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CHEMICALLY BOUND WATER AS MEASURE OF DEGREE OF HYDRATION
Method and potential errors

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INTRODUCTION

"Degree of hydration" is defined as *the fraction of portland clinker* (including gypsum addition) that has fully reacted with water. In this report, degree of hydration is assumed to be directly proportional to the amount of chemically bound water. Thus, it is assumed that a certain quantity of portland clinker binds exactly the same amount of water, may it be at the beginning of the hydration process, or at the end of this.

All chemically bound water is assumed to be lost at igniting the sample to 1000 ºC. No chemically bound water is assumed to be lost at heating to +105 ºC. The degree of hydration is therefore determined by weighing the sample after drying to +105 ºC and after ignition to 1000 ºC. The weight difference corresponds to the chemically bound water content.

The cement may contain components, other than cement clinker, that loose weight at ignition, for example limestone filler that contains bound CO_2 which leaves the sample after +105 ºC, but before 1000 ºC.

The clinker may be partly pre-hydrated (moisture damaged) when the sample is manufactured. Water in pre-hydrated cement shall not be included in the determination of degree of hydration.

The sample may be more or less carbonated. CO_2 from a carbonated cement sample is released at ignition and must be distinguished from chemically bound water in cement.

Aggregate in concrete may contain crystal water that is released at ignition. This water shall not be included in the calculation of degree of hydration.

Ways of making corrections for these potential sources of error are given in the report.

The way of defining the "dryness" of the sample before ignition has big influence on the measured amount of chemically bound water. The more intense the drying, the lower is the measured amount of chemically bound water. In this report, "dryness" is defined as the sample weight at equilibrium at drying at +105 ºC. Instead of drying at +105 ºC, drying can be made by exposing the sample to air of very low relative humidity. The effect of the drying procedure is discussed in APPENDIX 1.

For cement containing mineral admixtures like silica fume, chemically bound water in reaction products from the mineral admixture might be decreased with time, despite the fact that hydration proceeds. A method of compensating for this effect when calculating the degree of hydration of the portland component in the cement is discussed in APPENDIX 2.

I: CEMENT PASTE

Only portland cement paste, with or without mixed-in *inert filler*, is considered. When the cement contains reactive mineral admixtures, like silica fume, fly ash or blastfurnace slag, chemical reactions will occur that actually cause a gradual reduction in the loss on ignition with increased degree of hydration. In these cases, one cannot use the amount of chemically bound water as a measure of degree of hydration. The same restriction is valid if such materials are mixed into concrete. The question is treated briefly in APPENDIX 2.

I:1 Definition of degree of hydration of pure portland cement paste

Degree of hydration is defined as the fraction of cement that has fully reacted with water relative to the total amount of cement in the sample. In the total cement content is not included the part of cement that was pre-hydrated when the cement paste was mixed.

In the laboratory the amount of non-evaporable water content of the cement paste sample, $w_{n,sample}$, is determined by drying, followed by ignition of the same sample.

If the amount of cement in the sample c_{sample} is known the relation $w_{n,sample} / c_{sample}$ can be calculated. This relation is a measure of the degree of hydration.

The cement content c_{sample} in a sample containing no air pores can be calculated from the cement content $C\ (kg/m^3)$ and the specimen volume $V\ (cm^3)$ provided the water cement ratio *w/c* is known:

$$c_{sample} = C \cdot V = \frac{1}{0.32 + w/c} \cdot V \qquad \text{(I.1)}$$

Where the coefficient 0.32 is the specific volume of cement (cm^3/g).

The degree of hydration α of the sample is found by dividing $w_{n,sample}$ with the amount of non-evaporable water in *the same sample* when this is fully hydrated, $(w_n^0)_{sample}$.

$$\alpha = \frac{w_{n,sample}}{(w_n^0)_{sample}} \qquad \text{(I.2a)}$$

A general expression for degree of hydration is:

$$\alpha = \frac{\dfrac{w_{n,sample}}{c_{sample}}}{\dfrac{w_n^0}{c}} \qquad \text{(I.2b)}$$

where w_n^o is the chemically bound water at complete hydration of the cement quantity c.

The quotient w_n^0 / c varies between about 0.18 and 0.26 depending on the composition of the cement; [1]. Often the value 0.25 is used.

I:2 Experimental determination of degree of hydration

I:2.1 Without corrections.

A block diagram over hydrated cement paste is shown in Fig.I.1.

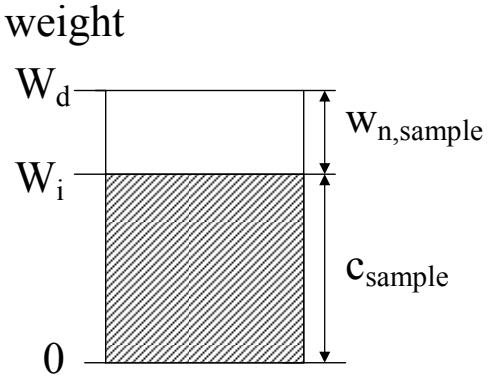


Figure I.1: Components in hydrated cement paste.

The amount of chemically bound water is obtained by drying effective enough that all evaporable water is released. Thereafter ignition at 1000 ºC

$$w_n = W_d - W_i \quad \text{where } W_d \text{ is the weight after drying, and } W_i \text{ is the weight after ignition} \tag{I.3}$$

For pure cement paste the weight after ignition is the same as the cement content in the sample, c_{sample}:

$$W_i = c_{sample} \tag{I.4}$$

Thus, the degree of hydration is obtained by the following equation, see Eq. (I.2b):

$$\alpha = \frac{W_d - c_{sample}}{\frac{w_n^0}{c}} \tag{I.5}$$

The assumptions behind this equation are; (1) the cement is not pre-hydrated at mixing, (2) the cement has no inclusion of limestone filler, (3) the sample is not carbonated. If these conditions are not valid, corrections according to paragraphs I:2.2 to I:2.4 must be made.

Gypsum added to the cement clinker in connection with grinding of this (about 5 weight-%) is included in the concept “cement”, i.e. it is included in the parameters c_{sample} and c as they are used in the equations above.

At calculation of the amount of chemically bound water, the dry weight, W_d, i.e. the weight before ignition, must be well-defined. The dry weight depends on the method of drying the sample. Also the quotient w_n^0 / c, which is used in the definition of degree of hydration depends on the drying method. The effect of drying method is discussed in APPENDIX 1.

Example

The dry weight of a sample is 103 g. After ignition the weight is 83 g. The ratio w_n^0 / c of the actual cement is 0.24.

The degree of hydration of the sample is:

$$\alpha = \frac{103 - 83}{0.24} = 0.83$$

I:2.2 Correction for pre-hydrated ("moisture-damaged") cement

The procedure described above requires that the loss on ignition of the cement before mixing is known, since this shall not be included in w_n. The loss on ignition of the cement before mixing is determined by drying and igniting a cement sample. The loss on ignition is found to be $\Delta w_{n,c} / c$.

A block diagram of a cement paste made with moisture-damaged cement is shown in Figure I.2.

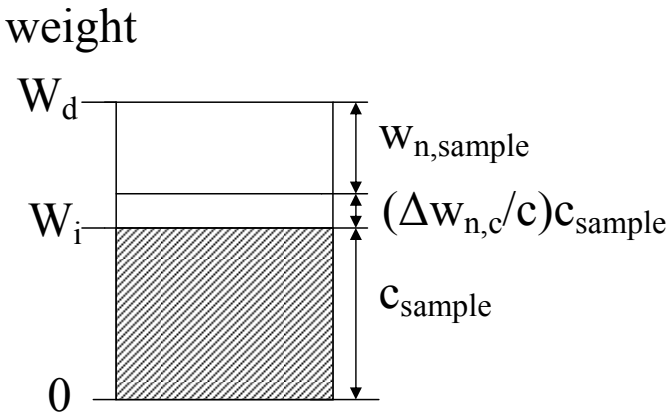


Figure I.1: Components in a cement paste when the cement was pre-hydrated before mixing.

After correction, w_n for a given sample is obtained by the following equation:

$$w_{n,sample} = W_d - W_i - \frac{\Delta w_{n,c}}{c} \cdot c_{sample} \tag{I.6}$$

Insertion in Eq. (I.4) gives:

$$w_{n,sample} = W_d - c_{sample} \cdot \left(1 + \frac{\Delta w_{n,c}}{c}\right) \tag{I.7}$$

At calculation of the degree of hydration the part of the cement that was pre-hydrated at mixing must be excluded. The residual ("effective") cement content in the sample is:

$$c_{sample,efff} = c_{sample} - \frac{\frac{\Delta w_{n,c}}{c}}{\frac{w_n^0}{c}} \cdot c_{sample} = c_{sample} \cdot \left(1 - \frac{\frac{\Delta w_{n,c}}{c}}{\frac{w_n^0}{c}}\right) \tag{I.8}$$

According to Eq. (I.2b) the degree of hydration is:

$$\alpha = \frac{\frac{w_{n,sample}}{c_{sample,eff}}}{\frac{w_n^0}{c}} \qquad \text{(I.9)}$$

Example

The loss on ignition of a certain cement is determined for a cement sample with dry weight 50 g. After ignition the weight is 48 g. This is the effective cement. The residual 2 g can be regarded as inert "filler".

The loss on ignition $\Delta w_{n,c}/c$ is (50-48)/50=0.04 g/g cement.

The sample on which $w_{n,sample}$ shall be determined has the dry weight 120 g. After ignition the weight is 102 g. According to Eq (I.7) $w_{n,sample}$ becomes:

$$w_{n,sample} = 120 - 102 \cdot (1 + 0.04) = 13.9 \text{ g}$$

If no correction was made the erroneous estimation of $w_{nsample}$ would be:

$$w_{n,sample} = 120 - 102 = 18 \text{ g}$$

The ratio w_n^0 / c for the actual cement is assumed to be 0.23.

According to Eq. (I.8) the effective cement content is:

$$c_{sample,eff} = 102 \cdot \left(1 - \frac{0.04}{0.23}\right) = 84.3 \text{ g}$$

The true degree of hydration is, according to Eq. (I.9):

$$\alpha = \frac{\frac{13.9}{84.3}}{0.23} = 0.72$$

Was no correction made, the following degree of hydration had been obtained:

$$\alpha = \frac{\frac{120 - 102}{102}}{0.23} = 0.77$$

Therefore, the error in calculated degree of hydration is big also when the cement has fairly limited pre-hydration.

I:2.3 Correction for limestone filler mixed in cement

Many cements contain limestone filler. Examples from Sweden are:

- CEM II/A-V (Swedish name ”Byggcement”): about 12-13 weight-% (According to the European cement standard, 25% is allowed)
- CEM I rapid hardening (Swedish name “SH-cement”): about 4 weight-%
- CEM I moderate heat of hydration (Swedish name “Anläggningscement”: about 4 weight-% (0% until April 2009)

CO_2 is leaving the limestone filler at ignition. 1 mole limestone, $CaCO_3$ (100 g) releases 1 mole CO_2 (44 g). Correction for this must be made at calculation of w_n. In the further calculations it is assumed that the filler is inert and that it does not bind water chemically.

It is assumed that the cement is not pre-hydrated.

A block diagram over the components in a cement paste containing limestone filler is shown in Figure I.3.

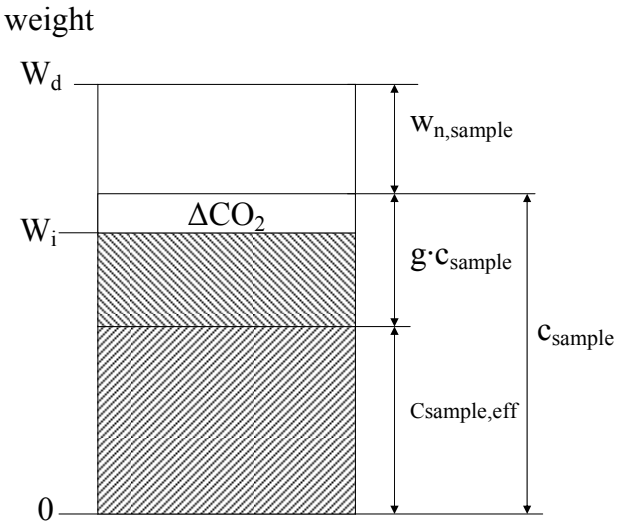


Figure I.3: Components in cement paste containing limestone filler in the cement.

The cement is assumed to contain g weight-% limestone. The weight loss at ignition of the limestone in cement is:

$$\Delta CO_2 = g \cdot c_{sample} \frac{44}{100} = 0.44 \cdot g \cdot c_{sample} \tag{I.10}$$

The amount of cement in the sample (including limestone filler) is:

$$c_{sample} = W_i + \Delta CO_2 = W_i + 0.44 \cdot g \cdot c_{sample} \tag{I.11}$$

Re-distribution of terms gives:

$$c_{sample} = \frac{W_i}{1 - 0.44 \cdot g} \tag{I.12}$$

The amount of chemically bound water is:

$$w_{n,sample} = W_d - W_i - \Delta CO_2 \tag{I.13}$$

Insertion of Eq. (I.10) gives:

$$w_{n,sample} = W_d - W_i - 0.44 \cdot g \cdot c_{sample} \tag{I.14}$$

Insertion of Eq. (I.12) gives after simplification:

$$w_{n,sample} = W_d - W_i \left(1 + \frac{0.44 \cdot g}{1 - 0.44 \cdot g} \right) \tag{I.15}$$

The effective cement content in the sample used for calculation of the degree of hydration of the limestone-free (”pure”) cement is:

$$c_{sample,eff} = (1-g) \cdot c_{sample} = (1-g) \cdot \frac{W_i}{1 - 0.44 \cdot g} \tag{I.16}$$

The degree of hydration of the limestone-free cement is obtained from:

$$\alpha = \frac{\frac{w_{n,sample}}{c_{sample,eff}}}{\frac{w_n^0}{c}} \tag{I.17}$$

Example. Cement with 12 weight-% limestone filler

A cement paste sample has the weight 120 g after drying and 97 g after ignition. The ratio w_n^0 / c for the clinker (incl. gypsum) in the cement is 0.25.

According to Eq. (I.15) the amount of chemically bound water is:

$$w_{n,sample} = 120 - 97 \cdot \left(1 + \frac{0.44 \cdot 0.12}{1 - 0.44 \cdot 0.12} \right) = 17.6g$$

According to Eq. (I.16) the effective cement content is:

$$c_{sample,eff} = (1 - 0.12) \cdot \frac{97}{1 - 0.44 \cdot 0.12} = 90.1g$$

The degree of hydration of the clinker part of the cement (incl. gypsum) is according to Eq. (I.17):

$$\alpha = \frac{\frac{17.6}{90.1}}{0.25} = 0.78$$

If the limestone filler was neglected, both when it concerns ignition, as when it concerns the effective cement content, the degree of hydration had been calculated as:

$$\alpha = \frac{\frac{120-97}{97}}{0.25} = 0.92$$

The error made when the loss on ignition of the limestone is neglected is therefore very big.

The same example, but lower filler content (4 weight-%)

A cement paste sample has the weight 120 g after drying and 97 g after ignition. The ratio w_n^0 / c for the clinker (incl. gypsum) in the cement is 0.25.

According to Eq. (I.15) the amount of chemically bound water is:

$$w_{n,sample} = 120 - 97 \cdot \left(1 + \frac{0.44 \cdot 0.04}{1 - 0.44 \cdot 0.04}\right) = 21.3g$$

According to Eq. (I.16) the effective cement content is:

$$c_{sample,eff} = (1 - 0.04) \cdot \frac{97}{1 - 0.44 \cdot 0.04} = 94.8g$$

The degree of hydration of the clinker part of the cement (incl. gypsum) is according to Eq. (I.17):

$$\alpha = \frac{\frac{21.3}{94.8}}{0.25} = 0.90$$

If the limestone filler was neglected, both when it concerns ignition, as when it concerns the effective cement content, the degree of hydration had been calculated as:

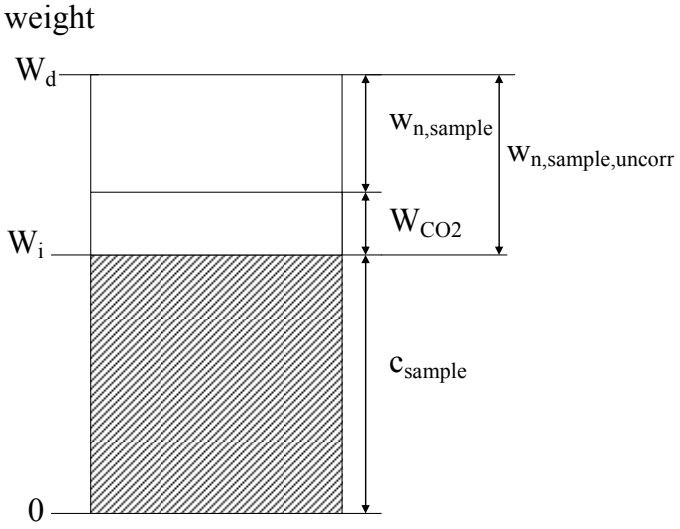
$$\alpha = \frac{\frac{120-97}{97}}{0.25} = 0.92$$

The error made when the loss on ignition of the limestone is neglected is therefore smaller at the lower limestone content.

I:2.4 Correction for carbonation

In the calculations below it is assumed that pure portland cement is used. Thus, no correction for loss on ignition of limestone filler is made. Furthermore, it is assumed that the cement is not pre-hydrated when the paste is mixed.

A block diagram over carbonated cement paste is shown in Figure I.4.



Figur I.4: *Components in carbonated cement paste.*

The density increases when cement paste carbonates. Carbon dioxide bound at carbonation is released at ignition of the paste. Thus, it will be included in weight W_d but not in W_i when Eq (I.3) is used for calculating the amount of chemically bound water content, $w_{n,sample}$. Consequently, if carbonation is neglected, the degree of hydration calculated by Eq. (I.2b) will be too high. The uncorrected value of $w_{n,sample}$ is:

$$w_{n,sample,uncorr} = W_d - W_i = w_n + W_{CO2} \tag{I.18}$$

where W_{CO2} is the weight of bound carbon dioxide in the sample.

All calcium compounds in cement paste except un-hydrated cement can carbonate. The amount of cement that is transformed to solid cement hydration products during hydration is (chemically bound water is excluded since it does not contain CaO):

$$W_{waterfree\,solid} = \alpha \cdot c_{sample} \tag{I.19}$$

Inserting Eq. (I.2b) gives:

$$W_{waterfree\,solid} = \frac{\frac{w_{n,sample}}{c_{sample}}}{\frac{w_n^0}{c}} \cdot c_{sample} = \frac{w_{n,sample}}{\frac{w_n^0}{c}} \tag{I.20}$$

where the parameter w_n^0 / c depends on the composition of the portland clinker

The weight fraction CaO in un-hydrated cement, and therefore also in solid hydration products (except hydration water), is assumed to be *x*. For ordinary Portland cements x is of the order 0.65 (65 weight-%). 1 mole CaO (56 g) reacts with 1 mole CO_2 (44g) to form 1 mole of $CaCO_3$ (100g).

100% carbonation

Complete carbonation of all calcium in the gel gives the following weight increase of the cement paste:

$$W_{CO2} = x \cdot W_{waterfree\,solid} \cdot \frac{44}{56} = x \cdot 0.79 \cdot W_{waterfree\,solid} = x \cdot 0.79 \cdot \frac{w_{n,sample}}{\frac{w_n^0}{c}} \tag{I.21}$$

Therefore, according to Eq. (I.18) the corrected value of $w_{n,sample}$ is:

$$w_{n,sample} = w_{n,sample,uncorr} - x \cdot 0.79 \cdot \frac{w_{n,sample}}{\frac{w_n^0}{c}} = W_d - W_i - x \cdot 0.79 \cdot \frac{w_{n,sample}}{\frac{w_n^0}{c}} \tag{I.22}$$

Re-distribution of terms gives the following expression for the amount of chemically bound water:

$$w_{n,sample} = \frac{W_d - W_i}{1 + \frac{x \cdot 0.79}{\frac{w_n^0}{c}}} \tag{I.23}$$

The degree of hydration is:

$$\alpha = \frac{\frac{w_{n,sample}}{c_{sample}}}{\frac{w_n^0}{c}} \tag{I.2b}$$

Incomplete carbonation

The most rapidly carbonating mineral (except for the small amount of Na_2O and K_2O also present in hydration products) is $Ca(OH)_2$ (calcium hydroxide) formed at cement reaction. The amount of calcium hydroxide in a normal portland cement is about 30 weight-% of the total solid hydration products (hydration water excluded).

Besides calcium hydroxide the solid hydration products also contain hydrates of the clinker compounds C_3S, C_2S, C_3A, C_4AF. These hydration products can also carbonate which is demonstrated by Figure I.5. At the surface the quotient between CO_2 and CaO is about 0.6 to 0.7. Had only calcium hydroxide carbonated, the expected quotient should have been about 0.2 corresponding to a degree of hydration of about 0.7.

The fraction of CaO in the solid reaction products that has carbonated is assumed to be y. Then, the weight increase of the cement paste caused by carbonation is; cf. Eq. (I.21):

$$W_{CO2} = x \cdot y \cdot 0.79 \cdot \frac{w_{n,sample}}{\frac{w_n^0}{c}} \tag{I.24}$$

The true amount of chemically bound water is; cf. Eq. (I.23):

$$w_{n,sample} = \frac{W_d - W_i}{1 + \frac{x \cdot y \cdot 0.79}{\frac{w_n^0}{c}}} \tag{I.25}$$

The degree of hydration is given by Eq. (I.2b):

Example: Completely carbonated cement paste

A cement paste containing 200 g portland cement is fully carbonated. The CaO content in the actual cement is 65%. The dry weight of the sample is 310 g. The weight after ignition is the same as the cement content, 200 g. The parameter w_n^0 / c is supposed to be 0.25.

The amount of chemically bound water is; Eq. (I.23):

$$w_n = \frac{310 - 200}{1 + \frac{0.65 \cdot 0.79}{0.25}} = 36.2 \text{ g}$$

The degree of hydration is; Eq. (I.2b):

$$\alpha = \frac{\frac{36.2}{200}}{0.25} = 0.72$$

Had no correction for carbonation been made, the calculated degree of hydration had been:

$$\alpha = \frac{\frac{310 - 200}{200}}{0.25} = 2.20$$

This is an unreasonably high value, since the degree of hydration cannot transgress 1.

Example: Partly carbonated cement paste

A cement paste with the cement content 300 g is carbonated to 20%. The CaO content in the cement is 65%.The dry weight of the sample is 390 g. The ignited weight is the same as the cement content, 300 g. The parameter w_n^0 / c is supposed to be 0.25.

The amount of chemically bound water is; Eq. (I.23):

$$w_n = \frac{390 - 300}{1 + \frac{0.65 \cdot 0.2 \cdot 0.79}{0.25}} = 63.8 \text{ g}$$

The degree of hydration is:

$$\alpha = \frac{\frac{63.8}{300}}{0.25} = 0.85$$

Had no correction for carbonation been made, the calculated degree of hydration had been:

$$\alpha = \frac{\frac{390 - 300}{300}}{0.25} = 1.20$$

This is also an unreasonably high value.

Measurement of degree of carbonation

The degree of carbonation expressed by the coefficient y in the equations above must be known. One method is to measure the gradual weight loss from a heated sample using TG. Within the temperature range 600-750ºC $Ca(OH)_2$ is decomposed and CO_2 released; [2]. The carbonated cement gel is decomposed already within the temperature range 380-600 ºC [2].

A problem is that also some hydrate water is leaving within these temperature ranges. For TG to be used safely it is therefore important to develop a method by which weight loss from release of CO_2 can be distinguished from weight loss due to release of hydrate water. Consideration must also be taken to carbon bound in limestone filler in the cement.

The safest method is to measure directly the amount of carbon in the sample using a so-called Leco-kiln. In Fig I.5 the result of such measurements are shown.

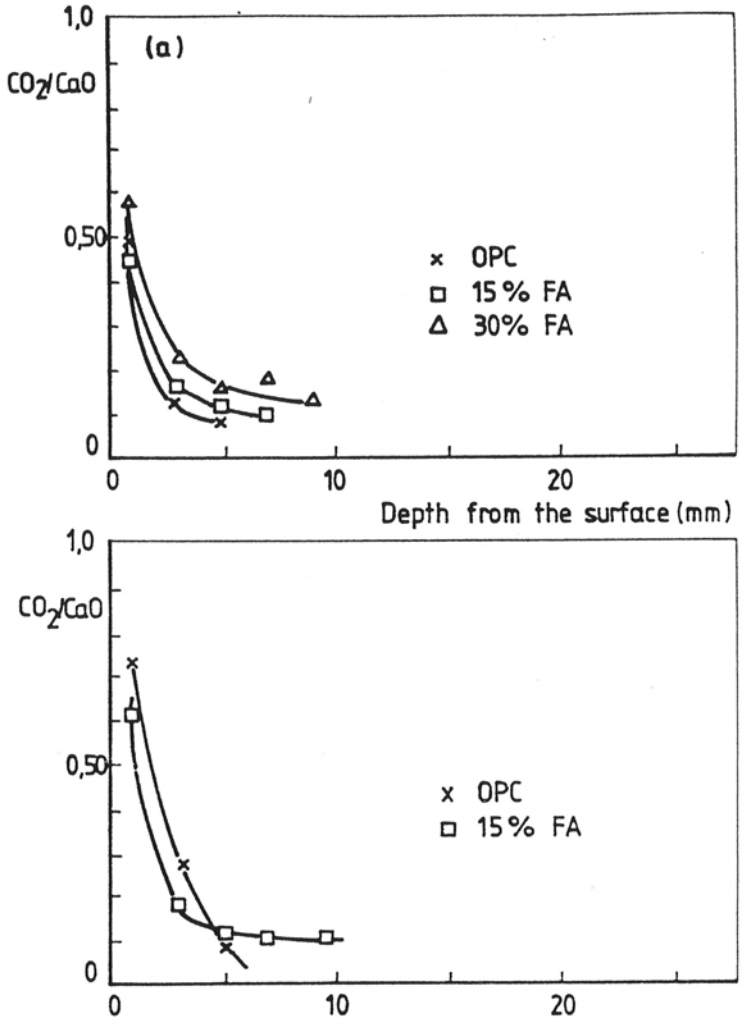


Figure I.5: Binding of carbon dioxide in cement paste stored for 2 years in air of 80% RH. Variables: 100% portland cement, 15% fly ash, 30% fly ash; [3]. (upper) 28 days in water before exposure. (lower) direct exposure to air.

II: CONCRETE

The same equations, given about for cement paste, can also be used for calculation of the degree of hydration of concrete. Eq. (I.2b) can be used, provided the measured amount of chemically bound water, and the (effective) cement content in the sample are introduced in the equations.

The aggregate might contain a certain amount of crystal water which leaves during ignition. This shall not be included in w_n.

The loss on ignition of an aggregate sample with the weight a is found to be $\Delta w_{n,a} / a$

A block diagram over a concrete sample with crystal water in aggregate and somewhat pre-hydrated cement is shown in Fig.II.1.

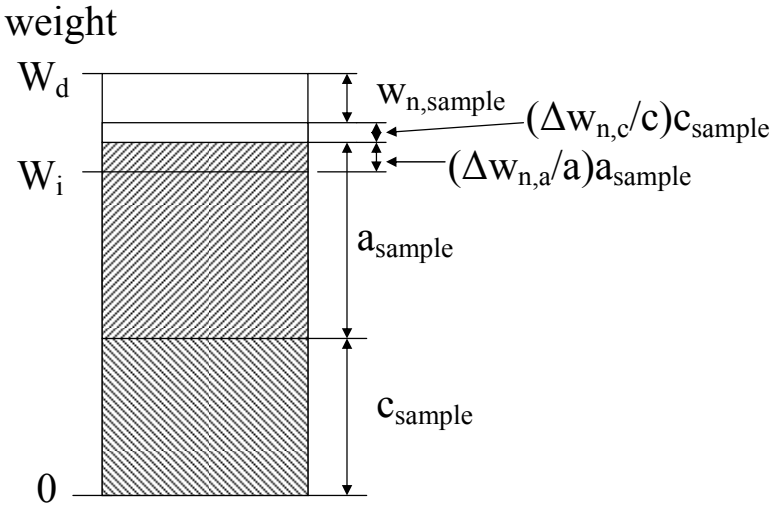


Figure II.1: Components in concrete.

After correction the chemically bound water content in the sample is:

$$w_n = W_d - W_i - \frac{\Delta w_{n,c}}{c} \cdot c_{sample} - \frac{\Delta w_{n,a}}{a} \cdot a_{sample} \qquad \text{(II.1)}$$

where c_{sample} and a_{sample} are the cement content and aggregate content in the sample.

The relation between aggregate and cement in the concrete is K.

$$\frac{a_{sample}}{c_{sample}} = K \qquad \text{(II.2)}$$

Inserting K in Eq. (II.1) gives:

$$w_{n,sample} = W_d - W_i - c_{sample} \cdot \left(\frac{\Delta w_{n,c}}{c} + \frac{\Delta w_{n,a}}{a} \cdot K \right) \qquad \text{(II.3)}$$

The effective cement content is given by Eq. (I.8):

The degree of hydration is given by Eq. (I.9).

An approximate value of a_{sample} can be calculated from the measured quantities W_d och W_i; see Fig. II.1 (the initial loss on ignition of cement and aggregate are neglected). It is assumed that the cement content is known, either from the concrete recipe, or from a direct determination of the amount of CaO.

$$W_d \approx c_{sample} + a_{sample} + \left(W_d - W_i\right) \qquad \text{(II.4)}$$

The aggregate content becomes:

$$a_{sample} = W_i - c_{sample} \quad [1]) \qquad \text{(II.5)}$$

Alternative equations for calculation of the degree of hydration of concrete considering loss on ignition of cement and aggregate are given in reference [4].

---

[1] An exact value of the aggregate content is calculated by the following equations. The cement content c_{sample} is calculated from a determination of the content of CaO in the sample (provided the aggregate does not contain calcium). The aggregate content a_{sample} is then obtained from the dry weight of the sample at which consideration is also taken to the loss on ignition of cement and aggregate at mixing.

The dry weight is:

$$W_d = c_{sample} + w_{n,sample} + \frac{\Delta w_{n,c}}{c} \cdot c_{sample} + a_{sample} = c_{sample} \cdot \left(1 + \frac{w_{n,sample}}{c_{sample}} + \frac{\Delta w_{n,c}}{c} \right) + a_{sample}$$

Thus, the aggregate content in the sample is:

$$a_{sample} = W_d - c_{sample} \cdot \left(1 + \frac{w_{n,c}}{c_{sample}} + \frac{\Delta w_{n,c}}{c} \right)$$

Thus, for an exact determination of the true aggregate content the amount of chemically bound water in the sample must be estimated as correctly as possible.

Example

The cement content in a concrete sample is 100 g. The aggregate content is 400 g, thus, K=4. Ignition of samples of cement and aggregate gave the following values:

$$\frac{\Delta w_{n,c}}{c} = 0.05$$

$$\frac{\Delta w_{n,a}}{a} = 0.005$$

The dry weight and the weight after ignition of the concrete are:

W_d=520 g

W_i=498 g

The amount of chemically bound water is calculated by Eq. (II.3):

$$w_{n,sample} = 520 - 498 - 100(0.05 + 0.005 \cdot 4) = 15 \text{ g}$$

The relation w_n^0 / c is supposed to be 0.25.

The effective cement content is calculated by Eq. (I.8):

$$c_{sample,eff} = 100\left(1 - \frac{0.05}{0.25}\right) = 80 \text{ g}$$

The degree of hydration is calculated by Eq. (I.9):

$$\alpha = \frac{\frac{15}{80}}{0.25} = 0.75$$

If no corrections were made for loss on ignition of cement and aggregate the following values should have been obtained:

$$w_{n,sample} = 520 - 498 = 22 \text{ g}$$

$$\alpha = \frac{\frac{22}{100}}{0.25} = 0.88$$

Thus, the degree of hydration should have been heavily exaggerated.

Example. The same as above, but crystal water in aggregate is neglected

$$w_{n,sample} = W_d - W_i - \frac{\Delta w_{n,c}}{c} \cdot c_{sample} = 520 - 498 - 0.05 \cdot 100 = 17 \text{ g}$$

The effective cement content is unchanged, 80 g.

$$\alpha = \frac{\frac{17}{80}}{0.25} = 0.85$$

This is also a considerable overestimation of the degree of hydration.

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APPENDIX 1: EFFECTS OF THE DRYING PROCEDURE

Error occurring during preparation of the sample

During drying made before ignition, some continued hydration might occur caused by water left in the pores. This hydration is also stimulated by the elevated temperature when drying at +105 ºC is used. This will led to an error in the measured degree of hydration. Therefore, it is essential that the ongoing hydration in the sample can be stopped before drying. The following technique, used at the Swedish Cement and Concrete Research Institute, has turned out to be appropriate. The method is as follows:

1. The sample is crushed and milled in pure ethyl alcohol (96%). Milling goes on for about 3-5 minutes.
2. The produced powder is left in alcohol for 2-4 hours. The time might be prolonged to 24 hours.
3. The powder-alcohol slurry is centrifuged for 2 minutes in order to remove surplus alcohol.
4. The remaining powder sample is dried in vacuum for 1-4 hours.
5. Drying at +105 ºC commences and goes on until equilibrium is reached.

By milling in alcohol much of the pore water is removed, which makes hydration stop. The only unwanted hydration occurring is restricted to a time less than ½ hour.

Examples of the use of this method are shown in Figure A1.1. It has been possible to follow the hydration process down to very low values. Probably, tests could also have been made at even lower concrete age.

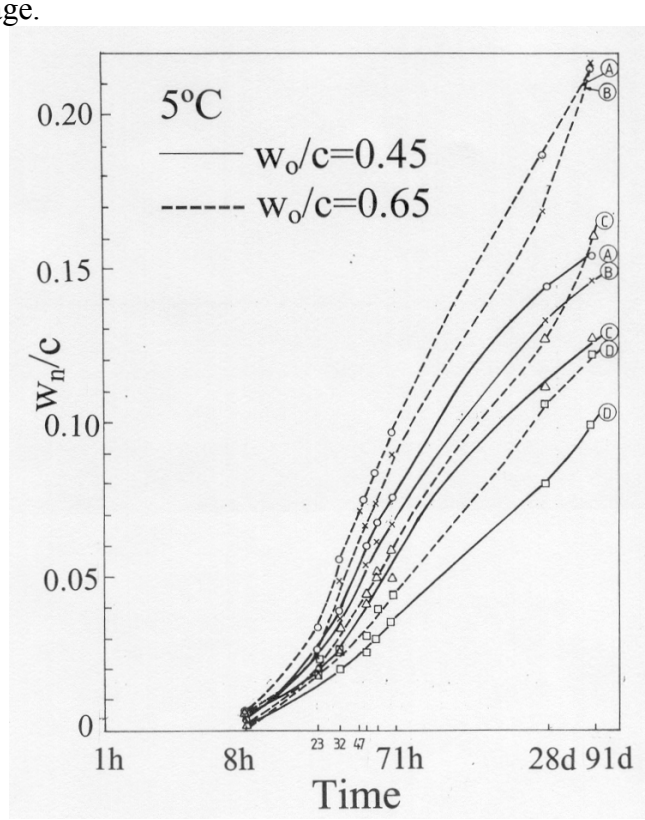

Figure A1.1: Chemically bound water as function of concrete age. Curing temperature +5 ºC. Four different concrete types (A, B, C, D); [A1.1].

Effect of the drying procedure before ignition

The calculated amount of chemically bound water depends on the method used for drying the sample before ignition. Reference [A1.2] presents a thorough study on the effect of drying procedure on the dry weight; W_d in equation (I.3).

There are four main methods for determination of the dry weight. The first method is most commonly used.

1. Drying at +105 ºC

The vapour pressure in the oven varies since it is the same as the vapour pressure in the laboratory. Thus, RH in the oven will depend on the climate in the lab.

Example: The room temperature is +20 ºC and RH of room air is 50%. Then, the vapour pressure in lab air is 0.5·17.5 torr=8.75 torr. The saturation vapour pressure at +105 ºC is 906 torr. RH in the oven becomes (8.75/906)·100=0.97%.
If the room temperature is +25 ºC and RH of room air is 50%, the vapour pressure in the oven is 0.5·23.8=11.9 torr, and RH in the oven becomes (11.9/906)·1000=1.31%.
Such fairly small variations in the vapour pressure of lab air affect the dryness and thus the amount of measured evaporable water. A method that makes it possible to keep RH in the oven constant, independently of variations in the outer vapour pressure has been developed; [A1.3].

2. Drying over magnesium-perchlorate-hydrate ($Mg(ClO_4)_2 \cdot 2H_20$), "P-dying"

Vapour pressure $8 \cdot 10^{-3}$ torr.

3. Drying over dry ice, "D-drying"

Vapour pressure $5 \cdot 10^{-4}$ torr. Drying temperature -79 ºC.

4. Freeze-drying, "F-drying"

Drying temperature -10 ºC.

The drying time is of big importance. In order to obtain the correct value of W_d and thus the correct value of $w_{n,sample}$, drying must proceed until the rate of drying is virtually zero. In reference [A1.2] it is assumed that the correct dry weight is obtained when the weight loss during 1 day does not exceed 0.001 gram per gram cement paste.

Different drying methods give different results for W_d. A less efficient drying method giving a high value of W_d brings about a higher calculated value of w_n than a method that is more efficient. This is visualized by Fig. A1.2. A less efficient method leaves a higher amount of evaporable water. This will be counted as chemically bound water at calculation of the degree of hydration using Eq. (I.3).

Measurements presented in [A1.2] of the efficiency of the four common drying methods are shown in Figure A.3. Furthermore, the effect of short drying time is shown for two methods; 12 hour D-drying and 3 hour +105 ºC drying.

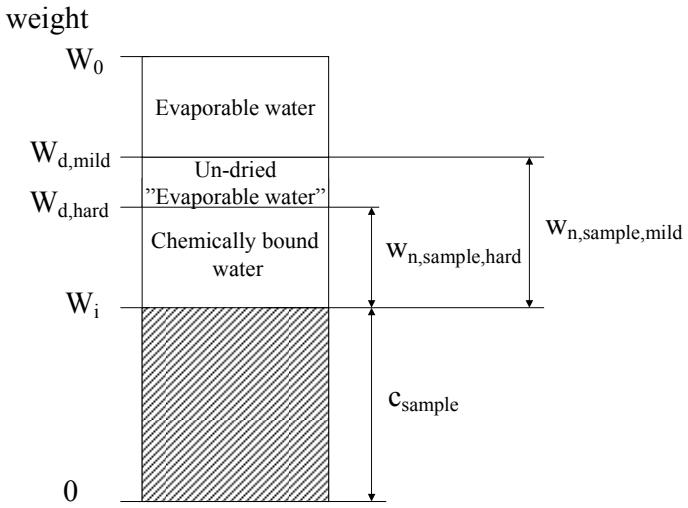

Figure A1.2: Effect of the drying efficiency on the estimated amount of chemically bound water.

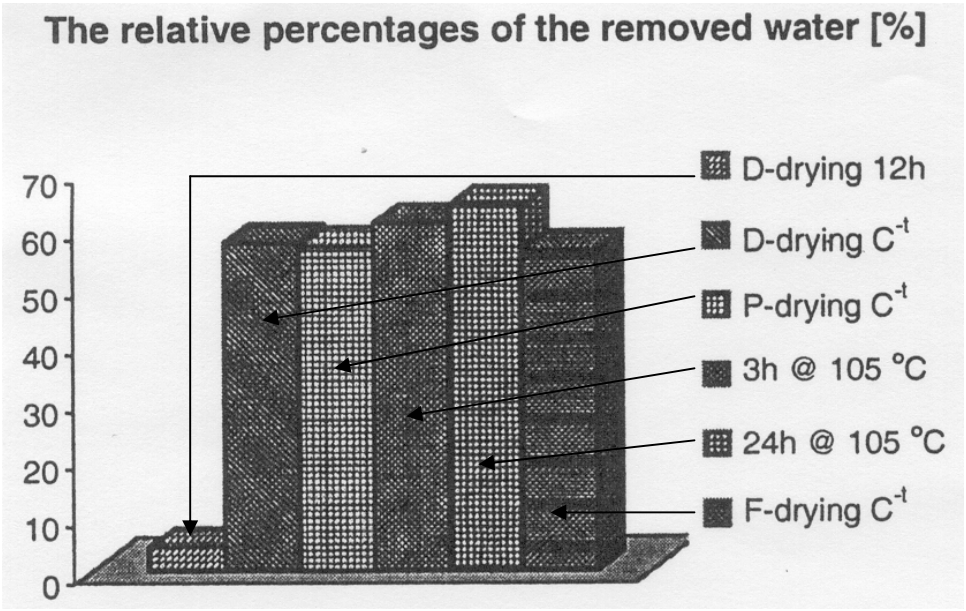

Figure A1.2: Drying efficiency of different methods of drying out evaporable water; [A1.2]. The drying efficiency is calculated by Eq, (A1.1). Two different drying times are tested for D-drying; 12 hours and drying to equilibrium. For +105 ºC drying values are given for 3 hours drying and 24 hours drying (equilibrium).

In A1.2 the following expression is used for estimation of the efficiency of different drying methods.

$$drying\ efficiency = DE = \frac{W_0 - W_d}{W_0 - W_i} \qquad \text{(A1.1)}$$

where W_0 is the weight of the cement paste before drying.

The higher the value of DE, the higher is the drying efficiency, and the lower is the chemically bound water; see Fig. A1.2.

In all cases, fine-ground water saturated cement paste with the water cement ratio 0.45 and 28 days of age, were tested. All samples had been pre-treated in exactly the same manner. Mixing was made in a glove-box in argon atmosphere and hydration occurred in air-tight containers in order to avoid carbonation.

The following values of the drying efficiency DE were observed.

Type of drying	Drying efficiency, DE
D-drying	0.571
P-drying	0.566
+105 ºC drying 24 hours	0.637
F-drying	0.560

Drying at +105 ºC is the most severe drying method giving the lowest amount of chemically bound water, and the lowest degree of hydration.

Since the samples were water-stored until start of testing the three parameters in Eq. (A1.1) can be calculated using the following equations:

$$W_0 = c_{sample} + w_{0,sample} + 0.25 \cdot w_{n,sample} \quad \text{(A1.2)}$$

where $w_{0,sample}$ is the water content in the sample at mixing. The term $0.25 \cdot w_{n,sample}$ is water taken up in the sample during curing. Water uptake is caused by chemical contraction of water when this is chemically bound to cement (the samples were stored in water).

$$W_d = c_{sample} + w_{n,sample} \quad \text{(A1.3)}$$

$$W_i = c_{sample} \quad \text{(A1.4)}$$

Thus, equation (A1.1) can be quantified by:

$$DE = \frac{w_{0,sample} - 0.75 \cdot w_{n,sample}}{w_{0,sample} + 0.25 \cdot w_{n,sample}} \quad \text{(A1.5)}$$

In the following discussion the cement is supposed to have no pre-hydration at mixing.

Dividing all terms in Eq. A1.5 by the cement content in the sample gives:

$$DE = \frac{w/c - 0.75 \cdot \dfrac{w_{n,sample}}{c_{sample}}}{w/c + 0.25 \cdot \dfrac{w_{n,sample}}{c_{sample}}} \quad \text{(A1.6)}$$

where w/c is the water-cement ratio (0.45).

Re-distribution of terms and exchange of c_{sample} for cement content in general, c, gives:

$$\frac{w_n}{c} = \frac{w/c \cdot (1 - DE)}{0.25 \cdot DE + 0.75} \quad \text{(A1.7)}$$

Data in Fig.A1.2 are valid for w/c=0.45. Thus, equation (A1.7) is transformed into:

$$\frac{w_n}{c} = \frac{0.45 \cdot (1 - DE)}{0.25 \cdot DE + 0.75} \qquad \text{(A1.8)}$$

NOTE

If water absorption during curing is neglected Eq. (A1.2) is changed to:

$$W_0 = c_{sample} + w_{0,sample} \qquad \text{(A1.2b)}$$

Eq. (A1.7) is transformed to:

$$\frac{w_n}{c} = w/c \cdot (1 - DE) \qquad \text{(A1.7b)}$$

Eq. (A1.8) is transformed to:

$$\frac{w_n}{c} = 0.45 \cdot (1 - DE) \qquad \text{(A1.8b)}$$

The relation w_n/c for the cement paste calculated by Eq. (A1.8) and Eq. (A1.8b) are given in the table below.

Drying method	w_n/c by Eq. (A1.8)	w_n/c by Eq. (A1.8b)
D-drying	0.216	0.193
P-drying	0.219	0.195
+105 ºC drying 24 hours	0.180	0.163
F-drying	0.222	0.198

The difference in measured amount of chemically bound water, using different drying methods, is considerable.

If the amount of hydrate water at full hydration is known (w_n^0 / c), the degree of hydration can be calculated by Eq. (I.2b), using the values in the table above.

Often the parameter w_n^0 / c is considered a material constant that is independent of the drying method. If it is assumed to be 0.25 for all drying methods the degree of hydration shown in the table below are obtained.

Drying method	Degree of hydration, Eq. (I.2b)	
	w_n/c by Eq. (A1.8)	w_n/c by Eq. (A1.8b)
D-drying	0.864	0.772
P-drying	0.876	0.780
+105 ºC drying 24 hours	0.720	0.652
F-drying	0.888	0.792

The relation in degree of hydration between the two most commonly used drying methods, D-drying and drying at +105 ºC is:

Eq. (A1.8): $$\frac{\alpha_{D-drying}}{\alpha_{+105}} = \frac{0.864}{0.720} = 1.20$$

Eq. (A1.8b): $$\frac{\alpha_{D-drying}}{\alpha_{+105}} = \frac{0.772}{0.652} = 1.18$$

The difference is as high as about 20%.

Comment on degree of hydration

The amount of chemically bound water, w_n, is depending on the drying method, as shown above. The degree of hydration α is however not influence as much as calculated above, depending on the fact that one shall not use the same value of the parameter w_n^0/c for all drying methods. This value shall be increased when a less effective drying method is used. The general value 0.25 used above is therefore not valid for all drying methods.

Effect of the drying technique on calculated porosity

A less efficient drying method will make the calculated total porosity bigger. This will be shown by the following equations.

The total porosity of cement paste is:

$$P_{tot} = \frac{w_0 - 0.75 \cdot w_n}{w_0 + 0.32 \cdot c} = \frac{w/c - 0.75 \cdot \frac{w_n}{c}}{w/c + 0.32} \qquad \text{(A1.9)}$$

where 0.75 is the specific volume of hydrate water (cm^3/g), 0.32 is the specific volume of cement (cm^3/g), and w_0 is the water content in the fresh cement paste at mixing.

The cement paste tested w/c=0.45. Thus Eq. (A1.9) is changed to:

$$P_{tot} = \frac{0.45 - 0.75 \cdot \frac{w_n}{c}}{0.77} \qquad \text{(A1.9b)}$$

The observed value of w_n/c for the different drying methods calculated by Eq. (A1.8) are inserted in this equation. The following porosities are obtained.

Drying method	Total porosity, %
D-drying	37.4
P-drying	37.1
+105 ºC drying 24 hours	40.9
F-drying	36.8

Evidently, the difference between different drying methods is fairly big.

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[A1.2] Korpa, A., Trettin, R.: *The influence of different drying methods on cement paste microstructure as reflected by gas adsorption: Comparison between freeze-drying (F-drying), D-drying, P-drying and oven-drying methods*. Cement and Concrete Research 2005.

[A1.3] Danielsson,U.: *An apparatus for easy determination of the amount of bound water in cement pastes yielding highly reproducible results*. Materials and Structures, 7:40, 1974.

APPENDIX 2:
EFFECTS OF REACTIVE MINERAL ADMIXTURES

The basic idea behind the method for determination of degree of hydration described in this report is that there is a direct proportionality between the amount of chemically bound water, as determined by ignition, and the amount of cement that has reacted:

$$\frac{w_n}{w_n^0} = const \cdot \frac{c_{reacted}}{c_{total}} \tag{A2.1}$$

Therefore, the amount of chemically bound water increases gradually with increased hydration time. Examples of the time development of chemically bound water are shown in Fig. A1.1.

When reactive mineral admixtures are added to cement or concrete the direct proportionality is no longer valid. One example is shown in Fig. A2.1 for cement paste containing silica fume. After about 90 days the amount of chemically bound water gradually diminishes with increased hydration time. The mechanism behind this phenomenon is not totally clarified. A hypothesis put forward is that a certain poly-condensation of the silicate chains occurs, at which previously bound water is released.

In [A2.2] the following expression for calculating the amount of chemically bound water in concrete containing *silica fume* is suggested:

$$w_n = \left(\frac{w_n^0}{c}\right) \cdot \alpha_{cem} \cdot c - \left(\frac{w_n^0}{Si}\right) \cdot \alpha_{Si} \cdot Si \approx 0.25 \cdot \alpha_{cem} \cdot c - 0.34 \cdot \alpha_{Si} \cdot Si \tag{A2.2}$$

where α_{cem} is the degree of hydration of the Portland cement, α_{Si} is the degree of reaction of the silica fume, c is the cement content, and Si is the silica fume content. The coefficients 0.25 and 0.34 are the chemically bound water at complete hydration of cement and silica fume in relation to the total cement and silica fume contents.

Thus, it is assumed that the cement reacts as if no silica fume is present, but that the reaction of silica fume releases water that was initially bound to cement hydration products.

According to Eq. (A2.2) the degree of hydration of the cement is:

$$\alpha_{cem} = 4 \cdot \left(\frac{w_n}{c} + 0.34 \cdot \alpha_{Si} \cdot \frac{Si}{c}\right) \tag{A2.3}$$

Thus, in order to calculate the degree of hydration of the portland cement in the concrete or cement paste one has to determine the amount of bound water by ignition of a sample in the normal way. Thereafter, a correction is made for the effect caused by the silica fume reaction. How the amount of reacted silica fume shall be determined is unclear. Possibly, it can be estimated from the amount of $Ca(OH)_2$ in the concrete, since silica fume reaction consumes lime.

Example

A cement paste sample containing silica fume that is 10 % of the cement weight is studied. The dry sample weight is 161 g. The ignited weight is 140 g.

The amount of cement+silica fume is the same as the ignited weight, 140 g. The cement weight is 140/1.1=127 g.

The amount of chemically bound water is 161-140=21 g.
The silica fume is assumed to be fully hydrated.
Then, the degree of hydration of the Portland cement is:

$$\alpha_{cem} = 4 \cdot \left(\frac{21}{127} + 0.34 \cdot 1 \cdot 0.10 \right) = 0.80$$

If the effect of silica fume was not considered the calculated degree of hydration is:

$$\alpha_{cem} = 4 \cdot \frac{21}{127} = 0.66$$

Thus, the effect of silica fume cannot be neglected.

Maybe, the effect of addition of other mineral admixtures, like fly ash or blast-furnace slag, can be treated in a similar way, by adding corrections to the measured ratio between bound water and cement content. How these corrections shall be made is, however, not known. Such materials are also used in much bigger quantities than silica fume. Therefore, for concrete containing fly ah or slag, it seems reasonable not to use the amount of bound water as a measure of degree of hydration.

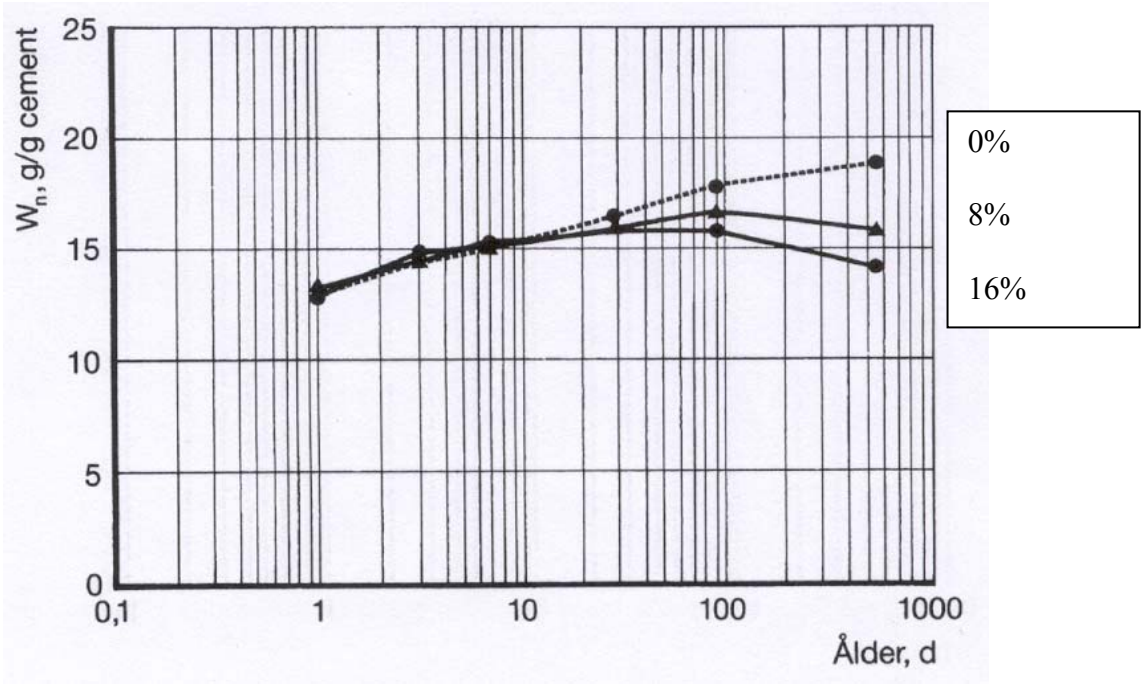

Figure A2.1: Measurements of the amount of chemically bound water in cement paste containing 0%, 8% or 16% silica fume (related to the cement weight); [A2.1] (Ålder=concrete age days)

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