SELFDESICCATION SHRINKAGE IN LOW POROSITY CEMENT-SILICA MORTAR

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ABSTRACT

It is a well known fact that the hydration re-
actions of sealed portland cement paste with a
low w/c-ratio may cause various selfdesiccation
phenomena. Above a certain degree of hydration
the chemical reactions are accompanied by

- a decrease in the internal relative humidity
in the cement paste

- a volume shrinkage of the cement paste matrix

This paper presents the results from a labora-
tory investigation of selfdesiccation shrinka-
ge mechanisms in hardening low porosity fibre-
reinforced cement-silica mortar. The experimen-
tal work carried out included measurements of

- the isothermal selfdesiccation shrinkage of
sealed specimens

- the coefficient of thermal expansion at
different hardening ages

- the thermal activation energy of selfdesic-
cation shrinkage

Parameterization of shrinkage curves has been
carried out, using the Dispersion Model,
suggested by T.Knudsen /1/.

Key-words: Selfdesiccation, Low-porosity,
Silica, Cracking, High strength, Shrinkage,
Mathematical modelling, Activation energy

1.   INTRODUCTION

In recent years the building industry has been engaged in the
development of new building components consisting of fibre-rein-
forced cement-bound thin slabs. The materials used in manufac-
turing these products are fibre-reinforced, silica-containing,

superplasticised cement mortars with low w/c-ratios; these mortars posess high strength combined with an outstanding workability.

However, manufacturing and use of low porosity cement-silica mortars have disclosed a number of technological difficulties. During the hardening process these mortars frequently develop crack-patterns. Experiences show that this may constitute a serious durability problem in service.

The observed tendency to crack formation may be caused by several different volume change mechanisms; of major importance is probably selfdesiccation shrinkage in the hardening mortar matrix.

It is a well known fact that the hydration reactions of sealed portland cement paste with a low w/c-ratio may cause selfdesic-cation. Implications of this phenomenon are found in earlier works by Powers and Brownyard /2/ from 1947; Powers and Brown-yard pointed out that the ultimate hydration of portland cement paste will be restricted at w/c-ratios less than app. 0.40. If the w/c-ratio is lower than 0.40 the hydration reaction will partly cease at a certain degree of hydration. At this stage further hydration is accompanied by a decrease in the internal relative humidity in the cement paste and by a volume shrinkage of the paste matrix. These phenomena are probably caused by chemical reactions taking up physically adsorbed water from the precipitated cement gel.
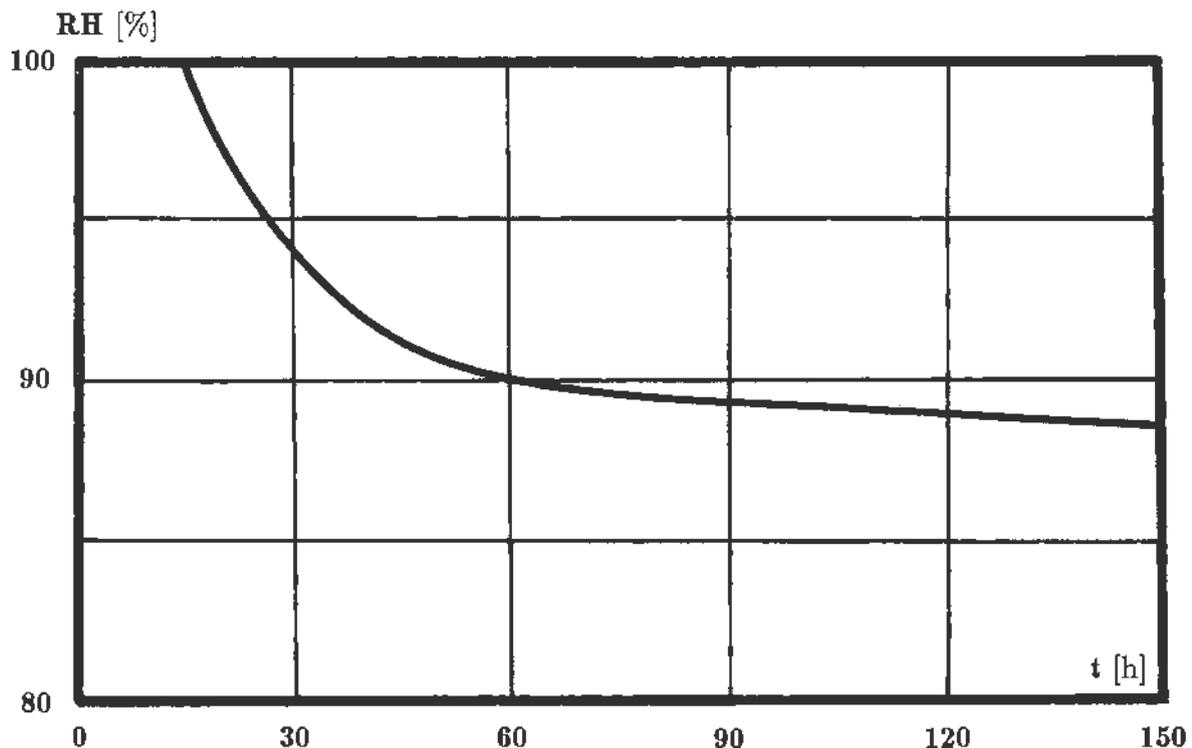

Figure 1. Change of internal equilibrium relative humidity during hardening of sealed cement-silica mortar with w/c-ratio 0.26; curing temperature 20°C /3/

At the division of Physics and Materials at the Danish Engi-
neering Academy various investigations have been carried out in
order to analyse the thermodynamic state of adsorbed water and
the mechanisms of selfdesiccation shrinkage in low porosity
cement-silica mortars (Nielsen,B.S. & Kronholm,F.L.:/3/,/4/,
Mejlhede Jensen,O.:/5/.) This paper is a progress report of
these investigations.

2.   SCOPE OF LABORATORY TESTS

The experimental work carried out included the following invest-
igations of fibre-reinforced cement-silica mortars cast with
w/c-ratio 0.26:

- measurement of the coefficient of thermal expansion at dif-
  ferent hardening ages

- measurement of equilibrium relative humidity at different
  ages
- measurement of isothermal selfdesiccation shrinkage during
  the early hydration period of sealed, unrestrained mortar
  specimens

- measurement of the thermal activation of selfdesiccation
  shrinkage by experiments on reaction rates at 20°C, 25°C,
  30°C, and 35°C.

The following theoretical analyses have been carried out:

- mathemathical modelling of shrinkage development, i.e. parame-
  terization of shrinkage curves using the Dispersion Model
  suggested by T. Knudsen /1/

- calculation of the activation energy E_a from the estimated
  rate constants in the Dispersion Model.

3.   MATERIALS

The tests comprised fibre-reinforced cement-silica mortar with
an effective w/c-ratio of 0.26; the materials used consisted of:

3.1   Cement

Rapid hardening white Portland cement: Blaine fineness 448
m^2/kg; chemical composition by weight-%:

C_3S	C_2S	C_3A	C_4AF	$CaSO_4$	free CaO	Na_2O eq
66.9	19.2	4.29	1.10	2.87	3.02	0.17

3.2 Microsilica

Specific surface after the BET-method: 15-20 m²/g; chemical composition by weight-%:

SiO₂	C	Fe₂O₃	Al₂O₃	Na₂O	K₂O	MgO	SO₃	LOI
89.1	1.7	1.80	0.80	1.10	1.30	1.9	1.3	2.9

3.3 Aggregate

Graded quartz sand 0-4 mm: water absorption 0.1%

Sieve size mm	4	2	1	0.5	0.25	0.125
Passing %	100.0	91.7	80.3	57.1	37.7	2.0

3.4 Fibres

Polypropylene fibres 6 mm, trade mark: "Krenit"

4. MIXTURE PROPORTIONS

A fibre-reinforced cement-silica mortar with the following mixture proportions was used:

Cement	Silica	Water	Sand	Fibres	SPC⁺
1193 g	119.3 g	262.5 g	1893 g	20.00 g	80.00 g

⁺ Superplasticiser, trade mark: "Sikament FF", 33% dry matter

The ingredients were mixed in a 5 l HOGBART mixer for 16 minutes. The mortar was introduced directly from the mixing bowl into the moulds, which were mounted on a vibrating table.

5. SAMPLES

The moulds consisted of 300 mm Ø25 mm steel tubes with a slit to admit a lenient demoulding of the test specimens. Before moulding the tubes were tightened by clamps to app. Ø24.5 mm and coated with hard wax. After pouring Ø24 mm discs of 18/8 stainless steel were anchored to the mortar specimens at both ends.

The mortar specimens were prehardened for 13 hours at 20°C before demoulding. At this age the specimens were transferred to 300 mm unslitted steel tubes, which were sealed with silicon rubber and coated with rubber gaskets (Fig.2). This moist-proofing arrangement ensured insignificant weight changes in the test period (6 months); less than 0.6% of the initial water

content in the specimens was lost by evaporation in all cases. At the same time the rubber gaskets ensured an insignificant restraining of the specimens.
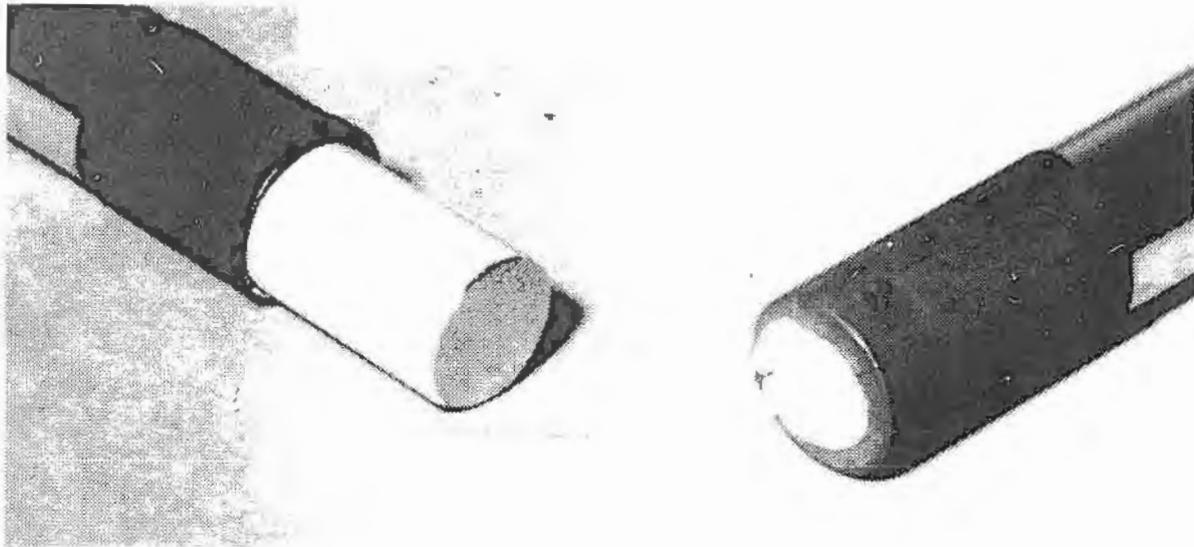

Figure 2. Close up of the moist-proof bearing: the prehardened mortar specimen transferred to the steel tube (left), and sealed with silicon rubber and gasket (right); a disc of stainless steel is anchored to the end of the specimen

6. INSTRUMENTATION

Equilibrium relative humidities of the hardening mortars were measured by a ROTRONIC Hygroscop DT equipped with two thermostatic controlled WA14TH (DMS 100H) measuring cells.

Thermal expansions and selfdesiccation shrinkage of the test specimens were measured by a specially designed dilatometer shown in figure 3. The dilatometer consists of a rigid bench made of NILO alloy 36 ("Invar") with a low thermal expansion coefficient. The investigated specimens were supported by two guide-bars with V-shaped notches. During the measurements the specimens were slightly wedged in between the adjustable pins and the gauging transducers by spring coils (not shown in figure 3).

Length changes of the specimens were recorded by three TRANS-TEK 350 inductance displacement transducers. The temperature of the dilatometer bench and the specimens were measured with copper-constantan thermocouples. External electronic circuits were formed by an MDP 8250 analog scanner transmitting recorded data to a host computer.

During the tests the dilatometer bench was built into a closed stainless steel box and submerged into a thermostatically controlled water bath. The relative humidity inside this box was controlled by NaCl salt to app. 75% RH.
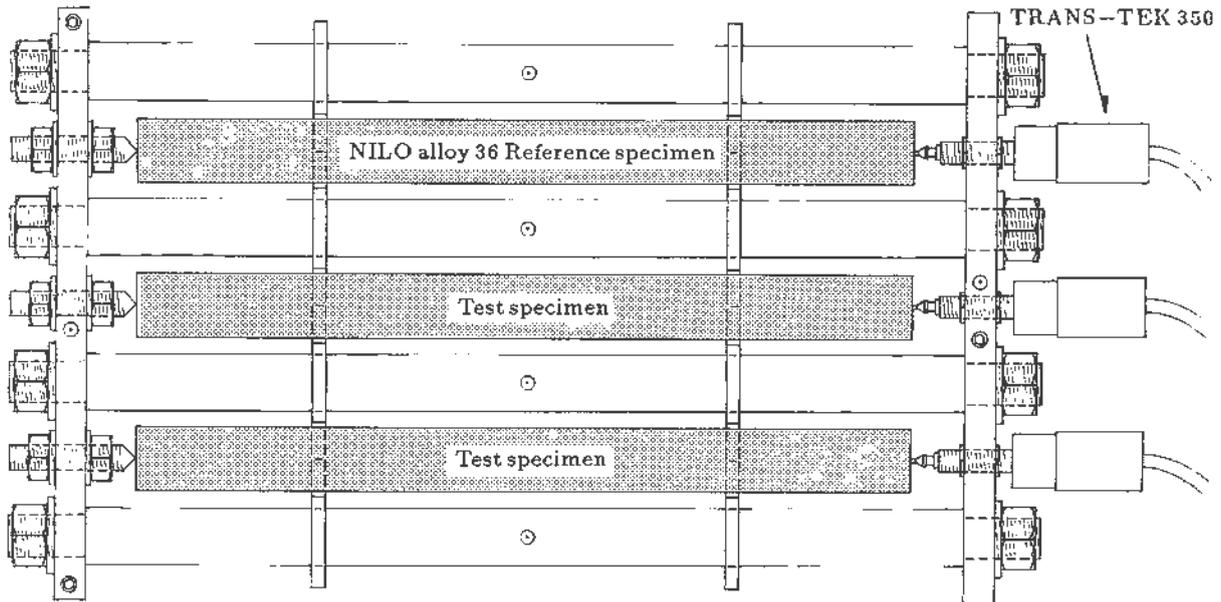
Figure 3. Dilatometer bench set up with three specimens. The bench is machined of NILO alloy 36 with a low thermal expansion coefficient. ⊙ point of temperature measurement.

The performance of the measuring system was tested on 300 mm long reference samples of NILO alloy 36, mild steel, and brass; the main results of this calibration were:

Stability: drift less than 1.5 μm (5.0 μstrain) for 5 weeks
Accuracy: app. 1 μm (3.3 μstrain) on length changes in a shrin-kage test for 2 weeks.

The temperature of the dilatometer bench and the specimens was controlled thermostatically to app. ±0.02°C during the tests at 20°C, 25°C, 30°C, and 35°C. In all cases measurements were carried out simultaneously with two mortar specimens and one reference specimen of NILO alloy 36.

7. COEFFICIENT OF THERMAL EXPANSION

The coefficient of thermal expansion α was determined by in-creasing or decreasing the temperature of the dilatometer and the test specimens in steps of 5°C in the range of 20°C to 35°C. The time necessary to equilibrate the dilatometer bench after each change in temperature was app. 10 hours; actually, 24 hour cycles were used in these measurements to ensure both thermal and internal sorption equilibrium in the sealed mortar speci-mens.

A total of 60 measurements of the thermal expansion coefficient was carried out; the mortar specimens investigated were cured in sealed conditions at 20°C for 2 weeks and 10 weeks respectively.

On specimens cured for 2 weeks, however, the readings were to some extent disturbed by superimposed selfdesiccation shrinkage.

It was not possible to identify any systematic effect of the curing time or of the level of temperature in these observations; average and standard deviation of thermal expansion coefficient:

$$\bar{\alpha} = 18.0 \cdot 10^{-6} \ K^{-1} \quad and \quad s_\alpha = 1.0 \cdot 10^{-6} \ K^{-1} \tag{1}$$

This value agrees reasonable well with observations on thermal expansion coefficients, discussed by Emanuel & Hulsey /6/.

8.   EQUILIBRIUM RELATIVE HUMIDITY

The equilibrium relative humidities RH in the sealed mortar specimens were determined at two hardening ages:

a) mortar cured for 14 days at 30°C .... RH ≈ 88%
b) mortar cured for 6 months at 20C .... RH ≈ 87%

Procedure: samples were crushed inside a plastic bag and immediately transferred to the ROTRONIC measuring cells thermostatically controlled at 25°C. The samples were left for 24 hours to reach equilibrium before readings.

These values are in reasonable accordance with the observations on the same mortar by Nielsen & Kronholm /3/ (figure 1). A tentative conclusion may be that the decrease in the internal relative humidity of the investigated mortar virtually ceases at app. 87% RH.

Later investigations on the same mortar by Christiansen, Andersen & Breengaard /6/ support this observation and indicate a marked influence of the silica-content on the reached level of equilibrium relative humidities.

9.   SELFDESICCATION SHRINKAGE

Measurements of selfdesiccation shrinkage of the investigated mortar were carried out at temperatures: 20.1°C, 24.6°C, 29.6°C, and 33.9°C, thermostatically controlled to ±0.02°C. The test period was in each case 14 days (336 hours). A total of 12 mortar specimens was examined. To secure a detailed picture of the shrinkage development each test run included 330 consecutive readings of length changes and temperatures.

The mortar specimens were prehardened for 13 hours at 20°C in moist proof moulds. At this age they were transferred to protecting steel tubes and sealed; subsequently the specimens were mounted in the dilatometer bench. Readings of length changes and temperatures began app. 13.5 hours after water addition.

Additionally, the long term effect of selfdesiccation was briefly examined by dilatometric measurements; shrinkage tests

were carried out on two mortar specimens, sealed, and precured for 4 months at 20°C.

Dilatometer measurements were carried out simultaneously with two mortar specimens and one reference sample of NILO alloy 36. In the case of 20°C the specimens were initially in thermal equilibrium with the dilatometer system. In case of 25°C, 30°C, and 35°C thermal expansion and selfdesiccation shrinkage were superimposed in the very first hours of measurement. The observed shrinkage ε_{obs}, therefore, must be corrected by a term $\bar{a} \cdot \Delta T$ to get the true shrinkage

$$\varepsilon = \varepsilon_{obs} + \bar{a} \cdot \Delta T \tag{2}$$

Reliable values for the coefficient of thermal expansion a at this degree of hydration are not present for the investigated mortar. Actually, a is expected to be slightly higher than the observed value $\bar{a}$ (1) at later ages; Emanuel & Hulsey /7/. In the final analyses, however, the measured value $\bar{a} = 18.0 \cdot 10^{-6}$ K^{-1} was used to calculate the correcting term in equation (2).

The over all features of the selfdesiccation shrinkage of the investigated mortar are:

- selfdesiccation shrinkage seems to coincide in time with the decrease in internal equilibrium relative humidity of the mortar, reported by Nielsen & Kronholm /3/

- approximately 80% of the ultimate shrinkage has been gained within app. 2 days of sealed curing

- the ultimate selfdesiccation shrinkage of the investigated mortar is 900-1100 µstrain, largely gained within 14 days of sealed curing

- the rate of shrinkage development increases with rising temperature; the ultimate shrinkage, however, sligthly decreases with rising temperature

- the rate of selfdesiccation shrinkage of mortars after four months sealed curing at 20°C is app. 2 µstrain/week, i.e. practically negligible.

Figure 4 shows these characteristics of the observed shrinkage curves at 20.1°C, 24.6°C, 29.6°C, and 33.9°C.

It is interesting to compare the observed value of the ultimate selfdesiccation shrinkage - app. 1000 µstrain - with published values of the ultimate tensile straining of mortars and concrete. According to Kasai, Okamula /8/, the ultimate tensile strain of cement mortar is normally less than 100-200 µstrain, i.e. 1/10th to 1/5th of the observed selfdesiccation shrinkage of the investigated mortar.
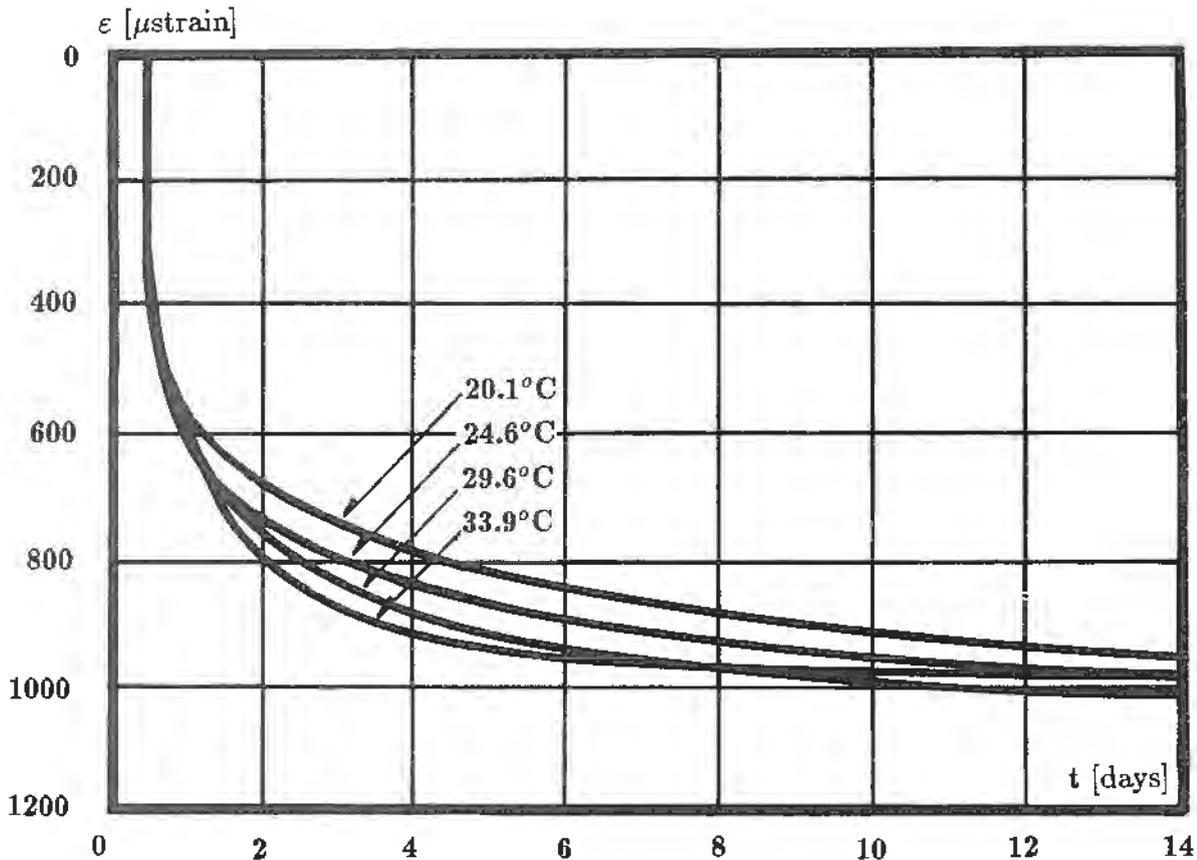
Figure 4. Selfdesiccation shrinkage of sealed, unrestrained cement-silica mortar; w/c-ratio 0.26.

10.   MATHEMATICAL MODELLING

A closer analyse of the selfdesiccation shrinkage phenomenon has been carried out, using the Dispersion Model suggested by T.Knudsen, IMI, The Technical University of Denmark (Knudsen,T. /1/). The Dispersion Model is originally derived for mathematical modelling of hydration kinetics of portland cement. As the origins of selfdesiccation shrinkage seem to be the chemical reactions in the hydrating cement paste, however, this model might prove valuable in analysing shrinkage data.

The basic assumption in deriving the Dispersion Model is that the particle size distribution of the cement is a dominant factor in the correct modelling of cement hydration. The effect of particle size distribution, so to say, overrides all but the gross features in the kinetics, governing the hydration of single particles in the system. According to this theory, only two basic groups of kinetics can be recognized in the hydration curves

- Linear kinetics controlled by diffusion through a highly impermeable membrane, formed at the surface of the particles

- Parabolic kinetics controlled by diffusion through a zone of precipitated reaction products, coating the particles.

Suppose the degree of hydration α is defined by $\alpha \equiv P/P_\infty$, where P is a measurable property like heat evolution, non-evaporable water etc., and P_∞ is the same property measured after infinitely long time. A distinct mathematical interpretation of Linear and Parabolic kinetics is :

$$\frac{1}{P} = \frac{a}{(t-t_0)^i} + \frac{1}{P_\infty}$$ (3)

where a is a rate constant, t is the time since mixing, and t_0 is the dormant period; then equation (3) expresses Linear kinetics when (i=1) and Parabolic kinetics when (i=½).

The experimental data were analysed in detail, using non-linear regression to estimate the parameters in equation (3). However, neither Linear nor Parabolic kinetics provided a satisfactory modelling at all. Graphical examination, plotting $1/\varepsilon$ against $1/(t-t_0)^i$, disclosed a distinct shift in kinetics in the time period investigated. A plot with (i=1) is shown in Fig. 5. This observation was verified by numerical inspection of the first derivative of the shrinkage curves. Further examination of the experimental data revealed that the observed shift in kinetics most likely is due to the onset of a secondary reaction in the cement-silica system.

Parameterization of the experimental data by superimposing two Linear kinetics almost exactly reproduces the measurements in the time period investigated; the standard deviation of residuals (SDR), each estimated by non-linear regression on 330 sets of data, are in the order of 2 - 4 μstrain. For instance, the shrinkage curves shown in figure 4 are reproduced by the Dispersion Model by superimposing the following two Linear kinetics according to equation (3):

$$\varepsilon(t)= \left[\begin{array}{ll} 0 & t \leq t_{01}; \\ F(t;\varepsilon_{\infty1},t_{01},a_1) & t_{01} \leq t \leq t_{02}; \\ F(t;\varepsilon_{\infty1},t_{01},a_1)+F(t;\varepsilon_{\infty2},t_{02},a_2) & t \geq t_{02}. \end{array} \right.$$ (4)

using the values from Table 1 as the parameters.

Summing up: preliminary examinations of the experimental data show that the Dispersion Model might be a valuable tool in analysing selfdesiccation shrinkage mechanisms.

Temperature °C	$\varepsilon_{\infty 1}$ µstrain	t_{01} h	a_1 h/µstrain	SDR* µstrain
20.1	835.3	10.741	0.00471	1.5
24.6	894.7	11.461	0.00330	2.4
29.6	867.3	11.145	0.00366	2.2
33.9	1020.7	10.430	0.00401	1.9

Temperature °C	$\varepsilon_{\infty 2}$ µstrain	t_{02} h	a_2 h/µstrain	SDR* µstrain
20.1	333	103.76	1.16277	3.8
24.6	312	75.38	0.80536	2.5
29.6	240	52.86	0.36617	1.6
33.9	173	40.99	0.21273	1.9

Table 1. Parameter values used in the Dispersion Model to reproduce the shrinkage curves shown in figure 4, superimposing two Linear kinetics according to equation (4); *SDR is the Standard Derivation of Residuals estimated by non-linear regression
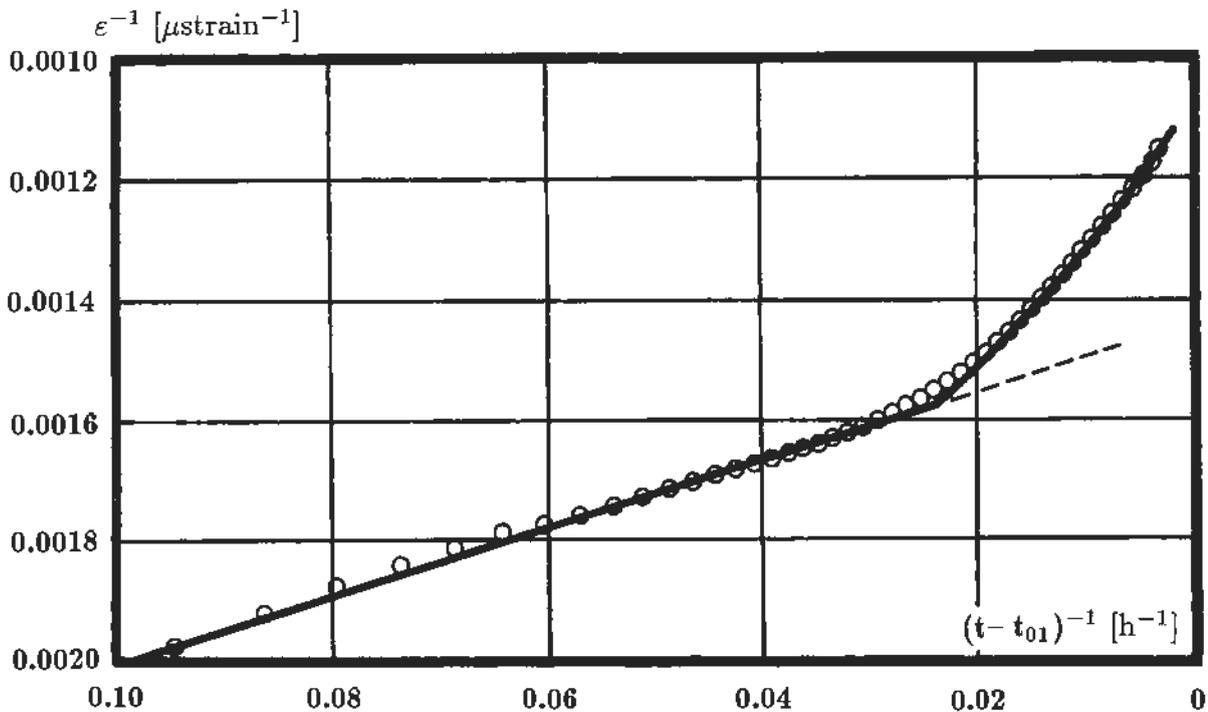

Figure 5. Graphical examination, plotting $1/\varepsilon$ against $1/(t-t_{01})$, discloses a distinct shift in shrinkage kinetics; the graph shows dilatometric shrinkage data from a test run at 29.6°C (only a part of the 330 data sets are shown).

11. ENERGY OF ACTIVATION

According to the Swedish chemist Arrhenius the increase in the rate v of chemical reactions with increase in reaction temperature can usually be expressed by

$$v = v_0 \cdot \exp\left[- \frac{E_a}{RT}\right] \qquad (5)$$

in which E_a is the activation energy, R is the gas constant, and T is the thermodynamic temperature in Kelvin; v_0 is a rate constant. A comprehensive discussion on numerical calculation of activation energy using (5) occurs in Korhonen & Vilhonen /9/.

Using the Dispersion Model in parameterization of the shrinkage curves tentative analyse of the experimental rate data seems to be legitimated. Of particular interest is information about the observed secondary reaction in the cement-silica system. Supposed to be a thermal activated rate proces the onset of this reaction is a measure of reaction rate, i.e. the change in (t_{02}-t_{01}) with temperature may be used to estimate the energy of activation.

Figure 6 shows a plot of $\ln(t_{02}-t_{01})$ from table 1 against T^{-1}; if the slope of this line proves to be linear, then, according to equation (5), the energy of activation E_a may be estimated as $-R \cdot (\text{slope})$. Actually, the regression line shown in figure 6 has the slope 7308 K, corresponding to an activation energy $E_a \approx 61$ kJ/mole.
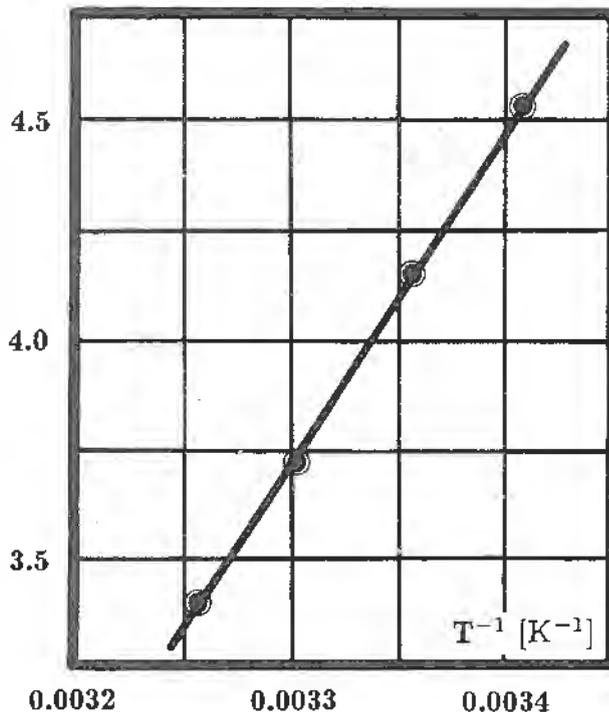

Figure 6. Graphical evaluation of the energy of activation, using time constants from table 1. From the slope of the line, the activation energy E_a is estimated to be 61 kJ/mole

In "Studies of Portland Cement Hydration" Geiker,M. /10/ has published a comprehensive study of chemical shrinkage and hydrating of portland cement. By systematic evaluation of

hydration curves using the Dispersion Model, Geiker,M. estimated the energy of activation E_a for hydration reactions of ordinary portland cement, rapid hardening portland cement, and white portland cement. It was showed that activation energies for Linear kinetics were 57-61 kJ/mole and for Parabolic kinetics app. 22 kJ/mole.

Actually, this is in agreement with the above estimated activation energy $E_a \approx 61$ kJ/mole for shrinkage development modelled by Linear kinetics with the Dispersion Model.

12.   DISCUSSION

The very fact that the Dispersion Model to a great accuracy reproduces experimental data for selfdesiccation shrinkage reveals a close connection between the kinetics of hydration reactions and the shrinkage development. As a matter of fact, the Dispersion Model is derived for mathematical modelling of hydration kinetics.

This means that the observed shift in shrinkage kinetics may very well be due to the onset of secondary chemical reactions in the hydrating cement paste. In proposing further investigations, thorough discussions of phenomena like:

- the kinetics of dehydration of alumina hydrates, especially ettringite, in an environment with decreasing relative humidity

- the onset of the lime-silica reaction in the cement paste as a function of time and temperature

- the balance and shift between different shrinkage mechanisms, i.e. capillary action, disjoining pressure, and surface forces, as a function of temperature and relative humidity in the cement paste

might be useful.

13.   · CONCLUSIONS

Measurements performed on moisture sealed fibre-reinforced cementsilica mortar with w/c-ratio 0.26 have shown the following characteristics:

- the coefficient of thermal expansion: $\bar{a} \approx 18.0 \cdot 10^{-6}$ K^{-1}

- the internal equilibrium relative humidity decreases and stabilizes at app. 87% RH within one week of hardening

- the measured shrinkage app. 1000 µstrain is 5 to 10 times the ultimate tensile strain of the mortar. Selfdesiccation shrinkage, therefore, is a probable cause of the observed

crack-pattern development in manufacturing of low porosity
cement-silica mortars

● superimposing two Linear kinetics the Dispersion Model almost
exactly reproduces the measured selfdesiccation shrinkage;
onset of the second linear kinetic probably is due to a
change in mechanism.

REFERENCES

/1/   Knudsen,T.: "The Dispersion Model for Hydration of
        Portland Cement", Cement and Concrete Research, 14,
        1984

/2/   Powers,T.C. & Brownyard T.L.: "Studies of the Physi-
        cal Properties of Hardened Portland Cement Paste",
        Journal of the American Concrete Inst., Vol.18
        No.6.,1947

/3/   Nielsen,B.S.& Kronholm,F.L.: "Physical Bonds of Water
        in Hardened Cement Paste", Project report, DIA-B,
        Division of Physics and Materials, Lyngby 1987

/4/   Nielsen,B.S.& Kronholm,F.L.: "Physical Bonds of Water
        in Hardened Cement Paste", Nordic Concrete Research
        1989

/5/   Mejlhede Jensen,O.: "Shrinkage of Fibre Reinforced
        Cement Mortars", Project report, DIA-B, Division of
        Physics and Materials, Lyngby 1988

/6/   Christiansen,A.F., Andersen,C.M & Breengaard,L.C.:
        "Selfdesiccation shrinkage of Fibre Reinforced Cement
        Mortar", Project report, DIA-B, Division of Physics
        and Materials, Lyngby 1989

/7/   Emanuel,J.H. & Hulsey,J.L.: "Prediction of the
        Thermal Coefficient of Expansion of Concrete", ACI
        Journal, April 1977, p.149-155

/8/   Kasai & Okamula: "The Initial Tensile Strength of
        Concrete", Japan Cement Association, 22nd General
        Meeting, p.172-176, 1968

/9/   Korhonen,U. & Vilhonen,E.: "On the Calculation of Ac-
        tivation Energy in Thermal Activation Rate Processes",
        Acta Polytechnica Scandinavica, No. 22, 1963

/10/   Geiker,M.: "Studies of Portland Cement Hydration,
        Institute of Mineral Industry", Technical University
        of Denmark, 1983.