THE ALKALINITY OF CEMENTITIOUS PASTES WITH MICROSILICA CURED AT AMBIENT AND ELEVATED TEMPERATURES

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ABSTRACT

The alkalinity in cementitious (Portland cement and Microsilica) pastes with low w/(c+s)-ratios and high dosages of Microsilica as a function of curing time at both ambient and initial elevated temperatures has been monitored utilizing Differential Thermal analysis (DTA)/Thermogravimetry (TG). In addition, the pH of the pore water has been measured for some mixes. Pastes based on Portland cement with 0 - 20 % replacements of cement by Microsilica and w/(c+s)-ratios ranging from 0.20 - 0.40 were subjected to initial curing at 20 or 50 °C, followed by a sealed cure at 20°C until 7, 28, 90, 360 or 420 days when the pastes were characterized. The results revealed that even though the CH content was below the detection limit in pastes with high dosages of Microsilica subjected to either long time ambient curing or initial elevated curing temperature, the pH of the pore fluid was still $\geq$ 12.5.

Key-words: Cement paste, Microsilica, Condensed Silica Fume, Alkalinity, Curing, Elevated Temperature, Light Weight Aggregate Concrete

1. INTRODUCTION

The object of the present study was to monitor the alkalinity of cementitious (Portland cement and Microsilica) pastes with low w/(c+s)-ratios and high dosages of Microsilica as a function of curing time at both ambient and initial elevated temperatures. The term alkalinity refers to the high pH (> 7) of the pore water created by alkali (e.g. Na, K) and/or alkali earth (e.g. Mg, Ca) salts (e.g. hydroxides, carbonates, silicates). If the pH of the pore water is high due to a slightly soluble salt of large deposits in the paste (e.g. calcium hydroxide), the alkaline reserve is vast (e.g. not easy to diminish pH by leaching). On the other hand, if the high pH is solely due to a minor amount of very soluble species in the pore water (e.g. potassium hydroxide), the alkaline reserve is small.

The task is carried out by utilizing Differential Thermal analysis (DTA)/Thermogravimetry (TG). In addition, the pH of the pore water has been measured for some mixes since the pH might have been lowered when the calcium hydroxide (CH) is consumed by the pozzolanic reaction with MS.

The current work is related to the production of low density, light weight aggregate (LWA) concrete, since the heat generated by hydrating cement then may create a temperature approaching 100°C in the interior due to the low heat capacity of the aggregate. The temperature gradient thus created in a construction may cause numerous microcracks due to thermal stress, but the high temperature may also affect the reaction products and the pore structure in the paste and the structure of the interphase with LWA. The reason why low w/(c+s)-ratios are investigated, is because the capillary suction of water by LWA in the fresh mix may reduce the effective w/(c+s)-ratio in the paste considerably.

This investigation is a continuation of a work recently presented by Justnes and Havdahl /1/, where they showed that long term curing of cementitious pastes with low w/(c+s)-ratios and high dosages lead to a depletion of calcium hydroxide (CH). Furthermore, only a slight elevation of the initial curing temperature lead to a drastic decrease in CH content and depletion at an early stage. However, it was shown that that the pH still was ≥ 12.5, even in mixes without detectable CH. Later, the high pH in cementitious pastes without CH was confirmed by Zhang and Gjørv /2/.

2. EXPERIMENTAL

The chemical analyses and mineral compositions of the cement (P30-4A) and Microsilica used are given in Table 1. A serie of cementitious paste mixes consisting of w/(c+s)-ratios = 0.20, 0.25, 0.30, 0.35 and 0.40 combined with 0, 5, 10, 15, and 20 % replacements of cement by Microsilica were sealed cured at 20°C and tested for chemical bound water and calcium hydroxide content after 90 and 420 days. Mixes in a second serie with w/(c+s) = 0.25 and 0.40 combined with 0, 8 and 16 % MS were cured initially (72 h) at 50°C. The CH content and the amount of chemical bound water were measured after 7, 28, 90 and 360 days for the second serie.

The paste samples were uniformly mixed in a high speed shear mixer (5 min). Adequate amounts (6 % dry when MS ≥ 15 %, else 3 %) of a sulphonated naphtalene-formaldehyde condensate based super plasticizer (SP) were used in order to secure uniform blends.

The samples cured at elevated temperature were cast in styrofoam bottles. When the temperature had reached 50°C due to the hydration reaction, the bottles were submersed in a water bath of 50°C and kept there for 72 hours. The rest of the curing periode was at 20°C.

The hydration was stopped after 28 days by crushing the samples and washing the powder with ethanol. The samples were then dried at

105°C for 1 hour prior to the DTA/TG analyses. The DTA/TG experiments were carried out at a NETZSCH 409 STA with a heating rate of 10 °C/min and nitrogen as a carrier gas. The sample (150 mg) was contained in an alumina crucible and alumina powder was used as a reference. Weight loss in the range of 105 – 1000°C was taken as non-evaporable water, while the weight loss around 500°C was interpreted as the decomposition of CH.

The pH of the water squeezed from the crushed paste in a pore water press (< 375 MPa) was analyzed by titration with HCl and phenolphtalein as indicator.

Table 1. Chemical analyses and mineral composition of cement and Microsilica

Oxide	P30-4A (XRF)	Microsilica
SiO_2	22.83 %	91.2 %
CaO	63.87 %	0.6 %
Al_2O_3	4.06 %	0.2 %
Fe_2O_3	2.88 %	1.3 %
MgO	1.82 %	1.1 %
Na_2O	0.27 %	0.8 %
K_2O	0.67 %	-
SO_3	2.85 %	0.3 %
Loss of ignition (LOI)	0.91 %	-
Fineness	405 m^2/kg (Blaine)	22600 m^2/kg (BET)
Minerals (Bogue calc.)		
C_3S	43.47 %	
C_2S	32.66 %	
C_3A	5.89 %	
C_4AF	8.76 %	
CS (gypsum)	4.85 %	
C (free lime)	0.87 %	

3. RESULTS

Non-evaporable water and CH-content in % of burnt weight, and some pH-data, for series 1 with w/(c+s) = 0.20, 0.25, 0.30, 0.35 and 0.40, and 0, 5, 10, 15 and 20 % MS cured at 20 °C are listed in Table 2 for 90 days ambient curing and in Table 3 for 420 days curing. The amounts of non-evaporable water for w/(c+s) = 0.20 & 0.25, 0.30 & 0.35 and 0.40 are depicted as a function of Microsilica dosage in Figures 1, 2 and 3, respectively, while the calcium hydroxide contents for the same samples are plotted in Figures 4, 5 and 6.

Table 4 contains analoguous data for series 2; pastes with w/(c+s) = 0.25 and 0.40 with 0, 8 and 16 % MS, cured initially at 50°C, and measured after 7, 28, 90 and 360 days sealed curing at 20°C. The

Table 2. The [weight loss 105 - 1000°C/*calcium hydroxide*/pH] of paste, w/(c+s) = 0.20, 0.25, 0.30, 0.35 and 0.40 and 0, 5, 10, 15 and 20 % MS replacement, sealed cured at 20 °C for 90 days

w/(c+s)	0 % s	5 % s	10 % s	15 % s	20 % s
0.20	11.11/ 7.79/-	9.87/ 3.45/-	9.58/ 3.13/-	9.89/ 1.88/-	10.41/ 0.00/-
0.25	13.74/ 9.97/-	11.94/ 7.01/-	10.98/ 3.17/-	11.53/ 1.60/-	11.83/ 0.00/-
0.30	15.92/12.57/-	13.58/ 8.79/13.59	12.65/ 3.88/13.52	12.89/ 1.30/13.00	15.30/ 0.00/-
0.35	17.44/13.57/13.90	15.58/11.21/13.59	14.27/ 5.85/13.52	14.81/ 1.97/13.05	- / - / -
0.40	18.55/16.01/13.86	16.85/12.38/13.61	15.49/10.97/13.30	15.89/ 0.06/13.13	17.12/ 0.00/12.63

Table 3. The [weight loss 105 - 1000°C/*calcium hydroxide*/pH] of paste, w/(c+s) = 0.20, 0.25, 0.30, 0.35 and 0.40 and 0, 5, 10, 15 and 20 % MS replacement, sealed cured at 20 °C for 420 days

w/(c+s)	0 % s	5 % s	10 % s	15 % s	20 % s
0.20	11.50/ 8.82/-	10.53/ 4.77/-	11.00/ 1.27/-	11.11/ 0.00/-	10.66/ 0.00/-
0.25	14.90/ 9.72/-	10.67/ 7.42/-	12.47/ 1.61/-	12.23/ 0.00/-	12.85/ 0.00/-
0.30	16.37/14.27/-	15.04/ 8.28/-	14.40/ 3.63/-	13.61/ 0.00/-	14.52/ 0.00/-
0.35	18.11/16.22/-	17.41/10.87/-	15.75/ 5.38/-	15.59/ 0.00/-	- / - / -
0.40	19.62/20.26/-	18.81/11.34/-	17.45/ 6.88/-	16.85/ 0.00/-	18.05/ 0.00/-

amounts of non-evaporable water as a function of curing time for
w/(c+s) = 0.25 and 0.40 are revealed in Figures 7 and 8, respectiv-
ely, while the same graphs for calcium hydroxide contents are drawn
in Figures 9 and 10.

Table 4. The [weight loss 105 - 1000°C/*calcium hydroxide*/pH]
of paste; w/(c+s) = 0.25 and 0.40 and 0 - 16 % MS
replacement, cured initially (72 h) at 50 °C and
measured at an age of 7, 28, 90 and 360 days age

w/(c+s) [age]	0 % s	8 % s	16 % s
0.25 [7 days]	12.82/*11.15*/-	10.51/*4.36*/-	10.93/*0.0*/-
0.25 [28 days]	12.50/ *9.50*/-	10.63/*2.49*/13.02	11.66/*0.0*/12.60
0.25 [90 days]	15.66/*11.58*/-	10.95/*2.20*/-	11.63/*0.0*/-
0.25 [360 days]	14.64/*11.01*/-	12.17/*1.59*/-	13.71/*0.0*/-
0.40 [7 days]	17.23/*17.48*/-	13.43/*7.15*/-	13.82/*0.0*/-
0.40 [28 days]	19.08/*20.51*/-	15.02/*5.81*/-	16.01/*0.0*/-
0.40 [90 days]	19.73/*16.97*/-	14.84/*5.19*/-	14.09/*0.0*/-
0.40 [360 days]	22.63/*23.06*/-	16.92/*6.69*/-	16.68/*0.0*/-
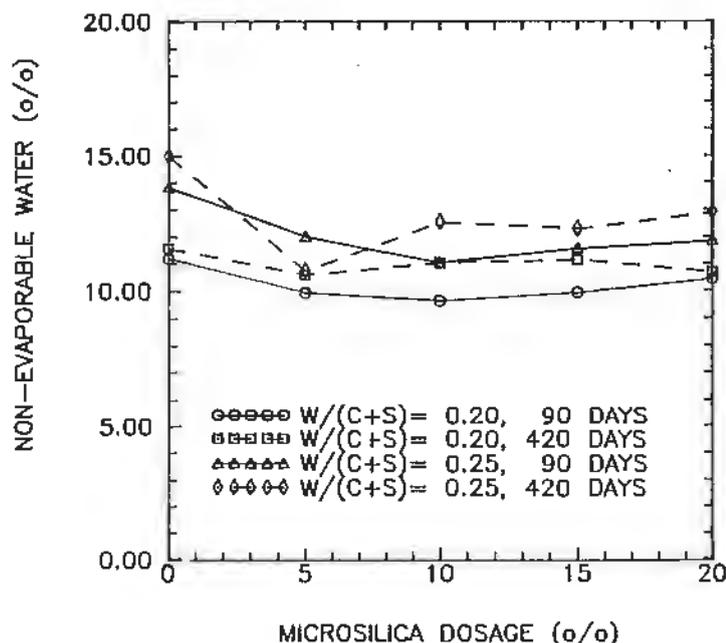
Fig. 1 Non-evaporable water in cementitious paste with
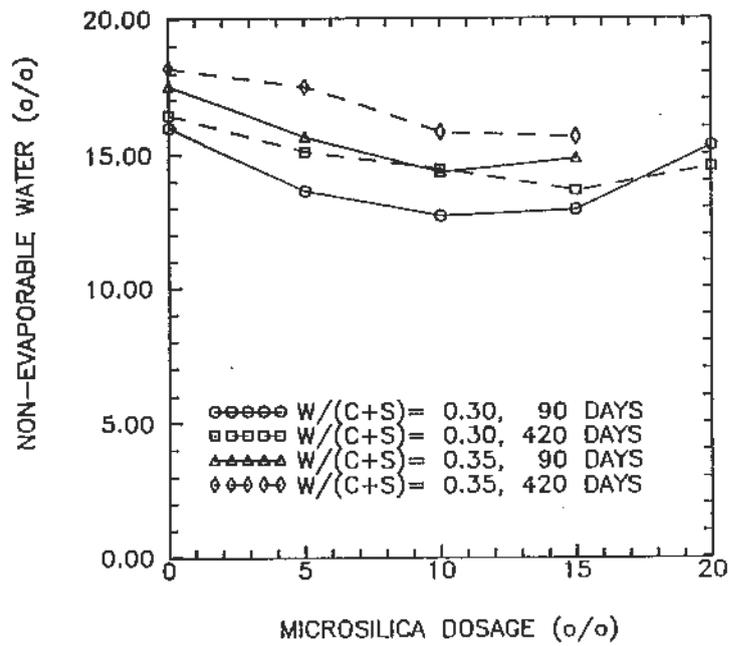w/(c+s) = 0.20 and 0.25 as a function of Microsilica
dosage at different ages.

Fig. 2   Non-evaporable water in cementitious paste with
w/(c+s) = 0.30 and 0.35 as a function of Microsilica
dosage at different ages.

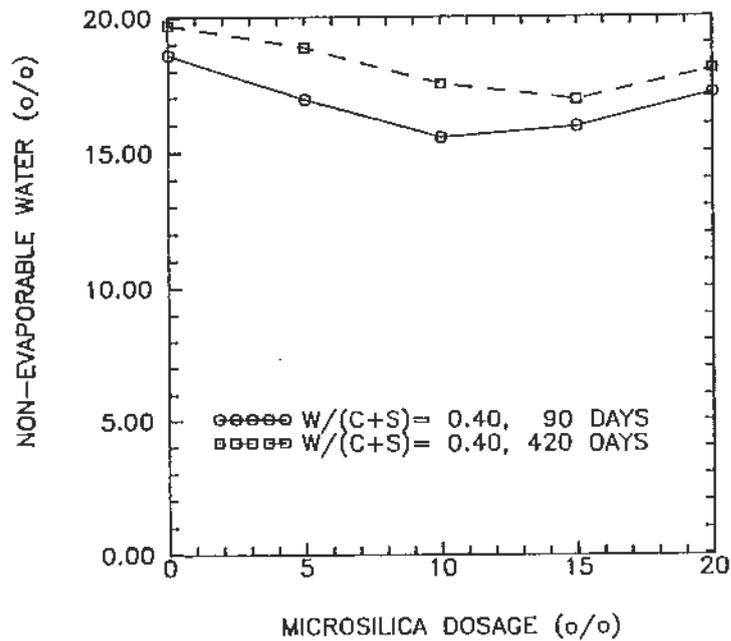Fig. 3   Non-evaporable water in cementitious paste with
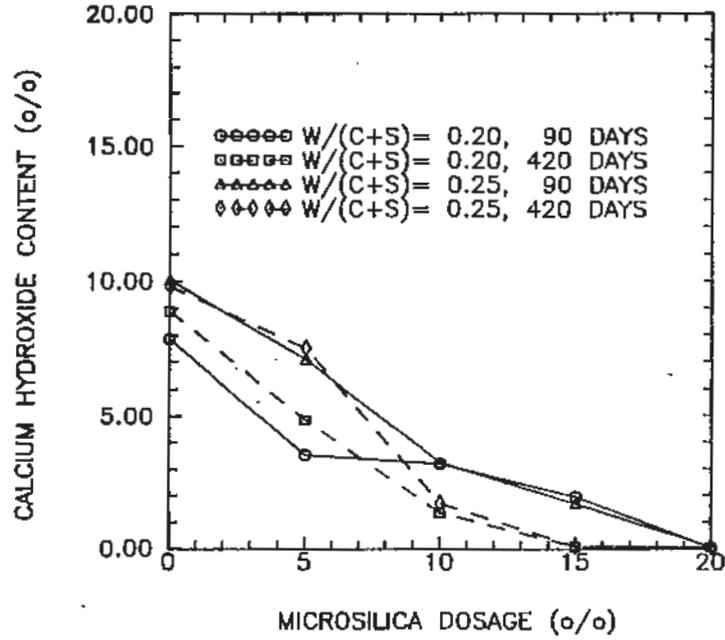w/(c+s) = 0.40 as a function of Microsilica dosage at
different ages.

Fig. 4   The calcium hydroxide content in cementitious paste
          with w/(c+s) = 0.20 and 0.25 as a function of
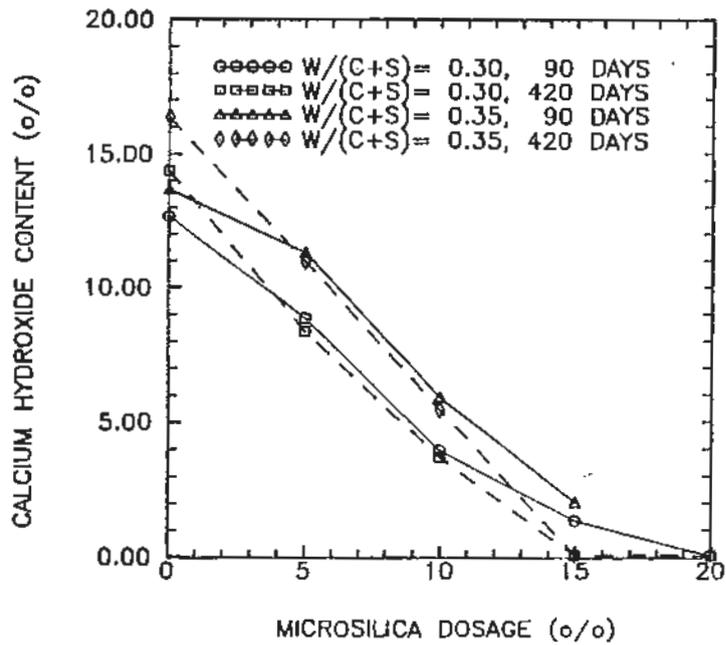   Microsilica dosage at different ages.

Fig. 5   The calcium hydroxide content in cementitious paste
          with w/(c+s) = 0.30 and 0.35 as a function of
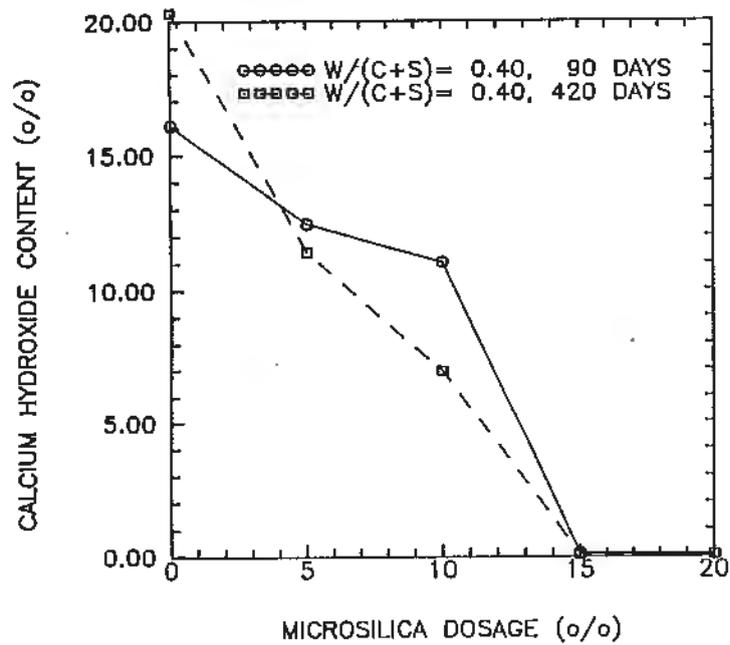   Microsilica dosage at different ages.

Fig. 6 The calcium hydroxide content in cementitious paste
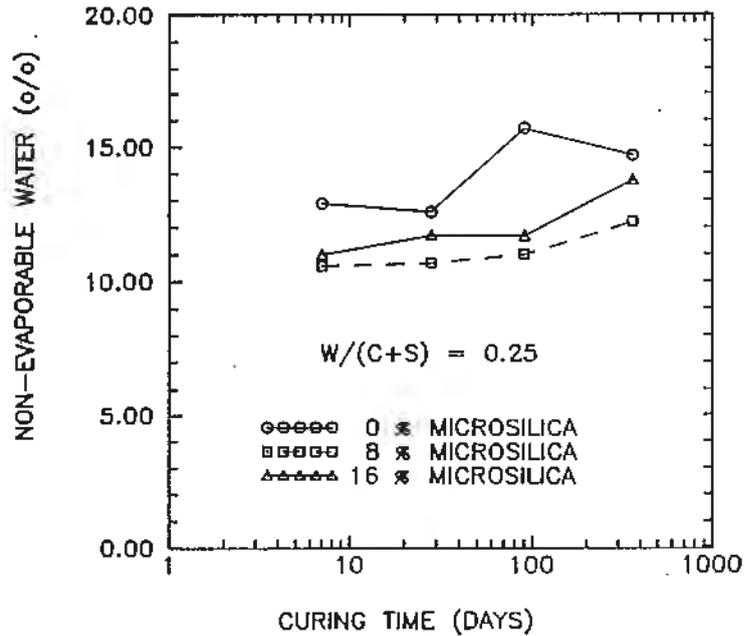with w/(c+s) = 0.40 as a function of Microsilica
dosage a different ages.

Fig. 7 Non-evaporable water in cementitious paste with
w/(c+s) = 0.25 and different dosages of Microsilica as
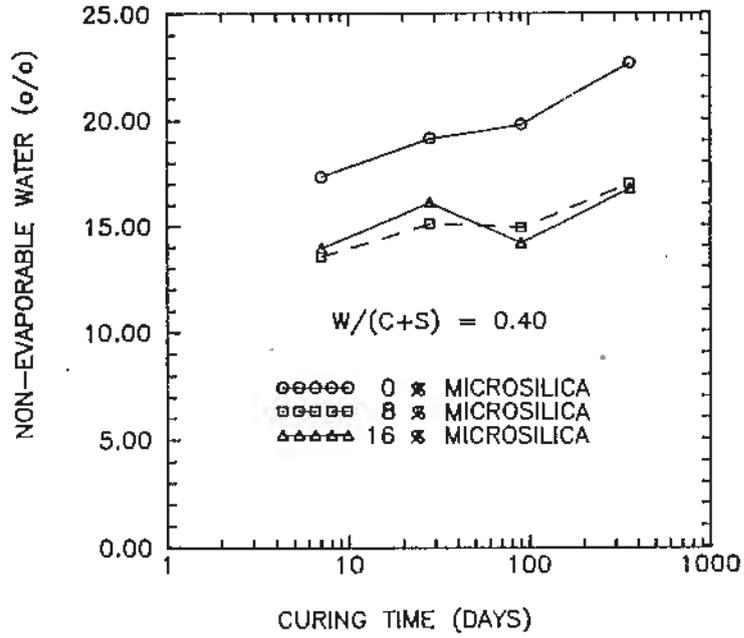a function of curing time (precured at 50°C).

Fig. 8 Non-evaporable water in cementitious paste with
w/(c+s) = 0.40 and different dosages of Microsilica as
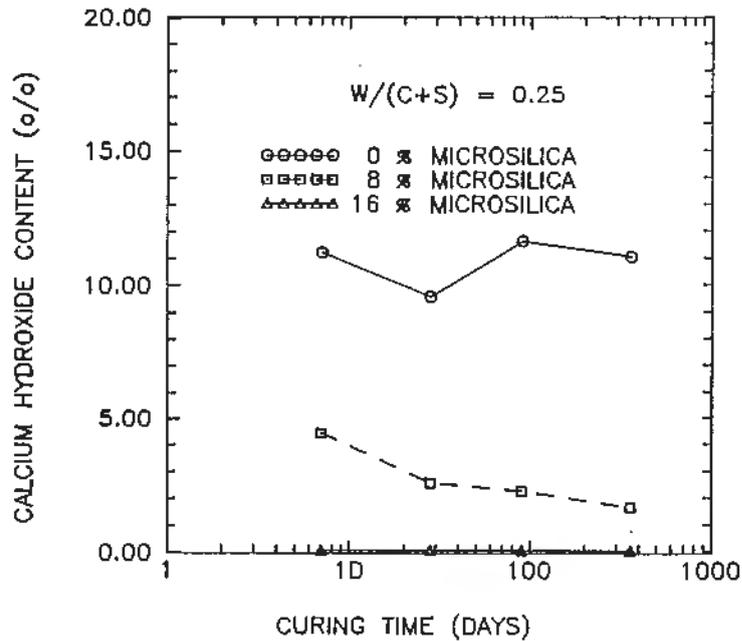a function of curing time (precured at 50°C).

Fig. 9 Calcium hydroxide content in cementitious paste with
w/(c+s) = 0.25 and different dosages of Microsilica as
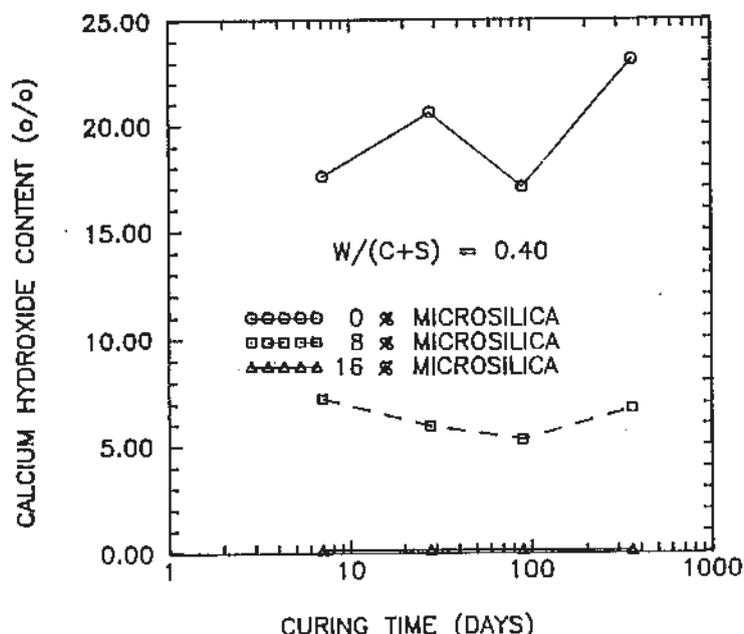a function of curing time (precured at 50°C).

Fig. 10 Calcium hydroxide content in cementitious paste with
w/(c+s) = 0.40 and different dosages of Microsilica as
a function of curing time (precured at 50°C).

4.   DISCUSSION

4.1   Paste series 1 (long term at 20°C)

There is a general tendency for series 1 (as seen from Figures 1 -
3) that the amount of non-evaporable water increases with increas-
ing w/(c+s), and that it slightly decreases with increasing
Microsilica dosages at a given w/(c+s). There is, however, a slight
tendency of a increase in amount of non-evaporable water for the
highest Microsilica dosage (20 %), which might be due to incomplete
drying caused by a denser matrix. The expected increase in non-
evaporable water with increasing w/(c+s) is due to increased degree
of hydration for the cement, while the slight decrease with
increasing Microsilica dosage might be due to a decreasing degree
of hydration with increasing Microsilica dosage at a given curing
time, as proven by Justnes et al /3/. The pozzolanic reaction
between Microsilica (MS) and calcium hydroxide (CH), vizualized as
a decreasing CH content with increasing MS dosage for a given
curing time in Figures 4 - 6, does not consume any additional water
to that bound in CH according to Justnes and Sellevold /4/.
However, Justnes /5/ showed that in a mix of CH and MS with the
molar ratio Ca/Si = 1.1, the MS consumed 35 % additional water
compared with what was contained in the CH.

From 90 to 420 days, the amount of non-evaporable water increases for all mixes, with the exception of the paste with $w/(c+s) = 0.30$ and 20 % MS. The observed increase is due to the increased degree of hydration, while a decrease may be caused by water expelled by the polycondensation process of the silicate anions in the CSH-gel as shown in Eq. 1. The hydration and polycondensation are simultaneous reactions, but the hydration (leading to more chemical bound water) is dominating by far before 28 days sealed curing. Zhang and Gjørv /2/ found a decrease in non-evaporable water as a function of time in cementitious mixes with MS, in contrast to Justnes et al /3/.

Figure 4 and 5 reveals that the CH is depleted in pastes with both 0.20, 0.25 and 0.30 at a 20 % MS replacement before 90 days curing at 20°C and before 420 days curing for a 15 % MS replacement (420 days data for $w/(c+s) = 0.35$ are lacking). The general tendency is a higher CH reserve for a given MS dosage with increasing $w/(c+s)$ (i.e. higher degree of hydration). However, for a paste with $w/(c+s) = 0.40$ (Figure 6), CH is depleted at both 90 (barely detectable) and 420 days curing when 15 % of the cement is replaced by Microsilica. The latter effect may be due to a more permeable matrix leading to a more rapid establishment of chemical equilibrium.

The pH values for the pore water of cementitious pastes listed in Table 2 reveal that when CH is still present in detectable (by DTA/TG) amounts, pH ≥ 13.0 (9 measurements). When CH is depleted, however, $13.0 > $ pH $ > 12.5$ (1 value). Note that the pH in equilibrium with solid CH is 12.5. The still high pH when CH is depleted might be due to minor amounts (about 1 -2 %) of alkali silicates (e.g. sodium metasilicate, Na_2SiO_3) formed by the reaction of alkalies (Na_2O & K_2O) with MS (SiO_2). As a comparison; a 0.1 N solution of sodium metasilicate exhibits pH = 12.6. Another possibility is that the CSH-gel itself is alkaline. In fact, the CSH-gel may incorporate free hydroxyl ions as a consequence of high C/S-ratio. Bentur et al /6/ found that a larger amount of CH could be __extracted__ from CSH than what could be measured by X-ray diffraction. May be such an amorphous CH will loose water at a different temperature than crystalline CH, and thus avoid registration as CH in DTA/TG.

4.2 Paste series 2 (initially cured at 50°C)

The amount of non-evaporable water as a function of curing time seems to increase with increasing curing time for pastes without Microsilica at both $w/(c+s) = 0.25$ and 0.40 (due to increased degree of hydration). When MS is included, the amount of non-evaporable water is at a lower level, but still increasing (apart from a few exceptions) with increasing curing time. The lower content of non-evaporable water may be explained by a halt of the hydration process caused by a densification of the CSH-gel around the cement grains or by the fact that the MS produces more gel which adsorbs water and thus cement hydration stops due to lack of "free" water /3/. The pozzolanic reaction may /5/ or may not /4/

what is bound in the CH, probably depending on the reaction conditions (w/(c+s), MS dosage etc). A decrease in the amount of non-evaporable water (as observed for some time intervals in Figures 7 and 8) over time when MS is included in the paste might be due to a polycondensation process of the polysilicate anions in the CSH-gel liberating water as visualized in Eq. 1. The changes in content of non-evaporable water as a function of time, MS dosage and w/(c+s) may be understood with the basis in the three preceding fundamental reactions.

The tetrahedra in Eq. 1 symbolize SiO_4-groups with oxygen in the corners and a silicon in the centre. The condensation can only occur when the silicate anions contain at least one hydroxyl group (Si-OH), each in place of a terminated Si-O⁻ bond. The result is a connecting Si-O-Si (siloxane) bridge.

(1)
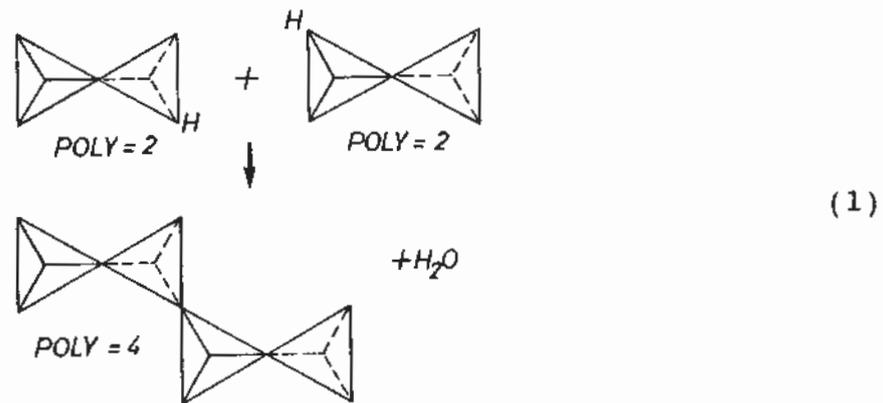
Evidence for the occurence of such a polycondensation process as described in Eq. 1 has been presented by Justnes et al /3/ by the use of Solid State ^{29}Si MAS NMR.

Zhang and Gjørv /2/ also found a decrease in non-evaporable water in cementitious pastes with w/(c+s) = 0.20, 0.30 and 0.40 between 90 and 550 days curing at 20°C when MS was included. The effect increased with increasing MS dosage. However, this tendency was not confirmed by Justnes et al /3/.

The calcium hydroxide content of series 2 depicted in Figures 9 and 10 reveals that at 16 % MS dosage and w/(c+s) = 0.25 and 0.40, the CH content is depleted already after 7 days curing. Thus, the effect of only a slight increase in curing temperature (50°C) the first days is strong (compared with Figure 6) with respect to the CH content. Justnes and Havdahl /1/ showed that the degree of hydration is similar at 20 and 50°C initially curing, but the pozzolanic activity increases. However, this is not sufficient to explain CH depletion if the reaction products should have the same composition. Thus, the CSH-gel formed at an elevated initially curing temperature is characterized by a higher molar C/S-ratio. This may be caused by the anomali of CH with respect to solubility as a function of temperature. The solubility of CH decreases with

increasing temperature; 1.15, 0.92, 0.80 and 0.59 g/l at 21, 50, 70 and 90°C, respectively. When intial gel is formed around the hydrating cement grains, the lower solubility of CH may reduce the diffusion rate through this gel and thereby favour the stabiliza- tion of a gel with higher C/S-ratio.

The findings regarding the relation between pH and CH content for series 1 are confirmed by series 2 (1 value with CH and 1 without). Furthermore, Justnes and Havdahl /1/ support the results with additional independent values; cementitious pastes with w/(c+s) = 0.25 and 16 % MS cured initially (72 h) at 20, 50, 70 and 90°C contained after 25 days additional sealed curing at 20°C pore waters with pH 12.94, 12.60, 12.48 and 12.58, respectively. Only the paste cured at 20°C contained detectable CH.

Zhang and Gjørv /2/ measured the pH in the porewater of a 550 days sealed cured cementitious paste with w/(c+s) = 0.20 and 16 % MS (without detectable CH) to be 12.7, while other samples with CH all had a pH > 13.2, confirming the results in the present investiga- tion.

Due to the high pH-level even when CH is depleted by the pozzolanic reaction, there should be no risk of rebar corrosion in a reinforc- ed concrete based on a matrix of Portland cement and Microsilica. However, if the pH is high due to minor amounts of alkali silicates when CH is depleted, the alkaline reserve is very low. As long as the concrete is not exposed to penetrating water, which is unlikely due to the very dense structure /1/, the reinforcing steel should be passivated. Note that the high pH of alkali silicates will not be lowered by carbonation. On the other hand, if the still high pH when CH is depleted is due to the CSH-gel itself, the alkaline reserve will be vast.

Justnes and Havdahl /1/ demonstrated that cementitious pastes with w(c+s) = 0.25 and 16 % Microsilica cured initially (first 72 h) at 90°C were impermeable to mercury in the MIP (Mercury Intrusion Porosimetry) test and had virtually zero porosity open to helium in the HEP (Helium Pychnometry) test. Consequently, leaching is very unlikely from such a paste.

5. CONCLUSION

The following conclusions may be drawn from the cementitious paste series long term cured at 20°C (series 1):

The amount of non-evaporable water increases with increasing w/(c+s) at a given Microsilica (MS) dosage and curing time, which is due to an increase in degree of hydration for the cement.

At a given w/(c+s) and curing time, there is a tendency of de- creasing amount of non-evaporable water with increasing MS dosage. This is explained by a decreased degree of hydration for the cement

and a pozzolanic reaction consuming little (if any) additional water other than what is bound in the calcium hydroxide (CH).

There is a general tendency of increased CH content with increasing w/(c+s) for a given MS dosage and a given curing time, which again is due to an increase in the degree of hydration for the cement.

The CH content in the cementitious pastes are depleted in pastes with both 0.20, 0.25, 0.30 and 0.40 at a 20 % MS replacement before 90 days curing and before 420 days for a 15 % MS replacement. Thus, it takes time before chemical equilibrium is established (diffusion controlled). However, a 15 % MS dosage is sufficient to consume all CH at ambient temperature.

Even in pastes where CH has been depleted, the pH in the pore water has been measured to > 12.5. This may either be due to minor amounts of alkali silicates or to an alkaline CSH-composition. In the former case, the alkaline reserve will be low.

The following conclusions may be drawn from the cementitious paste series subjected to an initial cure at 50°C followed by 20°C sealed curing (series 2):

The amount of non-evaporable water increases with increasing curing time for pastes without Microsilica and w/c = 0.40 due to an increased degree of hydration (analogous measurements for w/c = 0.25 are more dubious).

When MS is included, the amount of non-evaporable water is at a lower level, but still increasing with increasing curing time (apart from a few exceptions). The lower content of non-evaporable water may be explained by a halt of the hydration process caused by a densification of the CSH-gel around the cement grains or by the fact that the MS produces more gel which adsorbs water and thus cement hydration stops due to lack of "free" water. The pozzolanic reaction will not bind, or only bind minor amounts of, additional water. A decrease in non-evaporable water with increasing age (observed for some time intervals) might be due to a polycondensation process of the polysilicate anions in the CSH-gel liberating water (Eq. 1).

The CH content in pastes with 16 % MS and both w/(c+s) = 0.25 and 0.40 is depleted before 7 days curing. However, the pH of the pore water still exceeds 12.5. The reason for the rapid depletion of CH when the initial curing temperature is elevated, might be related to the anomal decrease in solubility for CH with increasing temperature, which in turn may stabilize CSH-gels with high C/S-ratios.

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