INFLUENCE OF CEMENT TYPE ON THE DESORPTION ISOTHERM OF MORTAR

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ABSTRACT

Water vapour desorption isotherms have been determined by the dessicator method on mortars made with seven different commercial cements. Both the chemical composition and the fineness of these cements varied. Two water-to-cement ratios were used; 0.40 and 0.60. The change in relative humidity due to chemical dessication was also registered on these mortars up to the age of one year.

The most obvious influence on the desorption isotherm is exerted by the fineness of the cement, especially above 45 relative humidity. A finer cement gives a finer capillary pore structure. Chemical desiccation also led to very different relative humidities when different cements were used.

Key words: Desorption isotherms, chemical dessication, cement type, pore structure

1.   INTRODUCTION

Several researchers have published aricles on water vapour desorption isotherms of cement paste /1,2/, mortar and concrete /3/. But the methods used to achieve these isotherms and the cements have not been the same. Some have used a method where one piece is run through the entire isotherm in small steps and others have left separate specimens dry in different relative humidities. But even if the methods are the same they have used different criteria for when eqilibrium could be assumed. Therefore it is difficult to compare the results and discern the influence of different parameters.

A project with the aim to investigate the influence of the properties of the cement on the desorption isotherm of mortar was

started at Chalmers University in 1987. Seven different commercial Swedish cements that were available on that occasion were involved in the experiment. Both the chemical composition and the fineness of these cements varied. Some preliminary results were briefly presented in 1989 /4/. The present article gives a detailed description and discussion of the results.

As an example of practical consequences that may arise from any differences in the shape of the isotherm, the change in relative humidity due to chemical dessication up to the age of one year was also registered for the different mortars.

2 EXPERIMENTAL

2.1 Materials

The cements came from three different cement factories; Degerhamn, Skövde and Slite. Some contained limestone filler and one fly ash. The properties of the cements are given in Table 1.

Table 1
Some properties of the cements

	Trade name	Spec. surf. area m^2/kg	Mineral ad- mixture	C_3A- con- tent %	N_2O- eq. %	
DLS	Degerhamns Anläggnings- cement	330	–	2	0.5	low heat sulphate resistent
DIC	Degerhamns Injekterings- cement	600	lime- stone 5%	2	0.5	
SKP	Skövde Standard Portland	380	lime- stone 5%	8	1.0	
SKR	Skövde Snabb- hårdnande P.	580	–	8	1.1	rapid hardening
SKM	Skövde Modifierat P.	580	fly ash 23%	8	1.1	
SLP	Slite Standard Portland	380	lime- stone 5%	8	1.1	
SLR	Slite Snabb- hårdnande P.	550	–	8	1.1	rapid hardening

The aggregate was quartz sand 0.25 - 2 mm, with a specific gravity of 2650 kg/m³. No admixtures were used.

2.2 Specimen preparation

From each cement two mixes of about $1 \cdot 10^{-3}\,m^3$ were prepared according to the following weight proportions:

Alt 1: W/C=0.40, Aggr./Cement=2.256

Alt 2: W/C=0.60, Aggr./Cement=3.741

The mortars were mixed in a laboratory mixer in the standard manner way and cast into steel moulds 40×40×160 mm. After 1 day in the covered moulds the prisms were tightly wrapped in several plastic bags. After 28 days the mortar prisms were wet sawed into discs 2 to 4 mm thick. The mortar discs weighed between 9 g and 20 g with a large majority around 13 g. 3 pieces per climate were prepared from each mix.

In order to determine the chemical dessication small amounts of the fresh mortars were put into glass tubes which were then sealed.

2.3 Test methods

The isotherms were determined by the desiccator method. Each point on the isotherm was obtained independently by letting separate saturated specimens dry in seven selected relative humidities (RH) until they reached weight equilibrium. The climate in the dessicators was controlled by saturated salt solutions, giving RH:s ranging between 11.3% and 96.5% The dessicators were specially fabricated sealed plastic containers that were equipped with a fan to assure an even climate in the container.

The weighing was carried out on an analytical balance in laboratory atmosphere. Steps were taken in order to disturb the climate around the pieces as little and as briefly as possible during this procedure. Previous to the dessication the pore systems of the specimens were water filled by capillary suction and the excess surface water was wiped off with a damp cloth immediately before the first weight registration. The intervals between weight registrations varied from once a month the first 6 months to every 2 to 4 months thereafter.

Weight equilibrium was assumed when a weight loss less than 0.001g between two registrations had been recorded twice. The specimen requiring the longest time to achieve weight equilibrium determined the experimental time, which was about one year. Since the weight losses for the parallell specimens were almost identical two specimens per climate were left for continuing experiments while one specimen per climate and mix was resaturated with water and then dried in 105°C. After that they were stored in an exsiccator with a desiccator until they could be analyzed thermogravi-metrically in a programmable thermobalance (LECO Mac-500). In order to distinguish different sources of the weight loss, a program with 5 temperature steps was used; 105°C, 380°C, 600°C, 750°C and 975°C. At each step the temperature remained constant until a weight loss less than 0.05% was recorded three times with a three minute interval.

Since the specimens had previously been dried in an oven the first temperature step (room temperature up to 105°C) only took away the evaporable water absorbed during the storage.

During the second step (105°C - 380°C) most of the hydrate water of the CSH-gel goes away and between 380°C and 600°C (step 3) the $Ca(OH)_2$ will dehydrate.

At the fourth step (600°C - 750°C) the calcium carbonate will decompose so that CO_2 will be liberated. Only minor weight losses originating mainly from other compounds and impurities were recorded during the fifth step between 750°C and 975°C.

The thermobalance could take 19 samples of about 5 grams simultaneously and it recorded weight losses down to 0.25 mg. Each specimen was divided into three samples for the analysis. The raw materials were also submitted to this procedure and the weight losses of the specimens were corrected for the weight losses of the raw materials.

The relative humidity was measured with RH-measuring tools as in /3/.

3. RESULTS AND ANALYSIS

3.1 Nonevaporable water content and carbonation

The thermogravimetric analysis was mainly intended to give the nonevaporable water content and the degree of carbonation of the specimens. The only measure that had been taken to avoid carbonation of the specimens during the experimental time was to keep them away from room atmosphere in sealed containers. However, the containers were opened each time the specimens were to be weighed, which also took place in a normal atmosphere. Therefore a restricted carbonation must be taken into account. Even if the carbonation is only superficial it may be of great importance for the results since the specimens are only around 3 mm thick. Consequently the actual recorded relative weight losses between 600°C and 750° (step 4) also varied considerably.

In order to quantify the carbonation the simple assumption was made that carbon dioxide first of all reacts with the calcium hydroxide forming calcium carbonate, liberating one water molecule:

$$CO_2 \;+\; Ca(OH)_2 \;\Rightarrow\; CaCO_3 \;+\; H_2O$$
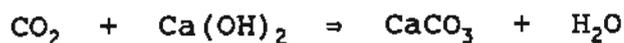
molecular weight: (44)   (18)
decompose at, °C: 380-600   600-750

So for each gram of CO_2 that has been fixed 18/44 grams of water has left the $Ca(OH)_2$ and the total weight gain is 26/44 grams.

Pieces of mortar from the interior of sealed prisms were used as totally uncarbonated references. Some cements contained limestone filler and thus had a large amount of calcium carbonate from the beginning. The thermogravimetrical analysis showed that when these

cements hydrated their calciumcarbonate content diminished, which indicates that the limestone is not a totally inert filler but some of it is transformed into aluminum- and other carbonates who will decompose at higher temperatures /5/. With these cements the recorded weight loss of the specimens between 750°C and 975°C also increased. Therefore the difference in loss above 600°C between the references and the specimens was assumed to be carbonation and the weight loss between 380°C and 600°C was then corrected according to the above proportions.

However, the degree of hydration may differ between the tested specimens and the references. The dehydration of the CSH-gel (step 2) is not particularly affected by a minor carbonation and thus the degree of hydration may be assumed to be proportional to the weight loss at this step.

The corrections were as follows:

$$\text{Step 4:} \quad \Delta S4 = - (S4 + S5 - (R4+R5) \cdot S2/R2)$$

$$\text{Step 3:} \quad \Delta S3 = - \Delta S4 \cdot 18/44$$

where S2, S3, S4, S5 and R2, R4, R5 are the weight loss per ignited cement at temperature step 2,3,4 and 5 of the specimens and the references respectively.

The nonevaporable water content is then defined as the total corrected weight loss of the specimens between 105°C and 975°C (S2+S3+S4+S5+ΔS3+ΔS4) and the amount of CO_2 due to carbonation is ΔS4.

Figure 1 shows the amount of nonevaporable water content in the specimens as a function of the relative humidity they have been submitted to. 'Ignited cement' is the remains of the entire cement (including mineral admixtures) after ignition to 975°C. The specimens were not fully hydrated at the start of the desiccation after one month of sealed curing. Therefore the curves are composed of two almost straight lines intersecting each other at 75% RH. When the relative humidity inside the specimen reaches below about 75% RH no further hydration will take place. The small inclination of the curve between 11% and 75% RH reflects the time it takes from the start of the desiccation until 75% RH is obtained in the specimens in the different ambient RH:s. The thickness of the specimen, which varies, also influences the time. Above 75% RH the hydration process continues during the whole experiment and increases with increasing RH.

The amount of nonevaporable water in the mortar with the cement containing fly ash is less than with the other cements. It is also declining at the highest RH (96.5%). This may be due to the pozzolanic activity of the fly ash. Similar tendencies have been observed in mortar with silica fume /6/. Among the Portland cements the highest amounts of nonevaporable water were obtained in the rapid hardening cements and the lowest in the low heat cement and the other three lie somewhere in between.
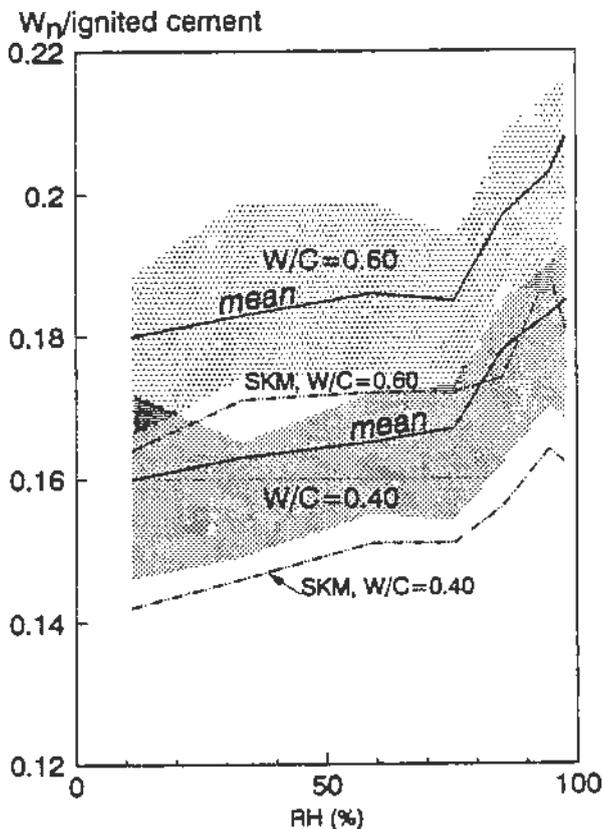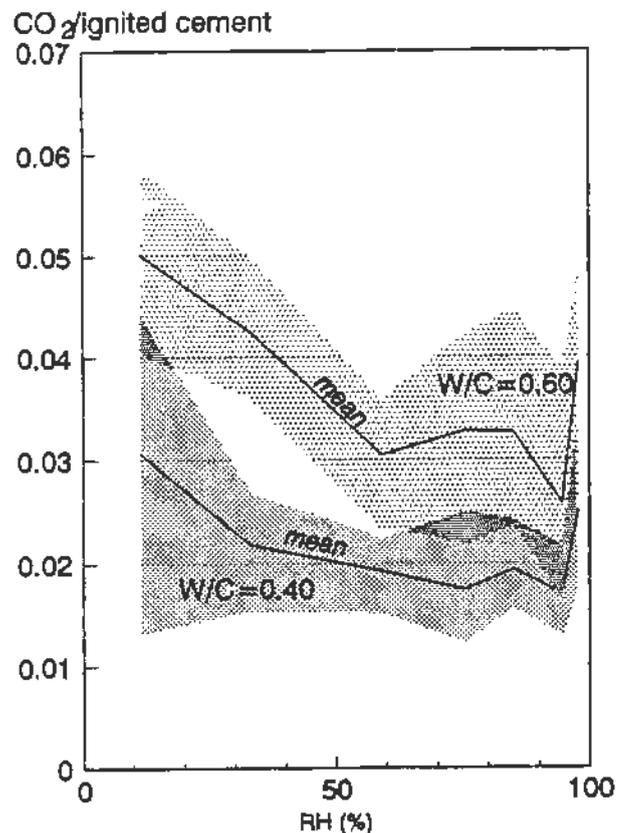
Fig. 1: Nonevaporable water content.

Fig. 2: Amount of CO_2 due to carbonation.

Unexpected results were obtained regarding the amount of fixed CO_2 due to carbonation in different relative humidities as can be seen in Figure 2. Most researchers have obtained more carbonation at a medium RH and less at low and high RH:s, for example Pihlajavaara /7/. In this case the opposite was experienced. This may however be due to the practical arrangements and since the CO_2-content in the containers was neither controlled nor registered in any way no definite conclusions will be drawn from this at this stage The degree of carbonation also varies with the thickness of the specimen. A thin specimen contains more CO_2 per ignited cement than a thicker one. Some cements carbonated more than others as for example the cements from Slite.

In any case only a part of the released $Ca(OH)_2$ in the hydrated specimens is needed for the modest degrees of carbonation experienced in this study.

3.2 Desorption isotherms

The desorption isotherms, i.e. the amount of evaporable water per ignited cement by weight at different RH:s, for all the prepared mortars is given in Figures 3 - 6. For the presentation the cements have been divided into two groups; coarser cements and finer cements with specific surface areas 330 - 380 m^2/kg and 550 - 600 m^2/kg respectively.
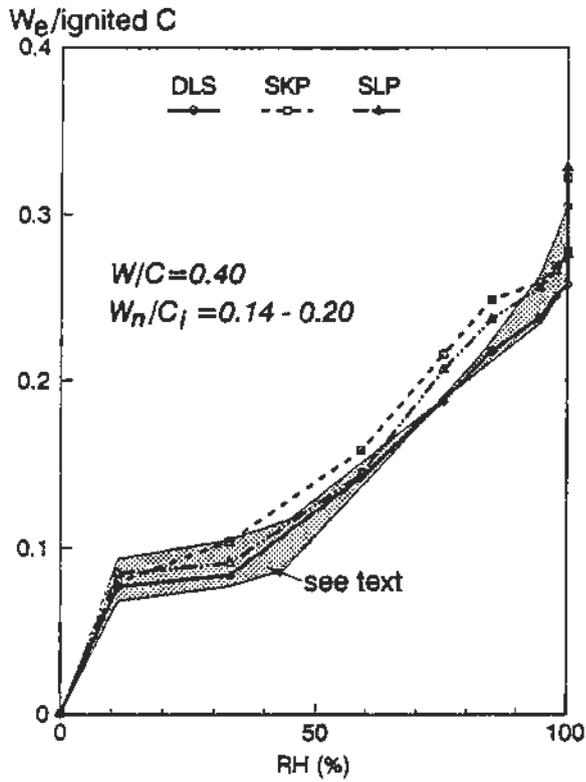
Figure 3: Desorption isotherms for mortar made with coarser cements. W/C=0.40

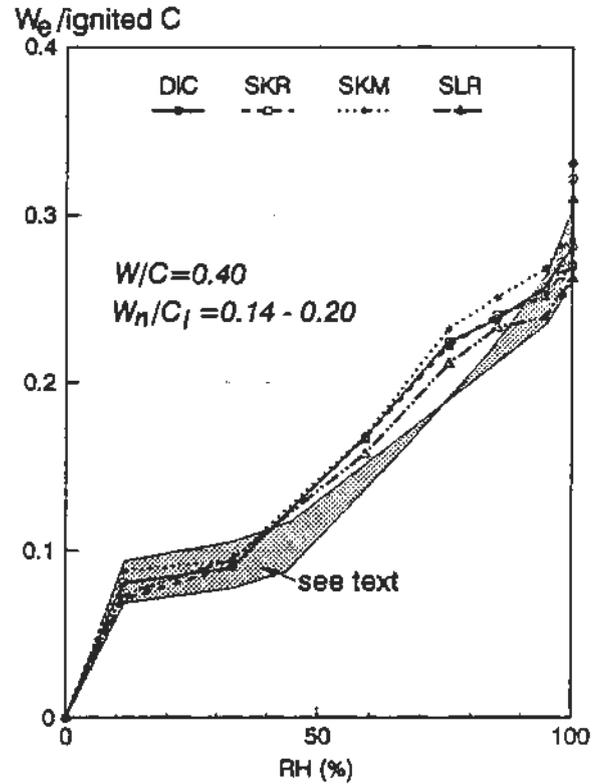

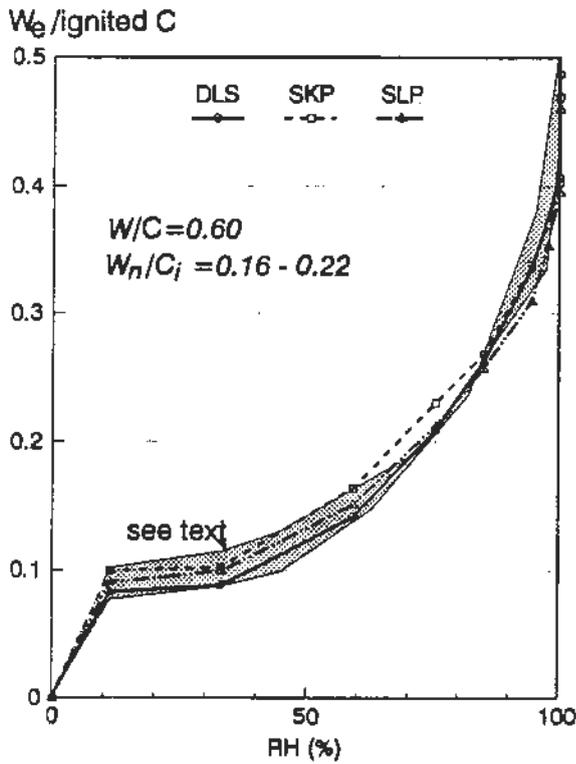Figure 4: Desorption isotherms for mortar made with finer cements. W/C=0.40

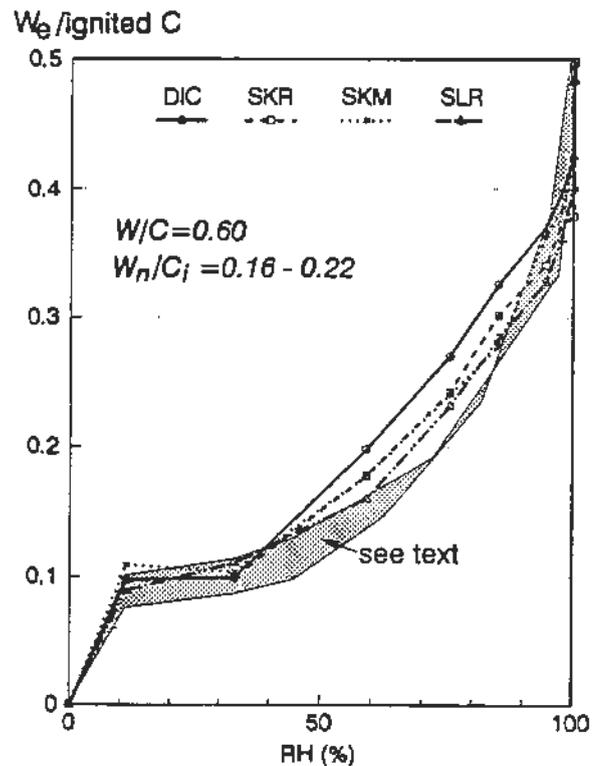Figure 5: Desorption isotherms for mortar made with coarser cements. W/C=0.60

Figure 6: Desorption isotherms for mortar made with finer cements. W/C=0.60

At 100% RH two evaporable water contents for each mix are shown. The lower value is the minimum obtained when filling the pore system by capillary suction at the end of the experiment (high degree of hydration) and the higher value is the water content at the start of the dessication when the degree of hydration was low.

The variation in degree of hydration or nonevaporable water content with ambient RH complicates the cvaluation of the isotherms. For comparision reference isotherm regions (shadowed) based on /3/ and the limiting degrees of hydration have been calculated and are marked in the Figures. To comply with older results the isotherm should lie at the lower side of this region, since lower degrees of hydration gives less evaporable water upto about 45% RH and higher degrees of hydration yields less total pore volume (We at RH=100%). The highest value at 100% RH should coincide with the upper part of the reference region. The ideal cement from this point of view is the low heat, sulphate resistent cement from Degerhamn, both at W/C-ratio 0.40 and 0.60. This is also a pure Portland cement with no admixtures and a moderate fineness; i.e. a traditional type of cement commonly used in the past. The other two coarser cements have a somewhat higher fineness which results in a higher degree of hydration. They also contain about 5% limestone filler. This does not affect the isotherm very much at a water to cement ratio of 0.60 but at W/C=0.40 the influence is obvious. The whole curve is lifted upwards and has a marked shoulder at higher RH:s. The total pore volume is higher even if the degree of hydration is higher. The effect would be even greater if the evaporable water content was given in proportion to the ignited weight of the pure Portland cement content, excluding the filler. The shoulder indicates a filler effect; the volume of larger capillary pores is diminishing and the amount of smaller capillary pores is increasing or at least the pore openings become smaller.

When the grain size diminishes as in the finer cements the capillary pore refinement is even more obvious and the dividing line is at about 75-80% RH which represents a pore radius of about $100 \cdot 10^{-10}$ m. The two rapid hardening cements (SKR,SLR) do not contain any limestone filler so the total pore volume is less than in the standard cements. In the injection cement from Degerhamn (DIC) the refinement effect of both the filler and the small grain size seem to be added to each other, giving an extremely distinct effect evident in both W/C-ratios. The fly ash substitution in the modified cement (SKM) does not influence the isotherm in any unpredictable manner except that it binds a larger amount of evaporable water at low RH:s than could be expected considering its lower amount of nonevaporable water.

3.2   Chemical dessication

The chemical dessication of the mortars is shown in Figures 7 and 8. Two test tubes were prepared from each mix. The evolution upto about 400 days was followed on test tube 1. The other tube was left sealed until the final measurement was to be carried out.
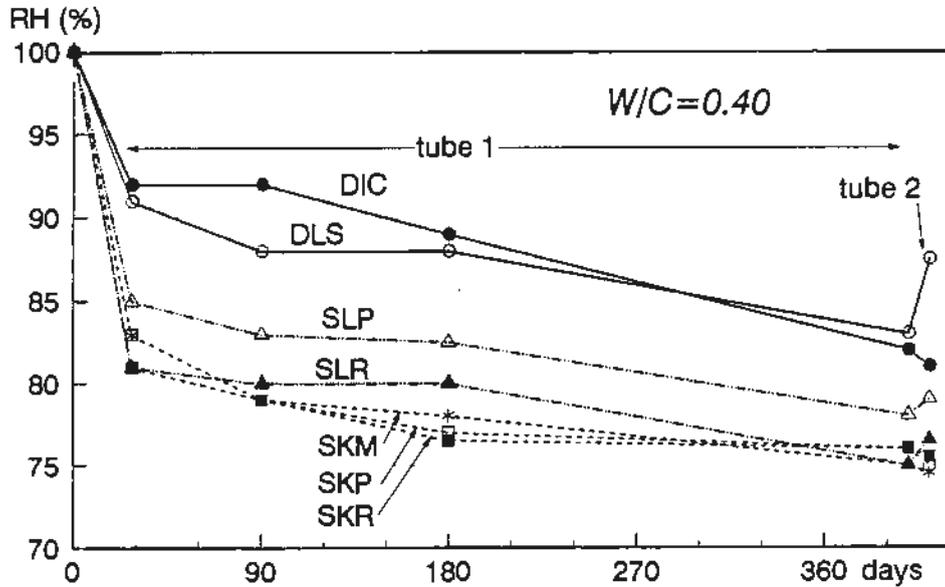
Figure 7:   *Relative humidity in chemically desiccating mortar with different cements.*
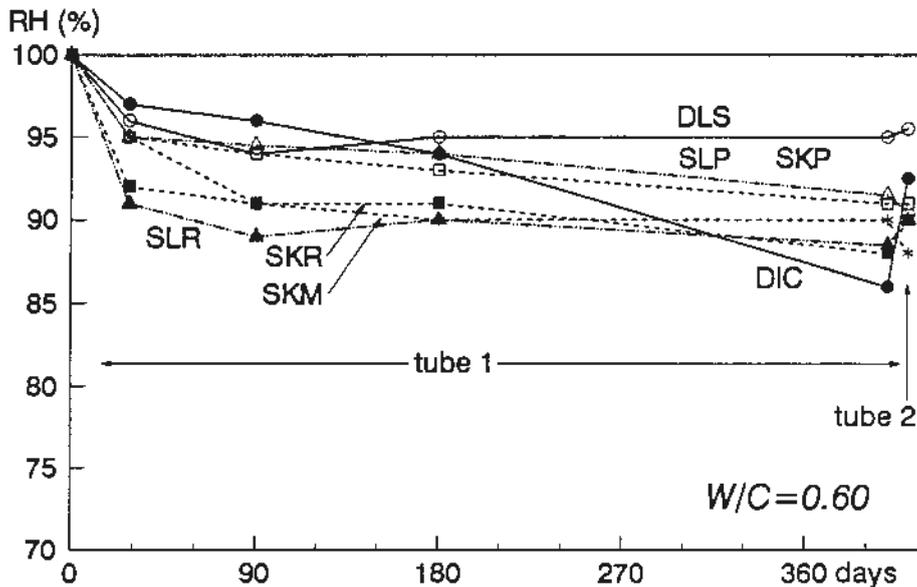*W/C=0.40*

Figure 8:   *Relative humidity in chemically desiccating mortar with different cements.*
W/C=0.60

Evidently two test tubes had not been well sealed between the two
last RH-recordings (DIC:W/C=0.6 and DLS:W/C=0.4) since there is a
great deviation between test tubes 1 and 2. In all the other cases
the difference is hardly more than the accuracy of the instrument
which is about 2 %-units.

The effect of the chemical dessication on the RH of the samples is of course greatest at lower W/C-ratios. There is however a clear difference between the cement types and the most important factor is the chemical composition of the cement. Cements from Degerhamn (which contain lower amounts of C_3A and alkalis) give a distinctly higher RH than cements from Skövde and Slite. The grain size only influences the levels marginally.

It is discussed whether the hydration under sealed conditions is controlled by the RH-level or the amount of evaporable water. Both these factors have been determined on the specimens but neither seem to govern the chemical dessication. However the degree of capillary saturation, i.e. $W_e/(W_e$ at saturation), has been calculated and it was found to be almost constant (90%) in all the samples, not only with the different cements but also at both W/C ratios. All these factors are illustrated in Figures 9 and 10.
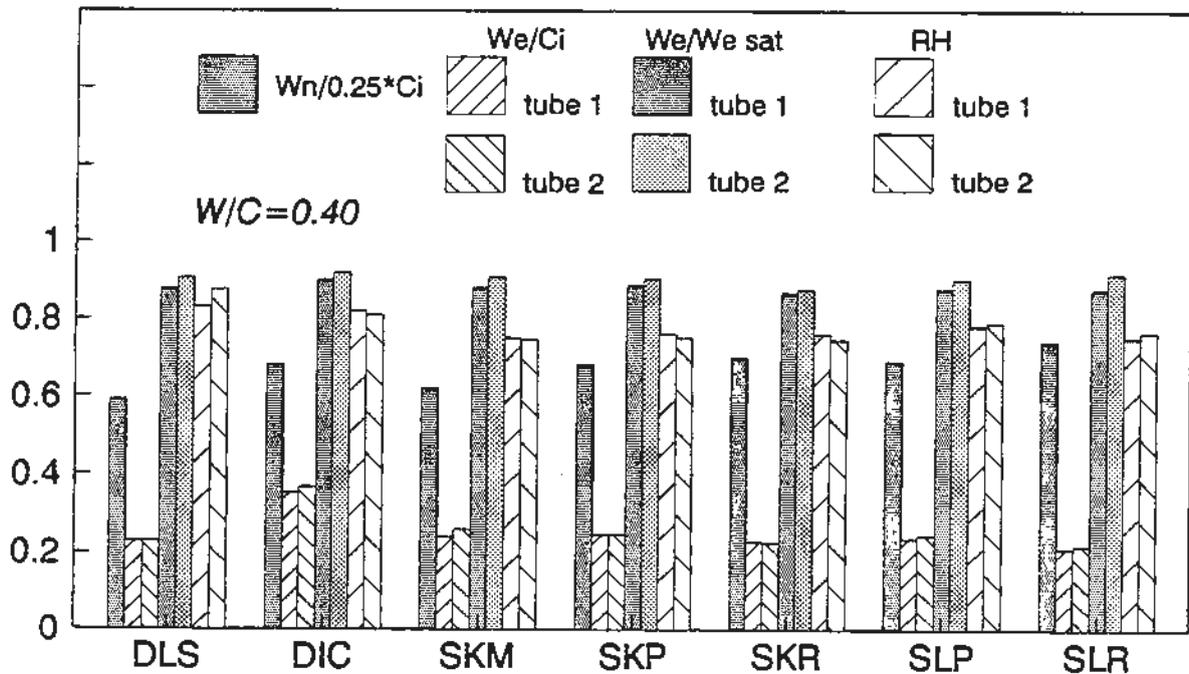

Figure 9: *Moisture parameters in mortar with different cements after 400 days of chemical desiccation. W/C=0.40*

If this is true it is the relative form of the isotherm curve that is important and not the actual levels. Consequently the upper part of the 'shoulder' which is an important point on the desorption isotherm could originate in chemical differences and not in fineness or filler effects. As a matter of fact the shoulder comes between 86 and 75% RH in the low C_3A/alkali-cement which contains filler and is finely ground (DIC) and not between 86 and 94% RH as in the other two finer cements (SKP and SLP). A high fineness of the cement will lower the RH but the filler may increase it by increasing the total pore volume, and it is possible that these

effects counteract each other in the DIC-cement giving it higher
relative humidities than the DLS-cement in the beginning.

One may wonder if the decrease in RH during chemical dessication
only reflects the change in the form of the isotherm and that the
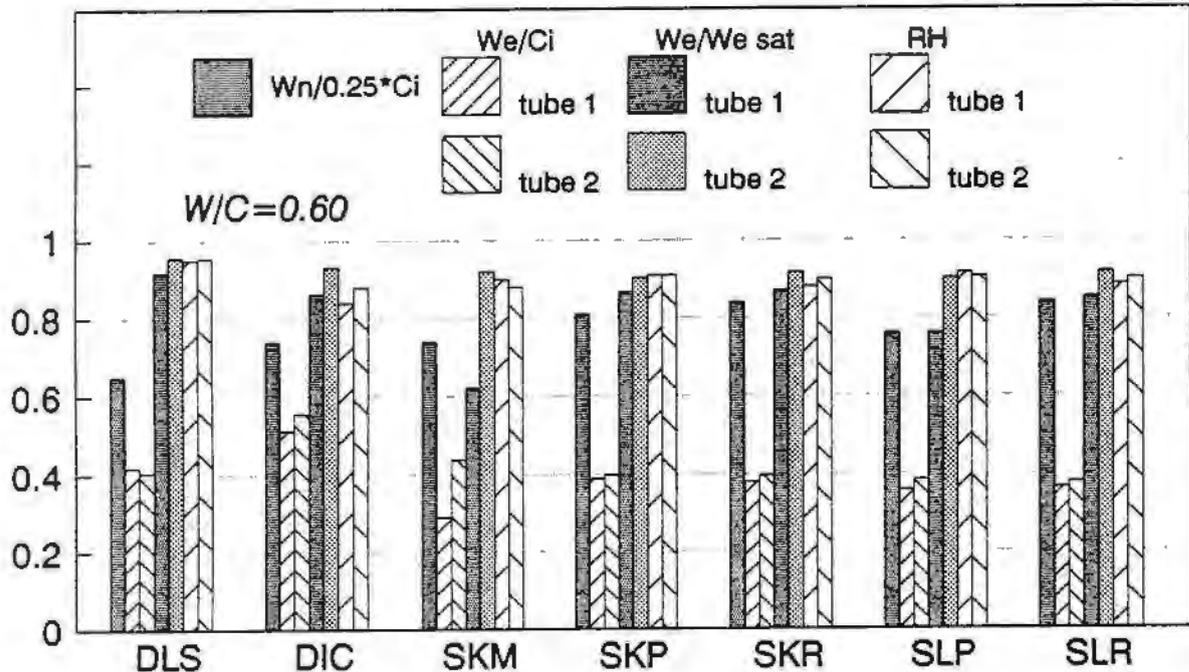degree of capillary saturation is constant after an initial excess
period.

Figure 10: *Moisture parameters in mortar with different cements after 400 days of chemical desiccation. W/C=0.60*

4.   CONCLUSIONS

* Grinding the cement to a high fineness refines the pore structure
or at least the pore openings so that the position of the
desorption isotherm in the capillary region (above 45% relative
humidity) is shifted upwards to the left but keeps the total pore
volume constant for a certain degree of hydration.

* Introduction of limestone filler refines the pore structure in
a similar manner but the total pore volume increases.

* The chemical dessication is greatly influenced by the chemical
composition of the cement; low amounts of C_3A and/or alkalis result
in higher relative humidities.

* The relative form of the isotherm is important for the chemical
dessication; measures giving shoulders high up on the isotherm will
give a faster decrease in relative humidity in the specimen.

5.   REFERENCES

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