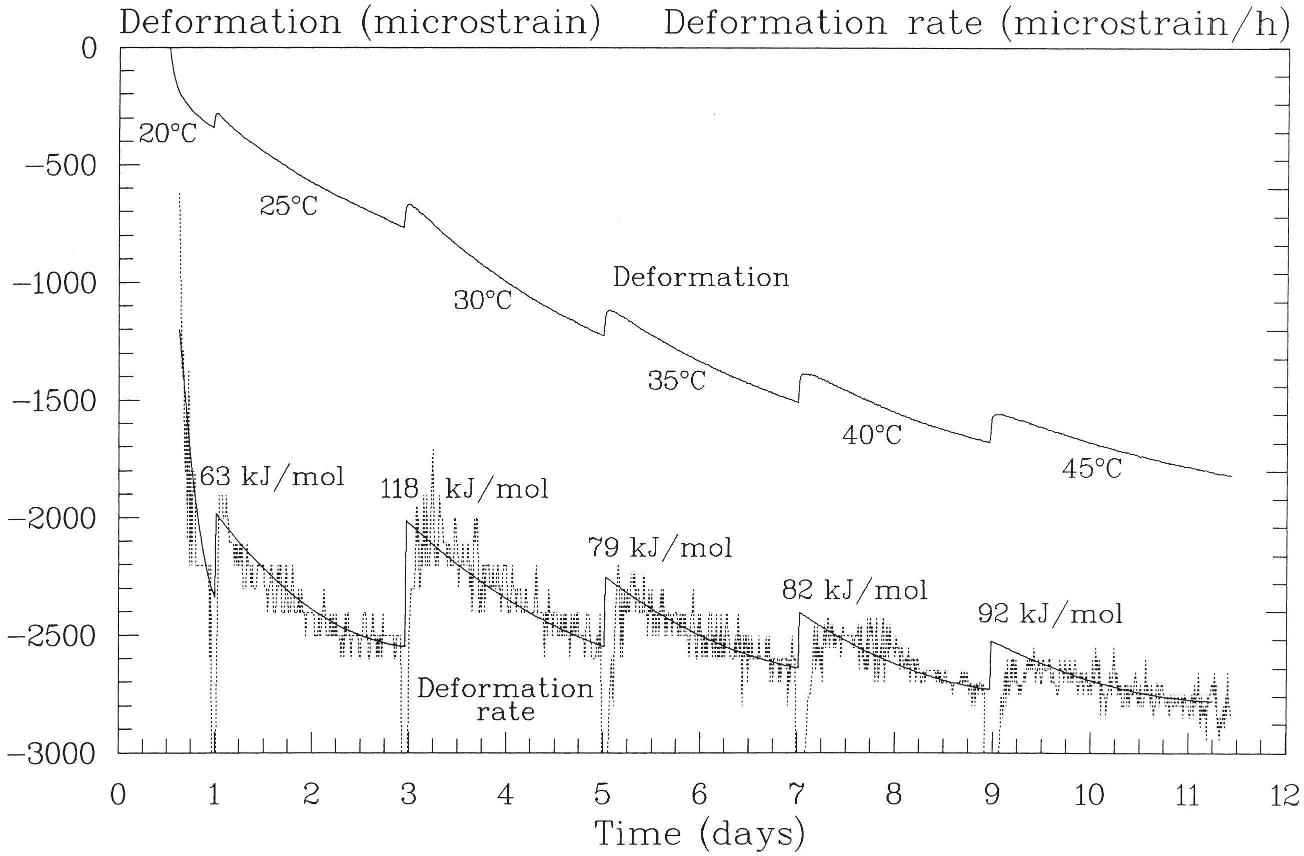

Fig. 7. Autogenous deformation and deformation rate during a stepped temperature course of white Portland cement paste at w/c = 0.3 and 20% silica fume addition. The temperature was changed in 5°C steps starting at 20°C. The deformation rate curve was obtained by numerical differentiation of the deformation curve. See text for further explanation.

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