

The degree of cement hydration in concrete

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The degree of cement hydration in Concreteby Pieter C. Kreijger^{x)}

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1. Introduction

Concrete gets its properties in the first place by the hydration of the binder, that is the cement and consequently therefore the degree of cement hydration is an important parameter for concrete. It is not certain however from which age (hours) this fact exists. Nevertheless it is advisable to select (a) measuring method(s) for the determination of this hydration degree also at the first stages of hydration.

Cement hydration is the gradually changing of free water to more closely bound water, in fact to water which is chemically bound in the hydration products of cement, the cement gel having a specific surface of about 250 m²/g. This increase in surface can be held responsible for the setting of cementpaste and later on for the gradual developping of all the properties of cementstone and consequently of the concrete if adhesion between cementstone and aggregates is guaranteed. So basically the concrete properties are determined by the specific surface and amount of cementstone and by the adhesion between cementstone and aggregates. These properties are inherently connected with the hydration reactions in which water is converted from free to bound. So measurement of chemically bound water (or non evaporable water) either directly or indirectly gives the degree of hydration, since the maximum amount of chemically bound water can be fixed at about 26% m/m of the cement. Therefore regarding the concrete considered, the first condition is to know the amount of cement in the concrete either by calculating or by direct measurement. The consequences of the accuracy in calculating the cement content in a sample of concrete can easily be shown by assuming a mix consisting of nominal 300 kg portland cement : 150 l H₂O : 1900 kg aggregate delivered by a well known ready mixed concrete plant while the cement factory has told that the loss on ignition of the cement in question is 3 ± 0,5%. Taking concrete samples of 1500 g at 3 stages of hydration (say 10 h, 3 days and 7 days) and determining the free evaporable water at 105-110°C and the non evaporable water at 1050°C.

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leads to the following calculation.

From an investigation [1] of the concrete composition of a 600 m³ fly-over deck (concrete delivered over 3 km in 9-3 m³ agitators during 11 h, no stock supply at ready mix plant) the following results (using a modified Thaulov method) were found for 21 fresh concrete samples taken each ½h at the end of the concrete pumplines at the deck:

coeff. of variation in cement content 3.5% (method 0.3%)
 coeff. of variation in aggregate content 1.0% (method 0.07%)
 coeff. of variation in water content 3.6% (method 0.9%)
 coeff. of variation in $\frac{w}{c}$ ratio 2.1% (method 0.8%)

So with 90% accuracy the variation in cement content was 5.7% and in the aggregate content 1.6%, which means that for practical calculations the variation in $\frac{\text{aggregate}}{\text{cement}}$ factor in our example can be taken as 6.33 ± 0.5 (= $\pm 7.9\%$). Admitting this variation gives the following (simplest) calculation of the non-evaporable water content (table 1)

Table 1 - Effect of cement-content calculation in concrete sample

	Concrete samples at		
	10 h.	3 days	7 days
weight of concrete sample (g)	1500	1500	1500
weight after drying at 110°C (g)	1410	1420	1450
evaporable water content (g,%)	$\frac{90}{1500} = 6.4\%$	$\frac{80}{1500} = 5.6\%$	$\frac{50}{1500} = 3.4\%$
weight of dried sample (g)	1410.0	1420.0	1450.0
weight after 50°C (g)	1398.5	1395.2	1410.5
loss in weight (g)	11.5	24.8	39.5
weight of cement in sample (g)	(192.3 \pm 13)	(193.6 \pm 13)	(197.7 \pm 13)
loss in weight in % m/m of cement	(6.0 \pm 0.5)	(12.8 \pm 0.9)	(20.0 \pm 1.4)
loss of ignition % m/m of cement	(3.0 \pm 0.5)	(3.0 \pm 0.5)	(3.0 \pm 0.5)
non evaporable water content (%)	(3 \pm 1)	(9.8 \pm 1.4)	(17.0 \pm 1.9)
deviation of average (%)	33.3	14.4	11.2
degree of hydration (26% = 1)	0.07 - 0.15	0.33 - 0.43	0.58 - 0.73

From table 1 it follows that if the degree of hydration is calculated from the non-evaporable water content, it will be advisable to test as well the cement content of the concrete as the loss of ignition of the cement used.

In the following the phenomenon of cement hydration is dealt with in more detail.

2. Cement and the principles of hydration, what is known and what not.

Cements are inorganic products that harden with and under water and so produce artificial stone for which reason they are called hydraulic cements. This in contrast to non-hydraulic, inorganic cementitious materials like gypsum plasters, lime etc. see table 2 [2].

Table 2 Types of inorganic cements

Hydraulic cements	Non-hydraulic cements
portland cements	gypsum plaster
(portland) blast furnace cements	lime
super sulfate cements	dolomitic lime
portland-porrolan cements	magnesium oxychloride
expansive cements	(= Sorel cement)
polymer cements	
ferro cements	
masonry cements	
oil-well cements	
aluminous cements	

Here we restrict ourselves to the hydraulic cements, based upon the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ (fig.1) and especially to the portland cements. The performance of concrete is mainly influenced by the quality of the cement paste and its characteristics are dependent on the composition of the clinker, reactivity of the clinker minerals, curing conditions and $\frac{W}{C}$ ratio used in preparing the paste or concrete. In the presence of water, each of the major crystalline compounds reacts, which is called hydration. But they differ in their reactivity with water, in the characteristics

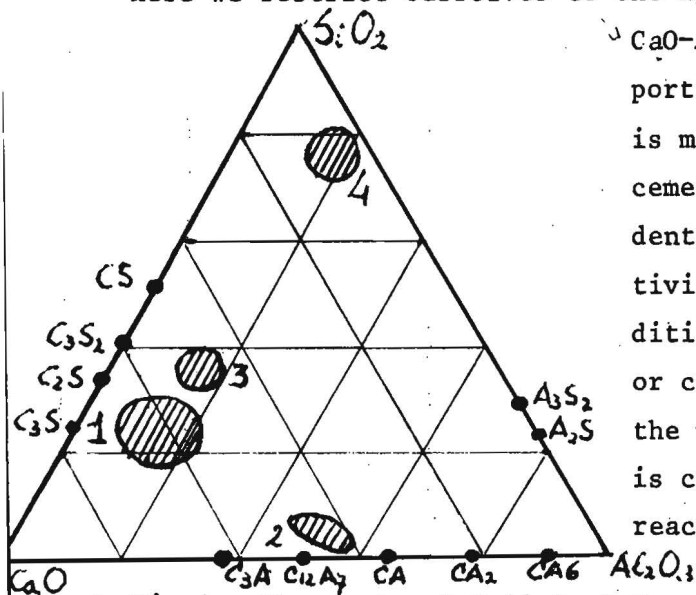


Fig.1 - The system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ with areas of basic cement and related materials composition [2]
 1 portland cement
 2 aluminous cement
 3 basic blast furnace slag
 4 volcanic (artificial) pozzolanas

of their hydration products and in the circumstances under which the pertinent hydration product is formed.

Lit. [3] gives an overall view of questions in the characterization of cements as well as in physical and mechanical behaviour of hydrated cements which are not yet solved:

- the characterization of hydraulic cements (unhydrated, starting materials) is not adequate to ensure that comparison of results obtained from different source materials and different workers is valid:
 - a. there is no agreement on how surface area of hemihydrate should be measured
 - b. the reactivity and the factors that determine it are not adequately defined; the question "What is reactivity?" will remain unanswered until the precise mechanisms of hydration reactions are known.
- the characterization of hydrated cements is equally unresolved:
 - a. there is much controversy regarding determination of surface area, especially that of hydrated portland cement, and its significance.
 - b. the precise chemical and mineralogical composition of some hydrated cement constituents remain obscure: precise lime/silica ratio, location of lime in the microstructure, effect of admixtures, etc.
 - c. the density of hydrated cement appears to vary with the method of measurement and the history of the sample.
- the relation of microstructure of hydrated cement, morphology, composition and strength has not been established and, although a relation between porosity and strength appears to exist, its use for prediction of these properties is limited because the relation is different for materials prepared in different ways:
 - a. Volume changes, involving both solid and total volumes, being connected with changes in moisture content are often determined on the basis "dry" or "wet" conditions, states not adequately defined and not representative of service conditions; the evaluation of sorption-dimensional change relations would be more useful and supplemented by measurements of several cycles to determine any irreversible changes (because these changes are involved in the time-dependent processes of deformation cracking, checking and deterioration).
 - b. Prediction of the behaviour of hydrated cements under freezing conditions is dependent on understanding of the behaviour of

adsorbed water in fine capillaries under freezing conditions.

- c. the sulfate attack of hydrated cement regarding the role of Al-ions entering CSH-system, the relative contribution of $\text{Ca(OH)}_2 \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ conversion to the total volume change, direct solid conversion or through solution of the sulfate conversion, the low or high sulfate being responsible for volume change, the gel-like or the crystalline ettringite being detrimental to cement, are some of the questions that must receive attention in further studies.
- d. the mechanism of carbonation shrinkage has not been determined fully.
- e. the coefficients of thermal expansion are different for the different components of concrete and depend on quite a lot of factors. There is some controversy regarding the role of differential expansion between aggregate and set cement (the α - β transformation of quartz and namely its expansion seems however to be absorbed by cement paste without disruption).
- f. a completely quantitative theory of strength and fracture is not available; the porosity/modulus relationship, extrapolated to zero porosity leads to different values by different researchers, the role of the solid part and the effect of the nature of the void spaces is not yet known, factors to be considered are total porosity, pore size distribution, microcracks and stress concentrations. On a more micro-scale the type of bond responsible for strength is not clearly defined: van der Waals forces may be operating in some regions and H-bonding in others while chemical bonding may predominate and surface forces may intervene. Although there is neither a linear nor a square proportionality between strength and amount of cement hydrated, there indeed seems to be a linear relation between total porosity and log modulus of elasticity or micro-hardness, independent of the way of preparing. The ratio of compressive strength to tensile strength is not yet explained although it seems that the nature of the surface (surface energy) is an important factor. The phenomenon of creep is not well understood and numerous theories are used to explain it although none of them do adequately explain all observed behaviour, while for polymer-impregnated concrete negative creep has been reported.

- Although from the foregoing it will be clear that a lot of basic questions are not yet solved, the engineer is obliged to look for approximations, trying to get estimations that will work in practice. In the following it is tried to assess the possibilities for determining the degree of hydration in practice and how to use the results.

From the foregoing it follows that the progress of hydration can be determined by different means, such as measurements of: the amount of Ca(OH)_2 in the paste, the heat evolved by hydration, the specific gravity of the paste, the amount of chemically bound water, the amount of unhydrated cement present (using x-ray quantitative analysis) and indirectly from strength properties of the hydrated paste. To study early reactions, thermogravimetric techniques and continuous x-ray diffraction scanning are used.

3. What happens during cement hydration?

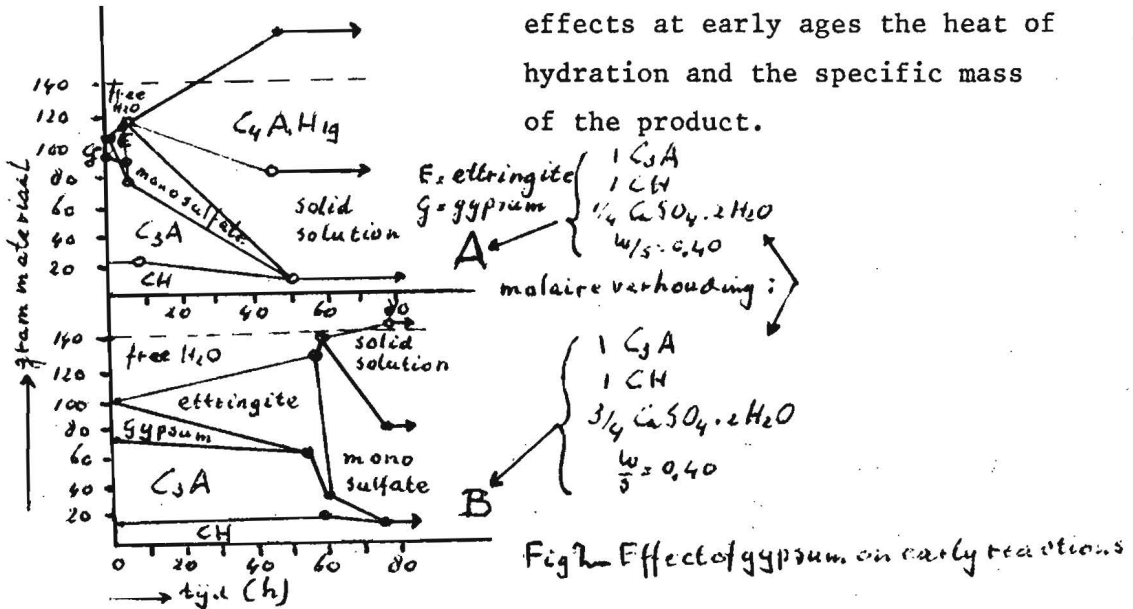
3.1 Heat of hydration, amount of Ca(OH)_2

Cement chemistry gives the composition of portland cements in the well-known compound-nomenclature: C_3A , C_3S , C_2S , C_4AF and $\bar{\text{S}}$ in which $\text{C} = \text{CaO}$, $\text{A} = \text{Al}_2\text{O}_3$, $\text{S} = \text{SiO}_2$, $\text{F} = \text{Fe}_2\text{O}_3$ en $\bar{\text{S}} = \text{SO}_3$. Simply stated the C_3A and $\bar{\text{S}}$ react with $\text{H} (= \text{H}_2\text{O})$ almost immediately to form crystalline hydrates, among which also ettringite ($\text{C}_3\text{AS}_3\text{H}_{32}$) that is formed on the surface of the unhydrated particle, thus preventing their fast hydration (set retardation by gypsum). C_3S and $(\beta)\text{C}_2\text{S}$ are considered the most important in their contribution to strength development after setting. Both give about analogue hydration products: CSH hydrates and $\text{CH} (= \text{Ca(OH)}_2)$. Table 2 gives often used simple hydration reactions [2,4] with heat of hydration evolved at full hydration .

From table 2 it follows that fully hydrated C_3S contains about 40% CH, while for fully hydrated C_2S this is about 18%. So in principle the amount of CH formed is a measure for the degree of hydration [6]. The same is true for the amount of water fixed in the hydration compounds (see 3.2)

simplified reactions	heat evolved (cal/g)
$\text{C}_3\text{A} + 6\text{H} \longrightarrow \text{C}_3\text{AH}_6$	207 } 320 in cement 347 }
$\text{C}_3\text{A} + 3\bar{\text{C}}\bar{\text{S}}\text{H}_2 + 26\text{H} \longrightarrow \text{C}_3\text{A}3\bar{\text{C}}\bar{\text{S}}\text{H}_{32}$	
$2 \text{C}_3\text{S} + 6\text{H} \longrightarrow \text{C}_3\text{S}_2\text{H}_3 + 3\text{CH}$	120
$2 \text{C}_2\text{S} + 4\text{H} \longrightarrow \text{C}_3\text{S}_2\text{H}_3 + \text{CH}$	62
$\text{C} + \text{H} \longrightarrow \text{CH}$	279
$\text{C}_4\text{AF} + 2\text{CH} + 10\text{H} \longrightarrow \text{C}_3\text{AH}_6 + \text{C}_3\text{FH}_6$	100

The time necessary for conversion of $C_3A + \text{gypsum} \rightarrow \text{ettringite} \rightarrow \text{mono-sulfate}$ depends on the ratio of C_3A to gypsum and for molar ratio's $\frac{1}{4}$ and $\frac{3}{5}$ Verbeck [5] shows (see fig. 1) the effect. Consequently this



The real composition of the cement determines the heat of hydration (which can be calculated on basis of table 2) and the speed of development for which practical values are given in table 3 [4]

type of cement	time of hardening			
	1 day	3 days	7 days	28 days
rapid hardening cement	50 - 65	70 - 85	85 - 90	90 - 100
normal cement	30 - 50	50 - 70	60 - 80	75 - 100
low heat cement (also p.b.cement with high slag content)	15 - 35	40 - 60	45 - 65	55 - 80

The range in table 3 is the consequence of variations in fineness of the cement, the temperature during the hydration and the amount of water available ($\frac{W}{C}$ ratio) For instance, for a $\frac{W}{C}$ ratio of 0.45, fineness 3100 \pm 200 cm^2/g Blaine and temperature 23 \pm 2°C, table 4 gives the development of the heat of hydration for the cementminerals per % of the mineral.

component	after a hardening period (days)					
	3	7	28	90	180	360
C ₃ A	1.7	1.8	1.9	2.0	2.1	2.2
C ₃ S	0.8	0.9	1.0	1.1	1.2	1.2
C ₂ S	0.1	0.2	0.3	0.4	0.5	0.6
C ₄ AF	0.2	0.3	0.4	0.5	0.6	0.7

With the help of the data of table 3 and/or 4, the temperature increase Δt of concrete under adiabatic conditions can be predicted:

$$\Delta t = \frac{c \cdot h}{a \cdot c_1 + w \cdot c_2}$$
 in which c, a and w respectively are the amounts of cement, aggregates and water in kg/m³ concrete, c₁= 0.2 kcal and c₂= 1.0 kcal while h=heat of hydration (kcal/kg cement).

On the other hand, if in a practical case the loss of heat at a certain place in the concrete (where temperature is measured) can be calculated, in principle it could be possible to calculate from the temperature recording the degree of hydration of the cementpaste in question (if the total heat of hydration of this cementpaste is known or calculated).

3.2 Changes of volume and mass, conversion of free water into bound water.

During hydration, the apparent volume of the hydrating system changes and can be related to the solid volume change associated with the nature of the new formed hydrated products and the conditions of hydration. According to Powers [7] and Brownyard, portlandcement can bind water chemically to about 26% of its weight at full hydration under water, during which a contraction of about 25% of the water volume takes place. So 100g. of cement can bind about 26g. of water and contracts about 6.5 cm³ after full hydration. Therefore measuring the contraction under water in a volumenometer can give the degree of hydration of a cement as function of time. Multiplying the contraction at a certain time with the factor 4, gives the amount of chemically bound water, which in fact determines the degree of hydration.

Diagram 1 [8] illustrates the transition from the system (cement + water) to that of the three-component system, in which W_0 = weight of water in fresh paste (corrected for bleeding and any dilation of the paste during hydration).

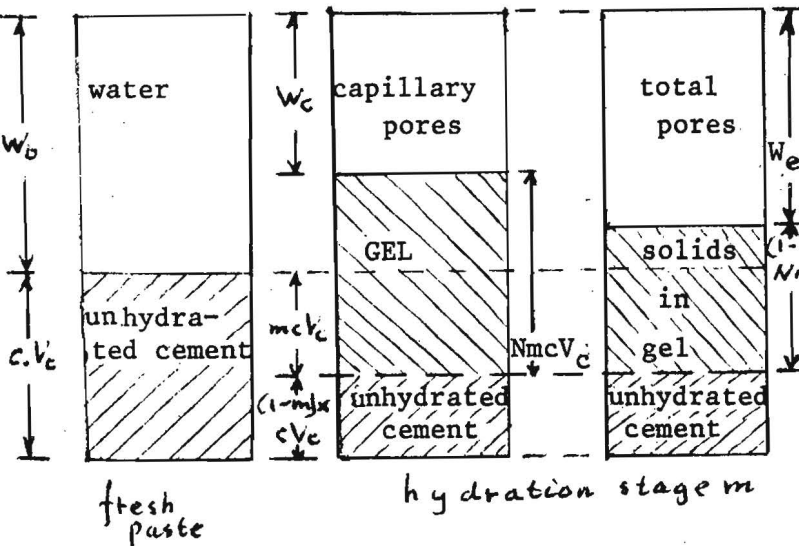


Diagram 1 - Hydration of cement.

- c = weight of original cement
- V_c = specific volume of original cement (cm^3 per gram)
- W_c = weight of capillary water at a stage when a fraction m of the cement has hydrated.
- N = volume of cement gel produced by the hydration of 1 cm^3 cement
- W_e = weight of evaporable water under specified conditions of drying at hydration stage m .
- P_g = inherent porosity of the gel.

Since the total volume of the system remains constant for any given paste at all stages of hydration, from diagram 1 it follows:

$$W + cV_c = W_c + NmcV_c + (1-m)cV_c = W_e + (1-P_g) NmcV_c + (1-m) cV_c$$

A more satisfactory expression for the volume of the gel solids is $V_{hc}(mc + W_n)$ in which V_{hc} = specific volume of hydrated cement in cm^3/gram and W_n = weight of non-evaporable water (under the specified drying conditions, at hydration stage m). However from a consideration of the values given by Powers, Fulton [8] concludes that for the purpose of diagrammatic illustration, no great error is involved in stating $V_{hc}(mc + W_n) = (1-P_g)Nm c V_c$.

The disadvantage of diagram 1 is that it illustrates volume relationship for only one paste at one specific stage of hydration. Fulton [8] therefore modified the relationship to:

$$W_e = W_0 + mcV_c - (1-P_g)NmcV_c \text{ and}$$

$$W_c = W_0 + mcV_c - NmcV_c.$$

For the values given by Powers : $N = 2.2 \text{ cm}^3/\text{cm}^3$ and $P = 0.28$

$$W_e = W_0 - 0.58 mcV_c \text{ and } W_c = W_0 - 0.38 mcV_c$$

From these relationships Fulton constructed the triangle phase fig. 3

which connects the amount of unhydrated cement $(1-m)cV_c$, the solid volume of gel $(1-P_g)N.m.c.V_c$ and the evaporable water W_e .

For example for $\frac{W_0}{c} = 0,40$ and $c = 100$ g gives $W_0 = 40$ g.

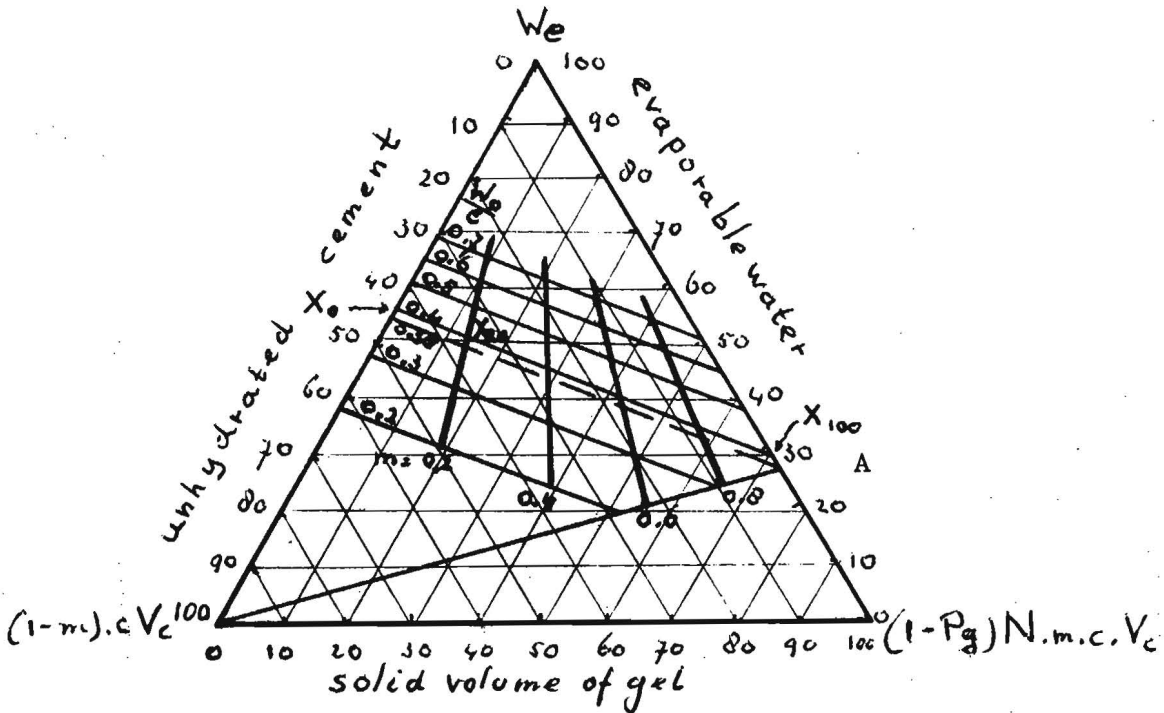


Fig 3 - Presentation of hydration of cement.

$$\begin{aligned}
 cV_c &= 100 \times 0.318 = 31.8 \text{ cm}^3 \\
 W_0 &= 40.0 \text{ cm}^3 \\
 \text{Total} &= 71,8 \text{ cm}^3
 \end{aligned}$$

or expressed as percentages :

$cV_c = 44.4\%$, $w_0 = 55.6\%$ ($V_c = \frac{1}{3.15} = 0,318$) These values establish the starting point X on the hydration curve for a paste of $\frac{W}{c} = 0.40$.

When $m = 0.20$:

$$W_e = 55.6 - 0.58 \times 0.2 \times 44,4 = 50.4\%; \text{ unhydrated cement} = (1-m)cV_c = 0.8 \cdot 44.4 = 35.5\% \text{ and}$$

consequently the volume of the solids in the gel = $100 - (50.4 + 35.5) = 14.1\%$. The point X₂₀ therefore can be plotted in the diagram.

Similar calculations establish the rest of the diagram, for every wished value of $\frac{W_0}{c}$. Since complete hydration is not possible for $\frac{W_0}{c} < 0.38$ (broken line through A) there always exists some proportion of unhydrated cement while at $\frac{W_0}{c} > 0,38$ there always will be capillary pores.

The stage at which all the space filled originally with water is completely filled by the porous gel may be estimated by substituting $W_c = 0$, that is

$$W_0 - 0,38 mc = 0 . \text{Hence } m = \frac{W_0}{0.38c} . \text{ For example for } \frac{W_0}{c} = 0.30, m = \frac{0.30}{0.38} = 0.79.$$

By calculating m for other values of $\frac{W_0}{c}$, the line OA which defines the limit of hydration may be drawn. The completed diagram can therefore be used to illustrate not only the progress of hydration of cement pastes of all possible $\frac{W_0}{c}$ -ratios, but also to depict the restriction of hydration in pastes of low ratios.

So for hydration in water, m can be estimated from as well the free water content as from the non evaporable water content, as from the density of the hydrated mass (changing from about 3.15 g/cm^3 to 2.15 g/cm^3 with a porosity of about 26-28% and a specific surface area of $650 \text{ m}^2/\text{cm}^3$ or $250 \text{ m}^2/\text{g}$ (the gel substance proper has an average density of 2.60 g/cm^3). These data always are given without corrections for the amount of CH present, or corrections for carbonation, which occurs for cement paste hardened in air. (densities of CH and CaCO_3 respectively are 2.23 and 2.71 g/cm^3)

The density of the hardened cementpaste (d_p) is according to the foregoing related to the non evaporable water:

$$d_p = \frac{V_c + 0.75 w_n \times c}{V_p} \text{ in which } \begin{aligned} V_c &= \text{cement volume} \\ w_n &= \text{non evaporable water} \\ c &= \text{cement mass} \\ V_p &= \text{Paste volume} = \text{concrete vol.} - \text{aggregate vol.} \end{aligned}$$

while the German School uses the formule: $d_p = \frac{V_c + w_n \times c}{V_p}$ [9]

Since due to the method of manufacturing, the contraction pores ($0.25 w_n \times c$) remain only partly in the hardened cement paste, the actual values of the density are between these two limits and either of them can be used.

3.3 Indirect relationships between concrete properties and degree of hydration

Since the degree of hydration controls the structure of the cementpaste, all properties of concrete have a certain relationship to the net $\frac{W}{c}$ ratio combined with the degree of hydration (or consequently porosity or paste density) and a large variety of formulæ has been developed from which strength, modulus of elasticity, creep, shrinkage etc. can be derived [9,10].

Consequently, the other way round, from such formulas and the property in question that is measured, the degree of hydration can be calculated. So, theoretically, it would be even possible to use the pulse velocity (from which modulus of elasticity can be calculated) of concrete to calculate the degree of hydration.

It will be clear that the reliability of such a prediction of the degree of hydration is low, the same will be true more or less for making use of other formulas meant above.

It may be doubted however if concrete strength can be derived from the porosity of the cementpaste (or density or degree of hydration) from concrete of young ages for, in such cases, the adhesion between aggregate and cementstone will determine mainly the concrete strength. At early ages (up till about 1-3 months) bond strength is lower than paste strength, at late ages the reverse seems to be the case, whilst paste strength is temperature dependent and bond strength practically not. [11,12] So fe. regarding tensile strength the formula $R_b = \gamma R_p + A(1-\gamma)$ is proposed [13] in which R_b and R_p respectively are the tensile strength of concrete and cementpaste, γ = amount of paste, A = adherence of aggregate to paste. If one should insist on the effect of cementpaste only, one is obliged to take into account the wall effect of the aggregates, since here for instance Powers' gel-space-ratio differs from the bulk value of the cementpaste.

4. The role of aggregates at the hydration of cement.

A contact zone is formed between cement and aggregates in concrete and the structure of the zone depends on the nature of the aggregate and the conditions of hardening [12,14]. The highest contact zone strengths are found in active aggregates which react chemically with the cement hydrates (i.e. carbonate rocks and quartz sand). Nevertheless up till about 3 months this boundary between aggregate and cementpaste is the weak point in the structure of concrete due to the formation in between 12-16h of $\text{Ca}(\text{OH})_2$ in the contact-layer [15] over a distance of about 2-3 μ and the formed adjacent intermediate layer (5-10 μ thick) consisting at early age for the most part of ettringite while at later age the number of CS crystals increases. Consequently fracture between cementpaste and aggregate occurs predominantly in this layer until its surface energy becomes equal to that of the contact layer and thus fracture shifts more and more into the contact layer.

This weakness can be increased by higher $\frac{W}{C}$ ratio (due to segregation or bleeding) especially at the underside of the aggregate particles. Of course in the foregoing it is accepted that aggregate strength $>$ layer strength which is true for normal weight concrete. Consequently not only the amount of aggregate but also type of aggregate, grading and surface texture influence concrete strength which means that the degree of hydration cannot be used alone to predict the strength of concrete.

5. The role of admixtures at the hydration of cement

Since accelerators and retarders react chemically with cement, they influence the hydration mainly chemically while the direct effect of surface active agents is physically. Accelerators primarily effect the hardening of cement while more rapid setting can be coincidental. Mostly chlorides are used which act more or less as catalyst for especially the reactions of C_3S -hydration; the normal hydration process of cement is not changed, only rate of heat liberation during the first period of hardening is increased depending on both chemical and mineralogical composition of the cement. Retarders give a delay in the setting of the cement paste and consist of sugar, carbohydrate derivatives, soluble zinc salts, soluble borates (real retarders) or lignosulphonic acids and their salts and hydroxylated carboxylic acids and their salts (waterreducing retarders which however belong to the group of surface active agents). Retardation in general is effected by adsorption of the molecules on the cement grains and increasing with the number of groups in the added molecules capable of forming hydrogen bonds with the cement grains.

Although the hydration is retarded in the early stages of the hydration, it is compensated later on by a higher rate of hydration so that the amount of bound water and heat of hydration are hardly changed at an age of about 28 days. Therefore in general it is thought that the degree of hydration still holds good as a measure of the cement paste characteristics if retarders or accelerators are added, although some (preliminary) chemical reactions are different from the cement-water interaction without these admixtures [16]. There is however a change in habitus of the gel-crystallites [17], the ratio between long fibres and short fibres will be different, leading to the wellknown strength-effects: high early strength in fact is given by a relative high degree of hydration, high strength at late ages are caused by an

increased amount of long fibred CSH and consequently by the relative high density. Therefore addition of about 2% finely grinded cementstone does increase strength at all stages with about 20%-30% because of the increased amount of long fibred CSH.

Surface active agents (nonionics, anionics and cationics) act by adsorption on the cement grains and as such effect its behaviour: anionics which make cement hydrophobic (AE agents), anionics which make cement hydrophilic (waterreducing retarders, fluidifiers) and nonionics which make cement hydrophilic (fluidifiers). The amount of bound water and heat of hydration are changed sometimes somewhat as function of time, the end values hardly are changed as is the case for the mechanism of chemical reactions [16]. There may be however a reduction of the pseudo-solid portion of the water [18] but not of the bound water. The strange fact that hydrated portland cements have a large positive ionic charge whereas CSH hydrate, the major constituent of hydrated portland cements carries an even larger negative ionic charge is an anomaly that can be readily interpreted by the availability of Ca(OH)_2 giving Ca^{++} precipitating in and on the CSH and the hydration products of C_4AF both having a positive charge. [19].

One can conclude by saying that in general the bound water content is a good measure to characterize the cementpaste, also in case of addition of admixtures.

6. Effect of walleffect and exposure conditions.

Roughly speaking, a concrete member has a woodlike structure [20], having a carbonated surface layer as a bark and a more or less wet cone as the pith. The properties of the various zones (cement skin, mortar skin, zone of drying/wetting, core) differ essentially from each other by reason of the possible different degrees of hydration, drying, carbonation, shrinkage and creep. Little research has taken these structural features into account.

The formation and effect of the layered structure is markedly dependent upon size and form of the member concerned, and it is probable that more or less unsolved dependence of properties of concrete upon size and form of a specimen could in many cases be attributable to these phenomena.

Since the hydration process stops when the moisture content of the cement paste is in equilibrium with a R.H of about 80%, the thickness of the layer at which this occurs has been approximated by [20] as $\sqrt{k \cdot h}$ in which k = moisture conductivity of concrete (usually $\approx 10^{-10} \text{ m}^2/3$) and h the duration of drying

which means that after 10 days drying the thickness of non-hydration layer varies from 40 mm (low strength concrete) over 4 mm (middle strength) to 0.4 mm (high strength).

So for thin concrete members, particularly of low quality, one should realize the importance of the place and largeness of the sample from which the degree of hydration is determined. This is even more the case if the evaporable water content has to be determined as a characteristic property, since (calculated mostly on basis of diffusion theory) the moisture content of the concrete only gradually reaches its max. and constant value. Consequently, because hydration only is possible when the $\frac{W}{C}$ ratio exceeds about 0,45, this too may effect the degree of hydration. Fig. 2 gives the principles of the effect of cementcontent and evaporable water content.

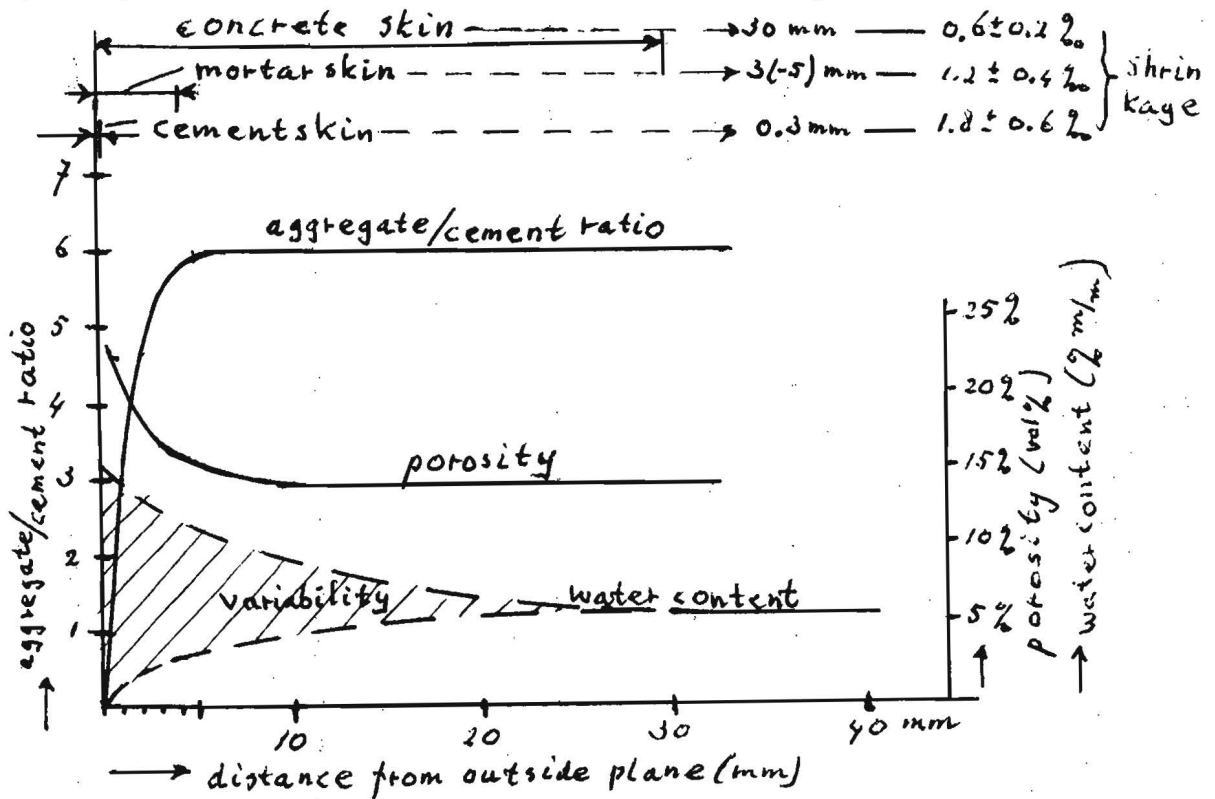


Fig. 2 - Layers in concrete members.

Next of course there is the effect of carbonation which changes the micro-structure of the cementpaste since the CO₂ take-up can be as much as 0.5 kg CO₂/kg dry cement [20] depending on permeability and internal humidity (in the very wet or the very dry state no carbonation occurs, max. is at 50 - 80% RH) Carbonation has a definite effect on properties like strength and shrinkage just like moisture and temperature [20].

The conversion of Ca(OH)_2 to CaCO_3 increases the volume, while in reality a shrinkage is measured; this anomaly has been explained best (to the authors opinion) by Powers [21] in his hypothesis that Ca(OH)_2 crystals are dissolved while under pressure and deposited as CaCO_3 in places not under pressure, while CSH hydration products become carbonated by topochemical reactions, about 2/3 of the Ca^{++} of gel-substance being available for such (rapid) reactions.

In determining the degree of hydration by the non-evaporable water content, the carbonate can give rise to mistakes by the difference in weight by the escape of H_2O from Ca(OH)_2 at the dissociation temperature of max 550°C and the escape of CO_2 from CaCO_3 gradually from above 100°C to the (almost) final dissociation temperature of 600°C from which fact lit. [22] defines the non-evaporable water content as that represented by the difference between total loss on ignition and the evaporable water plus total carbon dioxide content (which has to be determined, fe by taking up the CO_2 by anhydrous magnesium perchlorate in the way as given in [22] . If the degree of hydration of the bulk material of concrete has to be determined the sample has to be taken outside the carbonation zone which can be detected easily by using phenol phtalein or Alizerine. An estimation of the thickness of the carbonation layer can be made by using the various formulas developed for the rate of carbonation, preferably however lit [23].

An indication of the effect of carbonation also can be get from the evaporable water content, this being most favourable for carbonation if the values are between 6 and 18% of the cement (with a max at about 12% [22]).

The effect of moisture and temperature directly have their effect on the degree of hydration and as such are incorporated in it. A prediction of the effect of temperature on the degree of hydration has been given by

Pihlajavaara [20,24]: $m = \exp(-d \cdot h_{293}^{\frac{1}{2}})$; $h_{293} = h_T \exp \left[\frac{5900}{K} - \frac{5900}{293} \right]$

for $T = 283 \text{ K} - 303 \text{ K}$ ($10^\circ\text{C} - 30^\circ\text{C}$) in which $m =$ degree of hydration,

h_{293} is duration of hydration at T , K and d the parameter, dependent upon cement, $\frac{W}{C}$ ratio and moisture conditions.

7. Methods to determine the degree of hydration and its value

This chapter only gives a very rough overall view neither pretending completeness, nor precision because the author misses the necessary knowledge and experience in this particular field of measurements.

Therefore only formerly used methods are described in somewhat more detail while the latest development in this area is not dealt with other than by referring to some literature in this area.

7.1 Non evaporable water content

It all started with Powers definition and determination of the non evaporable water content W_n of cementpaste [25] from which the principles still are valid: sample preparation, removing evaporable water, determination on loss of ignition (of sample and original cement) and calculating the non-evaporable water content. For mortar and concrete containing no calcareous aggregates, the CaO content of the sample (of such size as to contain 5 g of the original cement) has to be determined which lead to the ratio $\frac{w_n}{c}$ (non evaporable water to cement in gr per gr original cement:

$$\frac{w_n}{c} = \frac{w_1}{w_2} (1-L)^{-1} \text{ for cement paste and}$$

$$\frac{w_n}{c} = \left[\frac{w_1}{w_2} (1-L)^{-1} \right] \times \left[\frac{\text{CaO g per g of original cement}}{\text{CaO g per g of ignited sample}} \right]$$

in which w_1 and w_2 are weights of dry and ignited samples in g and L = ignition loss of original cement in g per g of original cement.

For other types of aggregates it is advised to prepare neat cement specimens having the same $\frac{w}{c}$ ratio as the corresponding concrete while curing has to be done under the same conditions as the concrete. By determining the non-evaporable water content and assuming 26% at complete hydration, the degree of hydration can be calculated. If the evaporable water has to be determined, corrections for bleeding and adsorption by aggregates have to be made, which in fact means that bleeding water has to be determined and aggregates have to be used that do not absorb water (non absorptive or presaturated).

Copeland and Hayes [26] improved the method by using a vacuum desiccator connected to a trap held at the temperature of dry ice-alcohol (-79°C) in stead of using magnesium perchlorate dihydrate and-tetrahydrate as drying agent while the ignition is carried out at 1050°C in stead of at 1000°C . The improvement leads to a value of w_n which is about 8% smaller.

Danielson [27] uses the difference by heating at 105°C for 3 days and at 1050°C for 1 h which method (as far as is known) mostly is followed.

In [27] Daniélsón describes the total procedure (control of temperature and R.H) and gives corrections for deviations in $\frac{w}{c}$ ratio, use of admixtures, discusses the errors and gives comparisons with the former mentioned methods from which it follows that under the given conditions the method has a very good reproducibility. It should be noted however that in [27] Danielsson's notation differs from [25,26] in calculating the non-evaporable water content in relation to the ignited cement weight which is in better accordance with the determination of the heat of hydration (by heat of solution method BS 1370, 1947 p.20-27) which also is calculated per

unit weight of ignited cement, a linear relation consisting between these two values.

In between the Institut Central de la Recherche des Materiaux de Construction in Budapest reports in [28] to use a distillation apparatus, analytical balance and an oven and to add to about 20 g of the finally grinded sample of concrete 130 ml toluene of which 100 ml are distilled, filtrated and washed 3 times with benzol and later on 3 times with ether to constant weight and heats to 1000°C for the loss on ignition.

Hayden [29,30] gives the idea that 1 h boiling in 96% Alcohol and succeeded drying at 105°C gives the evaporable water content while treatment of the further ignited sample leads to the non evaporable water after correction with that of the cement itself. The CaO content in this ignited sample could be determined by again boiling with 96% alcohol by which method the CaO is said to rehydrate to $\text{Ca}(\text{OH})_2$ and is dried again. The loss of ignition caused by this uptake of water has to be multiplied by 3.111 to give the original CaO-content of the cement that has been hydrated to $\text{Ca}(\text{OH})_2$.

A short overall view of the estimation of $\text{Ca}(\text{OH})_2$ in set portland cement is given by Lea in [6, p 212 - 214].

7.2. Heat of hydration

The method suitable for long-period measurements is the heat of solution method, internationally everywhere standardized yet and further comments are not necessary-only that carbonation of the hydrated cement is a serious source of error (and therefore has to be prevented) for the absorption of 1% CO_2 causes an error of 5.8 cal/gm (24.3J/g) out of a total of between 60 and 100 cal/g (250 - 420J/g) in the heat of hydration. There is also uncertainty in the application of the method to pozzolanic cements since a proportion of the pozzolana usually remains insoluble and is not quite the same for the fresh and the hydrated cement [6,p 240-249].

On basis of measured differences with the nuclear magnetic resonance method, v.Gronow [31] gives a simple calculated table for the heat of hydration of no lesser accuracy then the complicated method of calculation and determination with the help of the heat of solution method, see table 2.

Table 2 Heat of hydration in cal/g per % clinkercomponent of portland cement at $23 \pm 2^\circ\text{C}$, $w = 0,45$, 3100 ± 200 Blaine

	Days					
	3	7	28	90	180	360
C ₃ A	1.7	1.8	1.9	2.0	2.1	2.2
C ₃ S	0.8	0.9	1.0	1.1	1.2	1.2
C ₂ S	0.1	0.2	0.3	0.4	0.5	0.6
C ₄ AF	0.2	0.3	0.4	0.5	0.6	0.7

He also mentions the fact that due to the way of cooling (leading to different glass content) the cement clinker, a difference in heat of hydration during the hardening proces may occur of about 4 cal/g while the heat of solution at room temperature is about 40 cal/g greater if glass is soluted in stead of crystallized substance. Since the German standard does not allow to vary more than 10% in glass content of total clinker amount the accuracy in the heat of hydration cannot be higher than about 5 cal. which is the same for table 2.

Regarding the effect of temperature, it can be said that its effect on the heat of hydration follows Arrhenius'law so there is a linear relation between the log.of the heat of hydration (cal/g,day) and the reversed value of the (absolute) temperature.

7.3 Modern methods

All the uncertainties in the degree of hydration basically are coming forth from the decision about what "bound" water is and the rough division into two types (hydrate water and pore water) no longer is thought useful since the binding energy of a hydrate H₂O molecule can be even smaller than that of a H₂O-molecule in the monomolecular adsorbtion layer. So there are various modifications : hydrate water, interlaying water as a kind of connecting link to pore water which can be devided into monolayer water (adsorbed on the surface of the gel), the water on top of this monolayer, the water condensed in the micropores ($r < 1 \mu$) and the macropore water. And just the porewater is so very important in practice for mechanical properties, shrinkage and creep of concrete.

A series of measuring methods has been developed during the last 15 years by which gradually more and more information is gathered about these phenomena. So in lit.[32] with its own list of literature already results are given of the methods of DTA (Different thermoanalysis),

TG (thermogravimetry) and NMR (nuclear magnetic resource).

Another method to follow hydration especially during the first period is IR (infa red) spectroscopy [33] while with the help of X-ray quantitative analysis the amount of unhydrated cement is measured [34]. There is no doubt the last 10 years a further development has taken place about which however the author unfortunately is unable to report. However in table 3 an overall view of the various methods and its basic principles are given while applications can be found in lit.[36 to 53].

Table 3 OVERALL VIEW OF SOME MODERN ANALYSING TECHNIQUES.

Principle	Examples	Surface characterization
<p>1. atoms in a surface, excited by primary radiation, give off a characteristic radiation for each element as the results of excitation or of a de-excitation process in the atom</p>	<p><u>XPS</u> = X-ray excited photo electron-spectroscopy <u>EMA</u> = electron microprobe X-ray analysis <u>AES</u> = Auger electron-spectroscopy</p>	<p>a. atomic composition</p>
<p>2. energy losses of primary radiation (see 1) give in certain cases a characteristic of the surface</p>	<p><u>ISS</u> = ion scattering spectroscopy <u>RBS</u> = Rutherford back-scattering spectroscopy</p>	
<p>3. mass spectroscopy by loosening atoms of a surface, bringing them in the gasphase and analyzing for mass</p>	<p><u>SIMS</u> = secondary ion mass spectroscopy <u>IMMA</u> = ion microprobe mass analysis <u>FDMS</u> = field desorption mass spectroscopy <u>GDMS</u> = glow discharge mass spectrometry</p>	
<p>x - y plane (parallel to the surface)</p> <p>1. using primary rays through the material or reflected optical microscopy <u>TEM</u> = transmission electronmicroscopy</p> <p>2. using secondary rays: <u>SEM</u> = scanning electronmicroscopy in case of use of detected X-rays the resolution can be ~ 1 μ use of secondary ions of certain mass in <u>ion microprobe</u> and in <u>SAM</u> = scanning Auger microscopy</p>	<p>z - plane (perpendicular to surface = "depth")</p> <p>1. interaction between radiation and material: limiting penetration of primary rays and depth for emitting secondary rays give limits <u>ISS</u> = (low energy ion scattering spectroscopy) <u>photo electronmicroscopy</u> using photons <u>RBS</u> = Rutherford back-scattering spectroscopy</p> <p>2. Removal of atom layers of a surface (mostly by ion-bombing) followed by mass-spectrometry or optical spectrometry or fe by electron spectroscopy</p>	<p>b. typological analysis = phase of components at/in a surface</p>

different types of structural information:

- ioncharge or valency of an element from X-ray photon-electronspectra
- direct chemical surrounding or presence of certain surface compounds by Auger - and photonelectronspectra and electronmicroprobe X-ray spectra (by comparison with standard compounds):
ESR = electronspinresonance and EXAFS (X-ray absorbtion) give indications about symmetry of surroundings and the amount of neighbours with its distance to the central ion.
- the nature of the chemical bound of adsorption complexes can be studied by UPS = UV excitited photon-electron spectroscopy and XPS (X-ray excitited) adsorptionbinds can be investigated by NMR (nuclear magnetic resonance)
- identification of adsorption complexes (also by UPS) by IR spectroscopy (infra red) with Fourier Transform techniques and by LEELS (low-energy electron loss spectroscopy) while Raman spectroscopy is somewhat disappointing because of fluorescency background
- ordered phases can be detected by diffraction techniques and electronmicroscopy fe XRD (X-ray diffraction) can distinct drystals $>, 30\text{\AA}$
thin layers can be analysed by HEED (high energy electron diffraction), two - dimensional layers are studied with LEED (low energy electron diffraction)
surface structures can be found with electronmicroscopy or FIM (field ion microscopy).

ξ.
information about chemical bounds by analysing the data of characteristic radiation,energylosses of primary rays and of masses of surfacematerial, and of adsorbed-reflected and diffracted radiation and of radiation excitited by electrical fields or by heating

8. Value of the degree of hydration and conclusion

Although at first sight everybody agrees that the degree of hydration of cement in concrete is a determining factor for all properties of concrete, it is doubtful if for practical purposes this characteristic can be used as a property. On one side there are the uncertainties in the determination of the degree of hydration, at the other side there is the lack of correlation to wished properties.

Since practice in the first place want to know strength values which not only are determined by the degrees of hydration of the cementpaste but too by the adhesion between paste and aggregate, it may be questioned if the degree of hydration can help practice in this stage of science. It may well be that properties derived from the degree of hydration, like for instance porosity [35] of cementpaste and concrete would prove to be of more importance for practical applications.

Finally there may be referred to the lack of information regarding electrical properties of cementpaste and concrete, although already in 1963 the idea was raised that cement clinkers and puzzolans probably are semi-conductors [36] and hydraulic action could be considered as semi conductor surface reactions and the rate of such reactions are governed by the position of bulk Fermi level. Cementing hydrators are claimed to owe their cementing property to their semi-conductivity which may be "p"-type semi conductors with some of the H^+ from the water molecules in these hydrates behaving as "holes" and this should distinguish the cementing hydrates from other inorganic hydrates. Adhesion between cement and aggregates should be a semi conductor surface reaction and the bond involved then is a "donor"-type bond. The author may have missed a follow up of this theory but would suggest to study its validity. Compared to the great development of semi-conductor-science, cooperation with scientists in this field seemed to be highly valuable.

LIST OF LITERATURE

1. Cornelissen HAW - Betonsamenstelling van viaduct te Eindhoven (concrete composition of fly-over at Eindhoven), rapport M 76-5 Lab. Materiaalkunde, TH - Eindhoven.
2. Skalny J, Daugherty K E - Everything you always wanted to know about portlandcement - Jan. 1972 Chemtech. p. 38-45
3. Sereda P J, Ramachandran V S - Predictability gap between Science and Technology of Cements - J of the Am. Cem. Society Vol 58 no. 3-4, p 94-99; Vol 58 no. 5-6, p.249-253 (Characterization of hydraulic Cements and Physical and Mechanical Behaviour of Hydrated Cements respectively).
4. Czernin, W - Zementchimie für Bauingenieure Bauverlag GmbH, Wiesbaden-Berlin 1968 - Dutch translation by K L A van der Leeuw - Verkoopassociatie ENCI-CEMY-ROBAR NV, Amsterdam 1968.
5. Verbeck, G - Cement hydration reactions at early ages - J of the PCA Res and Dev.Lab. Vol 7, no. 3, 57-63, Sept. 1965.
6. Lea, F M - The chemistry of cement and concrete, Edward Arnold (Publ.) Ltd., 2nd edition, 1956, p.212-214.
7. Powers, T C - The physical structure of cement and concrete - Cement and Lime Manufacture Vol XXIX, nr. 2 March 1956, p.13-24.
8. Fulton, F S - Simplified phase diagrams for cementpaste - Cement and Lime Manufacture Vol XXXIV, nr. 5, Sept. 1961, p. 65-68.
9. Wesche, K- Hermann, V- Waber, J W - On some concrete properties as a function of the pores of hardened cementpast - RILEM-IUPAC Symposium Pore Structure and Properties of Materials, Prague Sept. 18 - 21, 1973, Proc.part V, p. D177-D 187.
- 0.Fagerland, G - Connections between porosity and mechanical properties of materials (in Swedisch) Report 26, 1972, Division of Building Technology, Lund Institute of Technology (300p, 229 fig.)
- 1.Alexander, K M - A study of Concrete strength and mode of fracture in terms of matrix, bond and aggregate strength. Tewksbury symposium on fracture 1963, Melbourne, Engineering Faculty, Un. of Melbourne 1964, p. 141-168
- 2.Alexander, K M - Wardlaw, J- Gilbert, D.J.- Aggregate cement bond, cement-paste strength and the strength of concrete - Proc. of an Intern. Cong. London Sept. 1965, The Structure of Concrete and its behaviour under load.
- 3.Terrier, P - Contribution de recherches sur l'hydratation des ciments au problème de la liaison dans le béton - RILEM -

Colloque "Liaisons de contact dans les matériaux composites utilisés en génie civil". Toulouse, France, 22-24 Nov. 1972.

14. Lyubimova, T. Yu., Pinus, E. R. - Crystallization structure in the contact zone between aggregate and cement in concrete - Kolloidnyi Zhurnal Vol 24 nr. 5 Sept.-Oct. 1962, p.578-587.
15. Zimbelmann, R. - Zur Frage der Festigkeitssteigerung bei Beton - Betonwerk + Fertigteil - Technik Heft 2, 1978, p. 89-96.
16. Physico-chemical principles of the action of the admixtures with various cements and concrete - Topic II International Symp. on Admixtures for Mortar and Concrete, Brussels Aug. 30th and Sept. 1st 1967.
17. Richartz, W. - Über die Gefüge und Festigkeitsentwicklung des Zementsteins - Beton nr. 5, 1969, p.203-205, Beton nr. 6, 1969 p. 245-248.
18. Grün, W. - Grün, H. R. - Zur Frage der physiko-chemischen Verhaltenweise von Wasser der hydratisierenden Zementes im Beton - Zement - Kalk - Gips nr. 11, 1961, p.514-520.
19. Pike, R. G., Hubbard, D. - Source of Non-Migratable Ionic Charges developed by Portland and High-Alumina Cements during Hydration - Highway Research Board Proc. 37, 256 (1958)
20. Pihlajavaara S. E. - History - dependence, ageing and irreversibility of properties of concrete - Structure, Solid Mechanics and Engineering Design Proc. Southampton 1969 Civil Eng. Conference Part 1 Wiley - Interscience 1971, p.719-741.
21. Powers, T.C. - A hypothesis on carbonation shrinkage. J of the PCA, May 1962, p. 40-50.
22. Kroone, B. - Blakey, F. A. - Reaction between carbon dioxide gas and mortar - J of the ACI, Dec. 1959, p.497-509.
23. Martin, Rauen, Schiesze - Karbonatisierung von Beton aus verschiedenen Zementen - Betonwerk + Fertigteil Technik Heft.12 - 1975, p.588 - 590.
24. Pihlajavaara, S. E. - Notes on the drying of concrete - State Inst. Tech. Res. (Finland) Report Series III - Building 74.
25. Powers, T. C. - The non evaporable water content of hardened Portland Cementpaste - its significance for concrete research and its method for determination - ASTM Bulletin 158, May 1949, p.68-76.

26. Copeland, L E, Hayes, J C - Determination of non-evaporable water in hardened Portland-cementpaste - ASTM Bulletin 194, Dec. 1953, p.70.74.
27. Danielsson, U - An apparatus for easy determination of the amount of bound water in cementpastes yielding highly reproducible results - Matériaux et Constructions vol. 7 no. 38 - 1974, p. 231 - 246 (or CBI Report 2:75 of Swedish Cement and Concrete Institute, Stockholm).
28. Institut Central de la Recherche au Matériaux de Construction (Budapest, Hongrie) - Methode de mesure du degré d'hydratation des ciments - RILEM Bulletin, New Series No. 22, March 1964, p.56.
29. Hayden, R - Neue Versuche zur Bestimmung der freien Kalkes im Portlandzement - Zement - Kalk - Gips nr. 3; 1950, p.36.
30. Hayden, R - Das vom Zement gebundene Wasser - Zement - Kalk - Gips ? p.120-122.
31. Gronow von, H E - Die Erhärtungswärme von Portlandzement, unter besonderer Berücksichtigung der physikalisch - chemischen Natur des im erhärteten Zementmörtel gebundenes Wasser - Tonindustrie - Zeitung und Keramische Rundschau 86, 1962, H 10, p.209-222.
32. Englebert, G - Wittmann, F - Water in hardened cementpaste - Materials and Structures Nov.-Dec. 1968, no. 6, 535-546.
33. Haas de, G D - Kreijger, P C - Niël, E N M G - Slagter, J C - Stein, H N - Theissing, E M - Wallendael van, M - The shrinkage of hardening cement and mortar - Cement and Concrete Research vol.5, 1975, p.295 - 320.
34. Alegre, R - Applications des Rayons X en cementerie - Publ. Techn. no. 144 du Centre d'Etudes et de Recherches de l'Industrie des Liants Hydrauliques (CERILH) 1963.
35. Grudemo, A - Strength os. Structure in cementpastes - 6th International Symp. on the Chemistry of Cement, Moscow Sept. 23-27, 1974; CBI report 13:75 (Swedish Cement and Concrete Research Institute, Stockholm).
36. Beausoin, J J - Feldman, R F F - The significance of helium diffusion measurement in studying the removal of structural water in inorganic hydrated systems - Cement and Concrete Research Vol 8, no. 2 1978 p.223-232

(see also Vol 7, 1977, p.585-596)

- 37.Bensted, J - Raman spectral studies of carbonation phenomena
Cement and Concrete Research Vol. 7 1977 no. 2
p. 161 - 164.
- 38.Jazairi, Illaton, J M - A simultaneous semi-isothermal method of
thermo-gravimetry and derivative thermogravimetry
and its application to cementpastes. Cement and
Concrete Research Vol. 7, 1977 no. 3, p. 247-258.
- 39.Schneider, U - Weiss, R - Kinetische Betrachtungen über den thermischen
Abbau zementgebundener Betone und dessen mechanische
Auswirkungen - Cement and Concrete Research Vol.7
no. 3, 1977, p.259-268.
- 40.Lahajnar, G et al - On the use of pulse N M R techniques for the study
of cement hydration. Cement and Concrete Research
Vol. 7, 1977 no. 4, p.385-394.
- 41.Kristmann, M - Portland cement clinker, minerological and chemical
investigations part I - Microscopy, X-ray fluorescence
X-ray diffraction - Cement and Concrete Research
1977 no. 6, p.649-658.
- 42.Relis, M - Soroka, I - Variation in density of portland cement hydra-
tion products - Cement and Concrete Research 1977
no. 6, pp.673 - 680.
- 43.Hannawayga, F - Optimum thickness by X-ray test for clinker minerals
Cement and Concrete Research 1977 no. 6, pp. 695 - 702.
- 44.Setzer, M J - A method for description of mechanical behaviour
of hardened cementpaste by evaluating adsorption
data - Cement and Concrete Research Vo. 6, 1976
no. 1, pp. 37-48.
- 45.Wittmann, F H - On the action of capillary pressure in fresh concrete -
Cement and Concrete Research Vol. 6, 1976 no. 1
p. 49-56.
- 46.Fierens, P - Verhaegen, J.P. - Propriétés nucleophiles de surfaces de
C₃S - Cement and Concrete Research Vol. 6, 1976
no. 1, pp. 103 - 112.
- 47.Litonu, G G - Variability of the nitrogen surface area of hydrated
cementpaste - Cement and Concrete Research Vo. 6, 1976
no. 1, pp. 139-144.
- 48.Lachaud, R - Possibilités de la diffusion centrale dans l'examen
d'états altérés du ciment - Cement and Concrete Research
Vo. 6, 1976, no. 4, pp. 571-582.

49. Dent Glasser, L S- Lachowski, E E - The method of trimethylsilylation and studies of cement hydration: some possible pitfalls in interpreting results - Cement and Concrete Research Vol. 6, 1976 no. 6, pp. 811-812.
50. Wittmann, F H - Schlude, F - Microwave absorption of hardened cement-paste - Cement and Concrete Research Vol. 5, 1975 no. 1, pp. 63-71.
51. Fierens, P - Verhaegen, J P - The effect of water on pure and doped C_3S , using techniques of adsorboluminescence - Cement and Concrete Research Vol. 5, 1975 no. 3 pp. 233 -238.
52. Knudsen, T - Thaulow, N - Quantitative microanalyses of alkali-silica gel in concrete. Cement and Concrete Research Vol. 5, 1975 no. 5 pp. 443 - 454.
53. Luxán de, M P - Soria, F - Study and critical review of the pozzolanicity test - Cement and Concrete Research Vol.5 1975 no. 5, pp. 461-480.
54. Chatterji, AVK - Phatck, T C - Semiconductivity and cementing action in hydraulic - bond type cements - Nature Febr. 16th 1963, vol. 197, p.656-659.