

**PHYSICAL BONDS OF WATER IN HARDENED
CEMENT PASTE**



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ABSTRACT:

By means of a new measuring method based on measurement of relative equilibrium humidity, it has become possible to determine how the states of physical bonding of evaporable water changes in hardened cement mortar with low w/c-ratio, as a consequence of thermal and drying influences.

The tests primarily showed:

- The calculated values for differential wetting enthalpy, ΔH_b , correspond with values obtained by Powers and Brownyard /2/. Thus it is possible, by two completely different measuring methods (Powers and Brownyard's wetting enthalpy was carried out by means of heat of solution calorimeter), to describe the states of physical bonding of evaporable water in hardened cement paste.
- The previous history of the samples, i.e. the drying progress, affects the way in which the structure of the cement paste reacts to temperature influence.
- The calculated wetting enthalpies ΔH_b change with the temperature influence which the samples are exposed to during the measuring procedure. This indicates that a change takes place of the states of physical bonding of evaporable water.
- Measurements indicate an irreversible change of the cement paste structure, as

a consequence of changes in the states of physical bonding of evaporable water.

Keywords:

Low w/c-ratio, cement paste structure, thermo-dynamics, bonds of water, irreversible changes of structure, temperature influence.

1. INTRODUCTION

The project on which this article is based took its starting point in the fact that in recent years building industry has been spending considerable amounts on the development of fibre-reinforced, cement-bound thin slabs. Fibre-reinforced, silica-containing, superplasticised cement mortars with a low w/c-ratio are used for these products. A number of examples show that today manufacturers master the casting technique of the manufacturing process. High strength combined with workability has made it possible to manufacture a number of new, untraditional building components in fibre mortar.

However, the use of these thin slab products for building purposes has disclosed a number of material technological difficulties. Among other things, cracks/micro-cracks in the mortar matrix frequently develop during the hardening process. Experience shows that these initial cracks may constitute a durability problem. An important factor behind the mechanisms causing crack formation in the mortar matrix is the state of physical bonding of evaporable water in the matrix.

On the basis of these problems, the purpose of the project was

1. to develop a technique, based on measurement of relative humidity, for determination of bond energy of water adsorbed in hardened cement paste.
2. to investigate changes in the states of physical bonding of water in hardened cement paste with the temperature (in the range 20°C - 35°C), and how the changes were influenced by previous drying and heating processes.

2. BONDS OF WATER IN HARDENED CEMENT PASTE

The evaporation heat, ΔH_v , for adsorbed water is related to the energy required for adsorbed water molecules to break away from the solid phase (hardened cement paste) and become vaporous. Similarly, the heat of wetting, $-\Delta H_b$, is related to the amount of energy required to bring back adsorbed water to normal liquid phase. Thus, $-\Delta H_b$ is related to the bond energy existing between the evaporable water and the hardened cement paste. Evaporation heat, ΔH_f , is related to the energy required for the phase transformation of water into gas.

By introducing changes of the relative equilibrium humidity

with the temperature (range 20°C - 35°C) in the Clausius-Clapeyrons equation:

$$\frac{d \ln(p)}{d(1/T)} = - \frac{\Delta H}{R}$$

where: p = partial pressure N/m²
 T = absolute temperature K
 ΔH = difference in enthalpy between two phases J/mol
 R = gas constant

it becomes possible to calculate the heat of evaporation, ΔH_r (adsorbed phase to gas phase). By comparison with table values for the heat of evaporation, ΔH_f (liquid phase to gas phase), the heat of wetting, -ΔH_b (adsorbed phase to liquid phase) can be calculated by means of Hess' law.

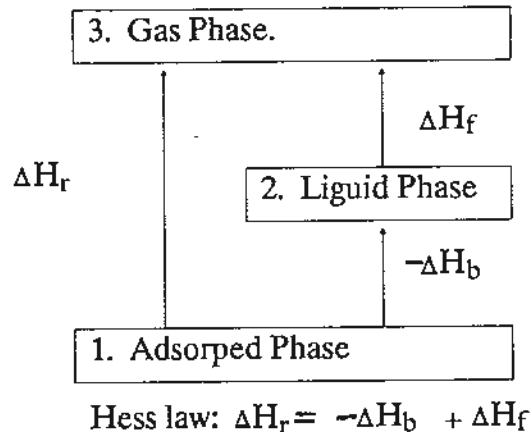


Figure 2.1 Hess' law: The total change in enthalpy by a process connecting two states of equilibrium is independent of the process.

3. EXPERIMENTAL BACKGROUND

3.1 Measuring Equipment/Test Set-Up

For measurement of the relative humidity and temperature, RH-equipment of the ROTRONIC brand was used. The model used was a Rotronic Hygroskop DT with two measuring stations type WA14TH (DMS 100H).

The set-up secures a constant and uniform temperature in the measuring chambers during the tests.

The measuring stations were placed in metal cans lowered into a thermostatically controlled water bath.

The water from the thermostat bath was circulated through bores in the single measuring chambers by a HAAKE E8 thermostat. A uniform water temperature in the thermostat vat was secured by a HETO circulating pump. During tests, the thermostat vat was

covered with an insulating lid of 100 mm polystyrene foam.

The measuring stations were connected to the Rotronic hygroskop showing temperature and RH in the measuring chambers.

Measurement of RH over the samples was done at temperatures 20°C, 25°C, 30°C and 35°C.

The test set-up ensured:

1. that there was thermal equilibrium in the measuring chambers during measurement of relative humidity (RH) over the sample;
2. that emission of humidity from sample to air volume in the measuring chamber was minimal at changes of temperature. The error of relative equilibrium humidity at a change of temperature of 5°C (20°C - 25°C) is estimated to $5.8 \cdot 10^{-4}$ % RH.
3. that no temperature fluctuations existed between sample and sensor.
4. that the temperature effect at the measuring station itself was very low.

3.2 Samples

The tests comprised mortar with a water/(cement+silica)-ratio of 0.2. The mixture is shown in figure 3.1.

	Cement	Silica	Water	Sand	Fibres	Superplastic
Weight percent	33.4	3.3	7.4	53.0	1.1	1.8

Fig. 3.1 Cement mortar mixture. The cement used was white Portland cement and the fibres used were polypropylene fibres.

The mortar was deposited in 250 ml powder glasses which were hermetically sealed after the depositing. The curing of the samples took place in a room with a constant temperature of 20°C.

After curing for 60 days, the samples were crushed and divided into two series (test series 4 and test series 5). After that, the measuring procedure was carried out on the samples from test series 4 whereas the samples from test series 5 were dried/moistured at different relative air humidities (34, 44, 52 and 98% RH) for 2 1/2 months before the measuring procedure was carried out on these samples.

3.3 Measuring Procedure

Each measurement included determination of relative equilibrium humidity RH over a sample at the following temperatures:

20°C, 25°C, 30°C, 35°C

The measuring procedure was divided into 3 measurements:

1st measurement: The measurement was made on a sample not tested before

2nd measurement: The sample was kept in the measuring chamber.
Measuring chamber and sample were cooled down to 20°C.

The measuring procedure was repeated.

The sample was sealed in a glass ampoule and heated for 4 days at 50°C.

3rd measurement: The measuring procedure was repeated on a heated sample.

After the measuring procedure in the measuring chamber, the moisture content of the sample was determined. Determination of the quantity of evaporable water took place by dehydration to constant weight at 105°C.

4. RESULTS

The following section presents the test results with comments and interpretation of general trends.

4.1 (T,RH) Graphs

Figure 4.1.1 shows the test results plotted into (T,RH) graphs. The points marked with (• * □) represent the last measurement made at the temperatures 20°C, 25°C, 30°C and 35°C.

The presentation of the test results on (T,RH) graphs gives a general view of the changes in the RH-level.

4.1.2 Test series 4.

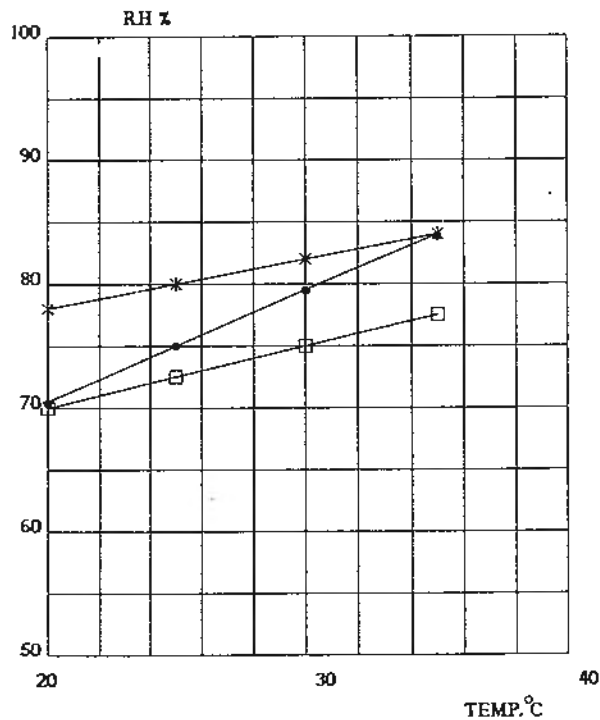


Figure 4.1.1 (T,RH) plot showing the trend in measurements for test series 4, on the basis of sample 4EK. The symbols represent measurements from
● 1st Measurement, * 2nd Measurement and □ 3rd Measurement.

The trends for the results of test series 4 are illustrated in figure 4.1.1. Note the following:

1. RH (20°C) of 1st measurement is below RH (20°C) of 2nd measurement. ΔRH (1-2 measurement) = 8%.
2. RH (35°C) is the same for 1st and 2nd measurement.
3. RH (20°C) is the same for 1st and 3rd measurements.
4. RH (35°C) of 3rd measurement is below RH (35°C) of 1st and 2nd measurement. ΔRH (3-1 measurement) = 8%.
5. As regards the inclination α of the lines through the points of the 3 measurement series, it is characteristic that $\alpha_1 > (\alpha_2 = \alpha_3)$.

4.1.3 Test Series 5.

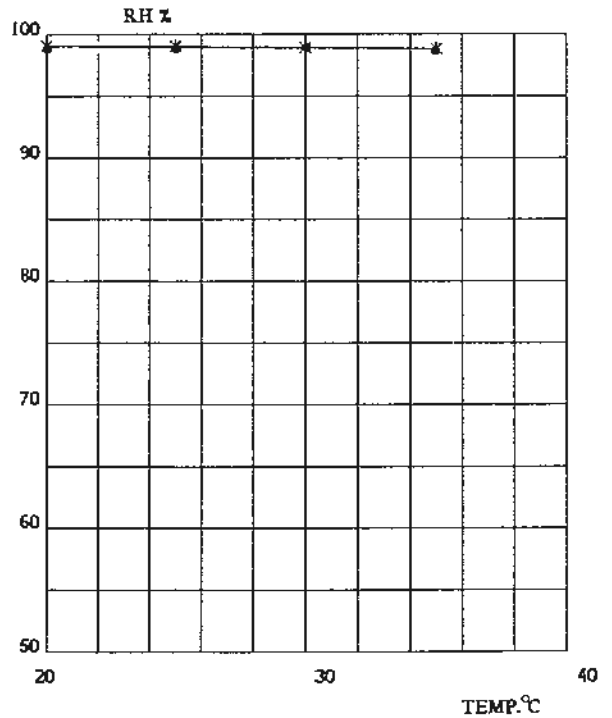
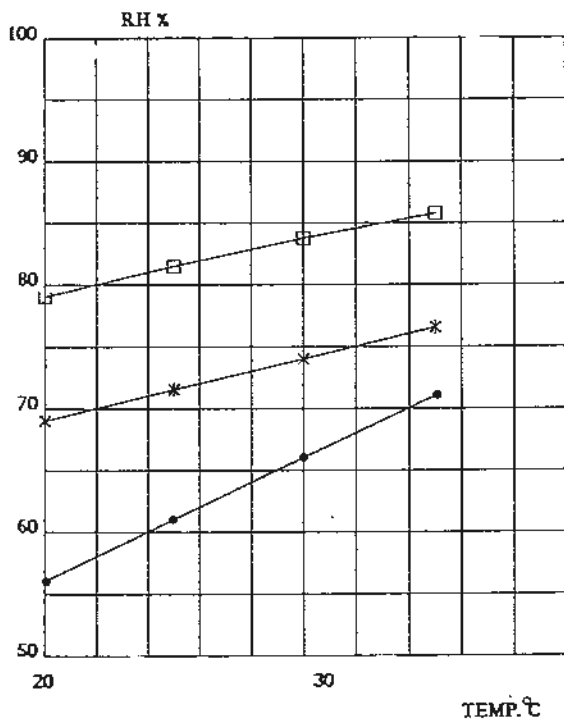


Figure 4.1.2 (T,RH) plot for sample 5A.

●1st Meas., *2nd Meas. and □3rd Meas.

Figure 4.1.3 (T,RH) plot for sample 5D.

●1st Meas., *2nd Meas. and □3rd Meas.

The trends for test series 5 are not as unequivocal as for test series 4. This is mainly due to the testing procedure which the single samples in test series 5 have been exposed to. Sample 5D was moistured to 98% RH.

The main differences and similarities between test series 4 and 5 are illustrated by test 5A (figure 4.1.2) and 5D (figure 4.1.3).

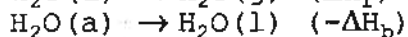
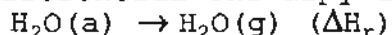
1. RH (35°C) of 2nd measurement is above RH (35°C) of 1st measurement.
2. The line through the points of 3rd measurement is above the lines of 1st and 2nd measurements.
3. As regards the inclination α of the lines through the points of the three measurement series, it is characteristic that $\alpha_1 > (\alpha_2 = \alpha_3)$.

The curves for sample 5D have a special course:

4. The points of 1st and 2nd measurement are approximately identical.
5. The inclinations for the lines α of 1st and 2nd measurement: $\alpha_1 = \alpha_2$.

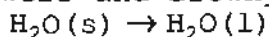
4.2 Calculation of Differential Wetting Enthalpy

Differential enthalpy for the following phase transformation



as well as calculation enthalpy in adsorbed phase are calculated from corrected (RH,temp.)-numbers, by means of electronic data processing.

As standard of comparison, values of $-\Delta H_b$ are used, measured by Powers and Brownyard /1/, and ΔH for the phase transformation:



For the above phase transformation at 0°C, $\Delta H = 6\text{kJ/mol}$.

The $-\Delta H_b$ curve is plotted from an empiric expression of $-\Delta H_b$, acc. to Powers & Brownyard /1/.

4.2.1 Test Series 4.

The results of 1st, 2nd and 3rd measurement for test series 4 are indicated by * in figure 4.2.1-4.2.3. The following is emphasized:

1. The values for $-\Delta H_b$ of the 1st measurement are between 5 and 8 kJ/mol. All values drop to the same level (4kJ/mol.) by the 2nd measurement. At the 3rd measurement, the $-\Delta H_b$ values are between 4 and 5 kJ/mol.
2. At the 1st measurement the $-\Delta H_b$ values are above the plotted curve. The values are almost identical to the curve of the 2nd measurement. At the 3rd measurement the $-\Delta H_b$ values, except one single value, are identical to the plotted curve.
3. One single $-\Delta H_b$ value is below the value of ΔH of the 1st measurement, the rest are above. Both 2nd and 3rd measurement show $-\Delta H_b$ values below the value of ΔH .

4.2.2 Test Series 5

The results of 1st, 2nd and 3rd measurement for test series 5 are indicated by □ in figure 4.2.1-4.2.3. The trends for test series 5 are not as unequivocal as for test series 4. This is primarily due to the curing history of the single samples of test series 5.

Sample 5D, which was moistured to 98% RH, is totally different from the rest of the samples in test series 5. The following is emphasized:

1. By 1st and 2nd measurement, sample 5D had a $-\Delta H_b$ value of approx. 0.0 kJ/mol. A 3rd measurement was not carried out on 5D.
2. The $-\Delta H_b$ values for the remaining samples were above the value for ΔH and the plotted curve, at 1st and 2nd

measurement. The values of 2nd measurement are closer to the plotted curve. At 3rd measurement, the values are below the value of ΔH and the plotted curve.

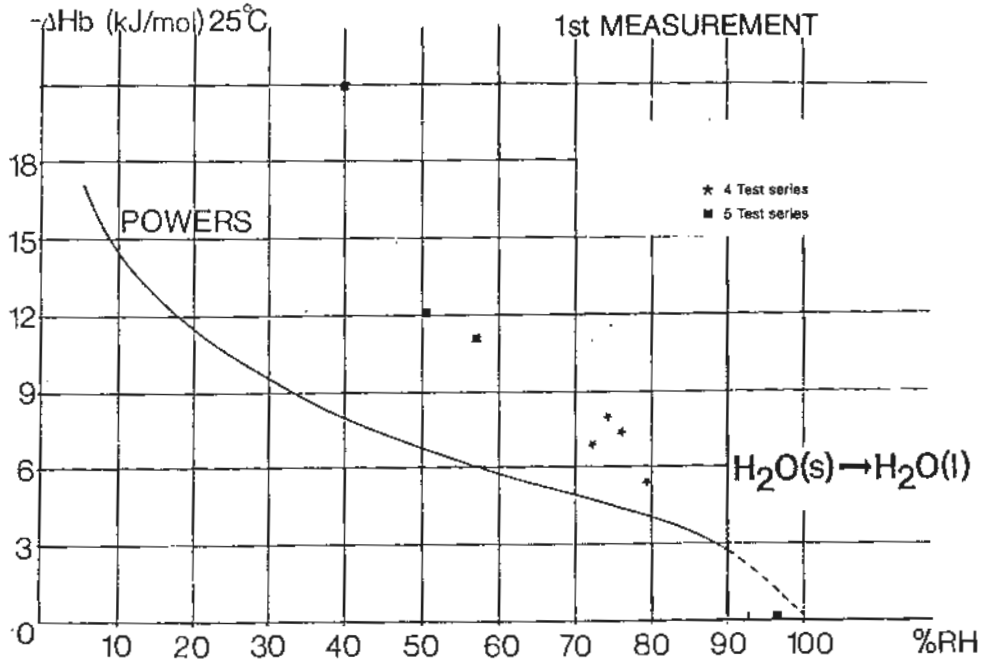


Figure 4.2.1 (RH, $-\Delta H_b$) plot showing trends in measurements for test series during 1st measurement. The plotted $-\Delta H_b$ curve appears from experimental data for $-\Delta H_b$, acc. to Powers & Brownyard /1/.

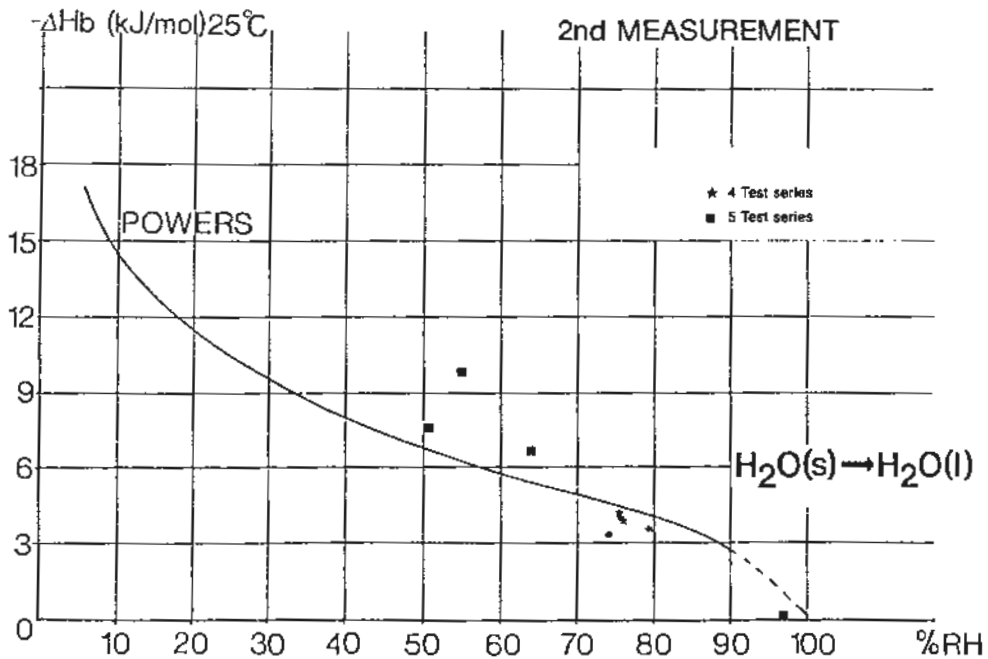


Figure 4.2.2 (RH, $-\Delta H_b$) plot showing trends in measurements for test series during 2nd measurement. The plotted $-\Delta H_b$ curve appears from experimental data for $-\Delta H_b$, acc. to Powers & Brownyard /1/.

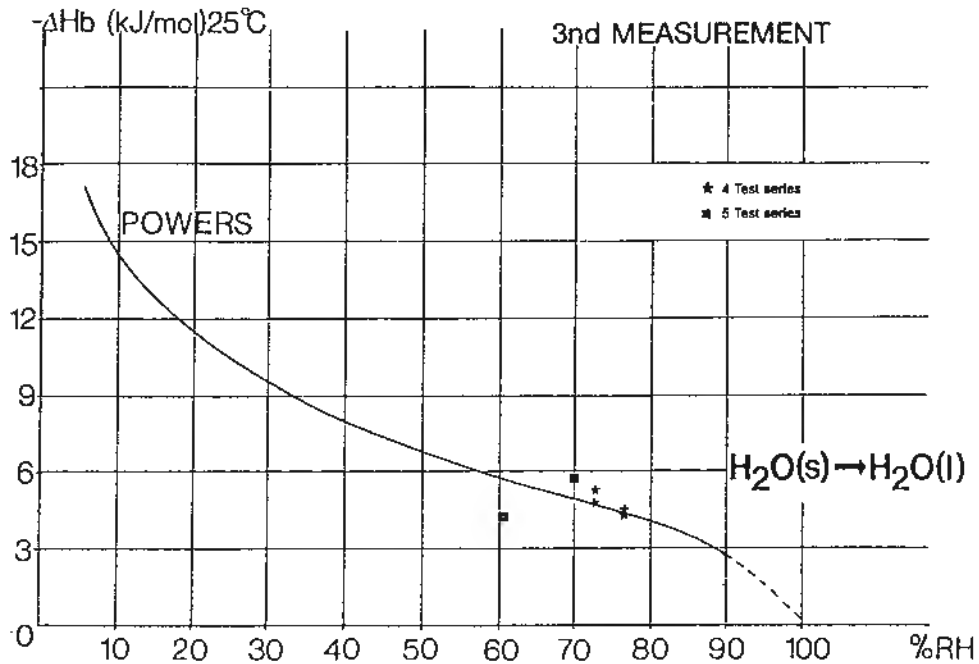


Figure 4.2.3 ($RH, -\Delta H_b$) plot showing trends in measurements for test series during 3rd measurement. The plotted $-\Delta H_b$ curve appears from experimental data for $-\Delta H_b$ acc. to Powers & Brownyard /1/.

5. DISCUSSION

5.1 Comparison with Powers & Brownyard

A comparison with Powers & Brownyard's values for ΔH_b was meant as a starting point, a reference to illustrate whether there was any "point" in the measuring results.

With Powers' testing background in mind, the results of the 2nd and 3rd measurements are in reasonable accordance with Powers & Brownyard's values.

Thus it has been possible, by two completely different measuring methods (Powers used heat of solution calorimeter for determination of the wetting enthalpy) to describe the states of physical bonding of evaporable water in hardened cement paste at given temperature influences.

5.2 Possible Changes in the Structure of the Cement Paste.

If there are any structural changes in the system, they are not unequivocal. Trends in test series 4 and 5 are different which may be ascribed to the previous history of the samples. Figure 5.2.1 and figure 5.2.2 describe schematically how the structure might change for test series 4 and 5.

The following description of structural changes is based on the presence of interlayer water ($H_2O(i)$).

5.2.1 Test Series 4.

1. The system does not gain equilibrium during the 1st measurement. The reason may be that interlayer water molecules penetrate from the structure during the total measurement.
2. The system has gained equilibrium after the 1st measurement and has been cooled down to 20°C. The influence of the temperature may assist in provoking a state of equilibrium in the system. Interlayer water molecules have penetrated from the layered structure and have been adsorbed on the surface. In a few places the structure has collapsed as a consequence of water molecule transport from the layered C-S-H gel. There is now a state of equilibrium between $H_2O(i)$, $H_2O(a)$ and $H_2O(g)$.

The trend in the 3rd measurement for test series 4 is in contradiction to the development of the sample during 1st and 2nd measurement. The sample gains equilibrium; but the relative level of equilibrium RH is below the RH-level for the 2nd measurement.

- 3A. Will some of the adsorbed water molecules penetrate into the collapsed layered structure? Measurements indicate that the oven treatment rearranges the structure.
- 3B. Due to the oven treatment at 50°C, there is a chemical bond of water molecules so that a further formation of hydrate is provoked. This chemical bond would in that case have to be of such a size that the water is liberated by heating to 105°C. The structure remains collapsed in the places where the water molecules have penetrated from the gel during the 2nd measurement.

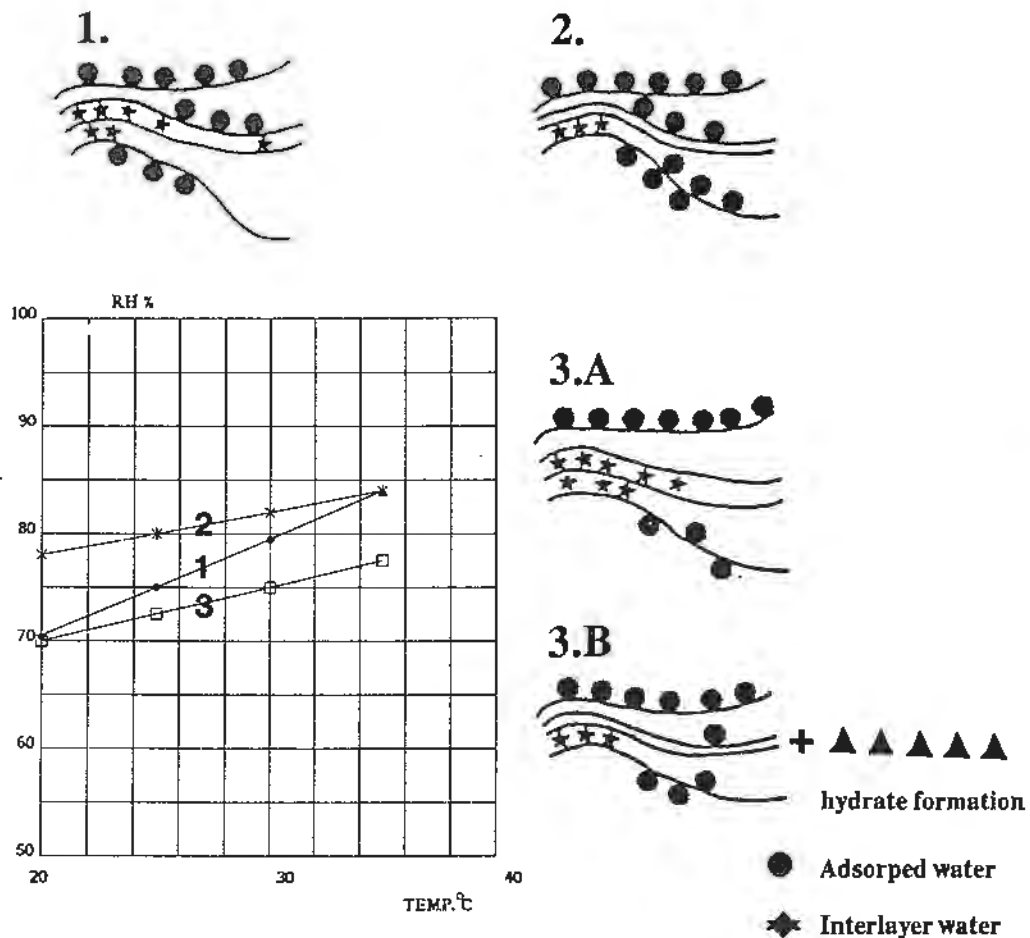


Figure 5.2.1 Schematic view of the structural changes in the hardened cement paste. Test series 4.

5.2.2 Test Series 5.

Figure 5.2.2 shows how sample 5A of test series 5 could change its structure, as a consequence of the influence applied to it during the measuring procedure.

1 & 2. The sample only deviates in the 3rd measurement from the changes described under test series 4.

3A. By an increased temperature influence on the system, more water molecules penetrate from the layered structure of the C-S-H gel. The sample is in a new state of equilibrium, compared with the state of equilibrium of the 2nd measurement.

3B. Concurrently with the changes described under point 3A, a further formation of hydrate might be possible.

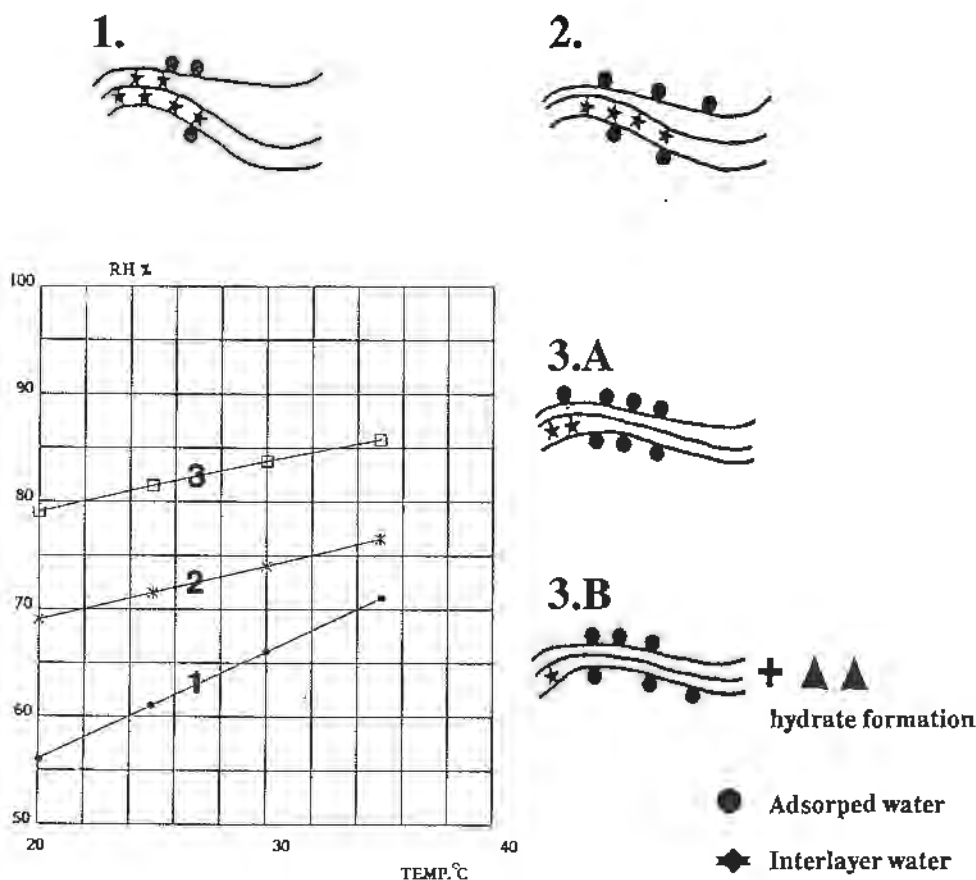


Figure 5.2.2 Schematic view of the structural changes in the hardened cement paste. Test series 5.

6. QUESTIONS

The structural changes in the hardened cement paste described above are based on a modest testing material. Therefore, it will be difficult to make conclusions on the basis of the measurements. However, it is possible to ask questions about the complex reversible/irreversible conduct of hardened cement paste. Questions such as:

A. Measurements indicate the presence of interlayer water.

A1. Will the water molecules be part of the gel structure already from the start of the hydration?

By a summing up of the results of test series 4 and 5, measurements indicate that some of the water molecules from the hydration process exist as physically bound water molecules in the gel structure. By a water molecule transport out of the gel this will collapse and the water molecules will not be able to penetrate into the layered structure again.

- A2. Measurements also indicate that a temperature influence, an increase of the temperature in the system, causes increased activity of the water molecules in the gel structure. Do the water molecules penetrate faster from the structure at 30°C than at 20°C? Can this be the reason for the samples gaining equilibrium in the 2nd and 3rd measurement?
- B. Will the oven treatment cause a further formation of hydrate?
- C. Measurements indicate that evaporable water in hardened cement paste does not have an unequivocal state of equilibrium. Does this mean that the state of equilibrium at a given temperature depends on previous temperature influences, as well as on the previous history of the samples?

7. CONCLUSION

It is possible to extract the following essential trends on the basis of the limited number of tests:

- The test set-up used for the project was able to secure a constant and uniform temperature in the measuring chambers. Temperature variations was 0.01°C between sensor and sample.
- The calculated values for differential wetting enthalpy ΔH_b of 2nd and 3rd measurement (measuring procedure consisting of 1st, 2nd and 3rd measurement) are in accordance with values obtained by Powers and Brownyard /2/. Thus it has been possible, by two completely different measuring methods (Powers and Brownyard's determination of wetting enthalpy took place by heat of solution calorimeter), to describe the states of physical bonding of evaporable water in hardened cement paste.
- The calculated differential wetting enthalpies (ΔH_b) for the samples depend on the temperature influence which the samples are exposed to during the measuring procedure. This indicates that a change of the states of physical bonding of evaporable water takes place.
- The previous history of the samples, i.e. drying progress, affects the way in which the structure of the cement paste reacts.
- Measurements indicate an irreversible change of the cement paste structure, as a consequence of changes in the states of physical bonding of evaporable water.

The developed technique, which is based on measurement of relative equilibrium humidity for determination of bonding energy, seems promising and may therefore form the basis of further studies of bonding energies, among other things for the

variety of special products developed within the last 10-15 years.

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