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Nilsson, Lars-Olof

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DIVISION OF BUILDING MATERIALS
LUND INSTITUTE OF TECHNOLOGY

HYGROSCOPIC MOISTURE IN CONCRETE - DRYING, MEASUREMENTS & RELATED MATERIAL PROPERTIES

LARS-OLOF NILSSON

REPORT TVBM-1003
LUND SWEDEN 1980

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by Lars-Olof Nilsson
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44	-4	Wajjar	Najjar
48	+5	on	in
56*	-4	slope	shape
58	+2	carboration	carbonation
58*	-9	driving of...	driving force at...
60*	-2	...y=0.25,..	...y=0.1 and 0.14 days/% change for y==0.25,...
67	-1	decrease	decreases
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90	+15	thickness	thicknesses
95	+10	drying the	drying of the
98	-3	moiature	moisture
100	+3	and	-
100	+4	carcied	carried
109	+10	role	rule
113	+15	then	than
115	-16	diviation	deviation
116	+1	construction	structure
117	-6	ralative	relative

* = essential correction

PREFACE

The division of Building Materials at the Lund Institute of Technology has done research and investigations on moisture problems ever since the division started in 1964 under the management of Prof. S.G. Bergström. Theoretical and experimental research were combined with investigations of damages and information to the building trade. This work gave rise to a high standard of knowledge by the staff of the division and it was quite natural to continue this work in 1972 when I joined the division as one of the successors to Dr. L. Ahlgren, who had built up the activity in the domain of moisture in building materials and written his thesis on moisture fixation.

The present work was initiated in 1973 by Dr. G. Fagerlund, at that time head of the division, as a research project with the title "Applied moisture problems in connection with material combinations and surface layers" with financial support from the Swedish Council for Building research. The project was soon concentrated on solving the moisture problems arising when tight coverings are applied on concrete floors. This was done by developing calculation methods for drying of materials with an excess of moisture, mainly concrete. Existing methods suffered from a lack of required material properties and this is where the main effort has been put in this work. The expected results were considered as having a great significance for use in practice since a great number of damages occur every year due to unsatisfactory drying-out of excess moisture. Also for other research projects, dealing with material properties influenced by the moisture content, the project was considered as having a significance.

Other connected problems have been dealt with. Damages due to additional moisture, especially soil moisture, were common and this problem was also dealt with to some extent. Later methods for the drying-out of excess moisture were studied and the possibilities of energy saving by using dehumidifiers were pointed out. New methods of moisture measurements have also been developed. The equipment is now available and the hygrometric methods developed are suggested for use in practice to replace the present methods. Some of this later work is also included in the thesis.

ACKNOWLEDGEMENTS

I would like to express my gratitude to all those who assisted in this work in various ways.

First of all I would like to thank Prof. Arne Hillerborg, head of the division since 1974, for his ever growing interest in moisture research. His advice, encouragement and constructive criticism has been of invaluable help to me. I also thank Prof. Sven G. Bergström and Dr. Göran Fagerlund for their way of introducing me to the subject and for still having an interest of and supporting the work done.

Most of the experimental work has been carried out by Bo Johansson in a most efficient way. I am deeply indebted to him for his accurate way of making use of his knowledge about concrete. I also express my sincerest thanks to Leif Erlandsson and Sture Sahlén, not only for their participation in the development of new equipment for moisture measurements, but also for solving most experimental problems and always having an idea of how to continue.

I am particularly grateful to Mrs Mona Hammar for the long devoted hours of translating my handwriting into a typed script in a very accurate way and to Mrs Britt Andersson, who made all the figures look like small pieces of art, using her personal handwriting on my request.

To all others who have participated in the work and supported me I would like to express my sincerest thanks.

Lund, March 1980

Lars-Olof Nilsson

CONTENTS

SUMMARY

The work presented in this thesis has been concentrated on developing a method of calculating the drying of moisture in hydrating concrete. A great number of theories have been available but could not be used because the necessary material properties regarding moisture were missing. The most essential material properties for several concrete compositions have therefore been determined by means of literary studies and extensive laboratory investigations.

From contraction measurements the progress and rate of hydration was found to be approximately described by simple mathematical expressions. By thermal methods the progress of hydration of different cements was determined and evaluated by means of equations expressing the actual amount of non-evaporable water. It is indicated that some 10% of this water is liberated when heating to above 600 °C and that it is not carbon-dioxide that causes this weight loss. The effect of composition and curing conditions was estimated by results from literature.

On the basis of literary information, in some cases contradictory, and some experimental results the desorption and absorption isotherms for concrete are evaluated with the effect of composition and age elucidated. Some examples of the moisture capacity are evaluated and the temperature dependence of the sorption isotherm is dealt with to a lesser degree. The amount of excess moisture affected by the composition is calculated in a few examples and the significance of a high cement content regarding this matter is shown.

By means of flow measurements with a modified cup method the moisture flow coefficient as a function of pore humidity have been determined for three cement mortars with different water-cement ratios. In several drying experiments the effect on the diffusivity of different factors in the composition of concrete is determined. Besides the water-cement ratio, the air content in particular has been found to be most important. A simple composite model, corresponding well with experiments, indicates a plain volume effect of the air. The effect of the aggregate content and gradation has been studied to some extent and the main effect has been found to originate from the different modulus of fineness. The effect of age is of course very essential at lower ages and the effect on the diffusivity is estimated.

In the case of an untreated concrete surface, the boundary conditions are found to be expressed rather accurately by assuming the concrete surface to be in equilibrium with the ambient air. The effect of some surface layers is also shown.

Approximate critical moisture conditions for some phenomena in concrete and materials sometimes combined with concrete are summarized on the basis of literary information.

A computerized calculation model using these material properties has been developed for the description of hygroscopic moisture under isothermal conditions. It is possible with the model to calculate the drying of concrete with different compositions and ages, as well as different concrete structures, taking the hydration into consideration. The model has been compared with a number of full scale control experiments and a good correlation has been found. There are however still some material properties lacking and if very good accuracy is requested some comparative measurement should be carried out in order to estimate the parameters.

With the calculation model the effect of some essential factors on the drying of concrete has been estimated. The usual quadratic rule for the influence of size is shown to be inaccurate and the true effect is calculated and proved to be dependent on the curing time. The effect of the drying climate is also calculated and a diagram for rough estimations is given. The effect of a combined heat insulation is calculated and the effect of e.g. mineral wood is found to be very great; the reduction of the required drying time can easily reach 40%.

Finally hygrometric methods of moisture measurement, used in the experiments and developed for use in practice, are presented. There are several advantages in measuring the relative humidity in a concrete instead of the moisture content. The RH expresses the moisture activity in a far better way, and it is certainly the activity and not the content, that is of interest in most cases. In addition the relative humidity can be measured on small samples, not necessarily representative for the concrete, with an accuracy shown to be much better than when measuring the moisture content.

LIST OF SYMBOLS

A	aggregate content	kg/m^3
A	area	m^2
a, b	variables in eq. (3:10)	-
a_θ, b_θ	weight losses of original constituents at heating to $\theta\,^oC$	kg/kg
C	cement content	kg/m^3
C	amount of cement in a sample	kg
D	diffusivity, cf. eq. (5:3)	m^2/s
d	thickness	m
F	moisture flow	$kg/m^2 \cdot s$
F_o	Fourier number $D \cdot t/L^2$	1
f	variable in eq. (3:11)	kg/kg
g	rate of evaporation	$kg/m^2 \cdot s$
i	number	1
K	symbol for a concrete quality with a compressive strength exceeding K with a certain probability	kp/cm^2 (~0.1 MPa)
k	moisture flow coefficient, cf. Appendix II	-
L	characteristic dimension	m
M	molar mass	kg/mole
M	maturity, cf. eq. (3:2)	days ^oC
m	mass	kg
m_θ	mass after heating to $\theta\,^oC$	kg
P	absolute pressure	Pa
P_w	pore water pressure	Pa
p	water vapour pressure; p_s at saturation	Pa
R	molar gas constant 8.314	J/mole·K
R	resistance to moisture flow; Fig. 8.2	s/m
RH	relative humidity	1

r	pore radius	m
r^2	correlation coefficient	1
s	degree of saturation	1
T	absolute temperature	K
t	time	s
$t(y)$	drying time to reach a degree y of drying	days
u	moisture ratio by dry weight	kg/kg
V	volume	m^3
V_m	molar volume	m^3/mole
v	water vapour content; v_s at saturation	kg/m^3
w	moisture content; $\bar{w}$ average	kg/m^3
W	amount of moisture in a sample	kg
w_e	evaporable moisture content	kg/m^3
w_n	non-evaporable moisture content	kg/m^3
w_o	mixing water	kg/m^3
w_{eo}	initial moisture content at drying	kg/m^3
$w_{e\infty}$	equilibrium moisture content	kg/m^3
w_o/C	water-cement ratio	kg/kg
x	coordinate	m
y	degree of drying = $(w_{eo}-w_e)/(w_{eo}-w_{e\infty})$	1
α	degree of hydration	1
β	surface coefficient of moisture transfer	m/s
δ	air content	(m^3/m^3)
θ	Celsius temperature	^oC
ρ	density	kg/m^3
σ	surface tension	N/m
ϕ	relative humidity (RH); pore humidity	1
ϕ_{cr}	critical moisture condition as RH	1

1 INTRODUCTION TO MOISTURE IN CONCRETE

The moisture content in a porous material is very influential in many ways. Most mechanical and physical properties are affected, for example creep and thermal conductivity, and certain phenomena, such as swelling and shrinkage, are directly induced by change in the moisture content. The durability of the moist material itself or the surrounding materials is greatly affected by moisture taking part in a deterioration in several ways.

This work is part of a research project aimed at solving the moisture problems which arise when a surface layer sensitive to moisture is applied to a concrete structure that has an excess of moisture. This moisture problem can be dealt with in the same way as a structural design, cf. Figure 1.1.

Structural design

$$\left.\begin{array}{l}\text{Loads}\\ \text{Structural mechanics}\\ \text{Material properties}\end{array}\right\}\Rightarrow \text{stress } \sigma$$

Criterium of failure, f
Safety factor, s

$$\boxed{\sigma \leqslant \frac{f}{s}}$$

Moisture design

$$\left.\begin{array}{l}\text{Moisture sources}\\ \text{Moisture mechanics}\\ \text{Material properties}\end{array}\right\}\Rightarrow \phi$$

Critical moisture condition, ϕ_{cr}
(Safety)

$$\boxed{\phi < \phi_{cr}}$$

Fig. 1.1 Comparison between structural design and design to protect against moisture damages.

The different parts of a structural design are well known. In norms the loads that a structure should be designed to tolerate are given as well as the mechanical material properties and maximum stresses permitted. Furthermore the calculation methods are well established.

A design against moisture loads suffers from lack of knowledge in almost every stage of the design. Only the calculation methods and the moisture mechanics are developed but these are of little use as long as neither the required material properties nor the critical moisture conditions are sufficiently known. The present work is an attempt to determine and estimate some of this information and together with the moisture mechanics, make it possible to describe the moisture phenomena in concrete in a quantitative manner.

Most of the work has been aimed at solving moisture problems of concrete floors, principally shown in Figure 1.2, but the results and methods are applicable to most cases concerning the effects of moisture in concrete.

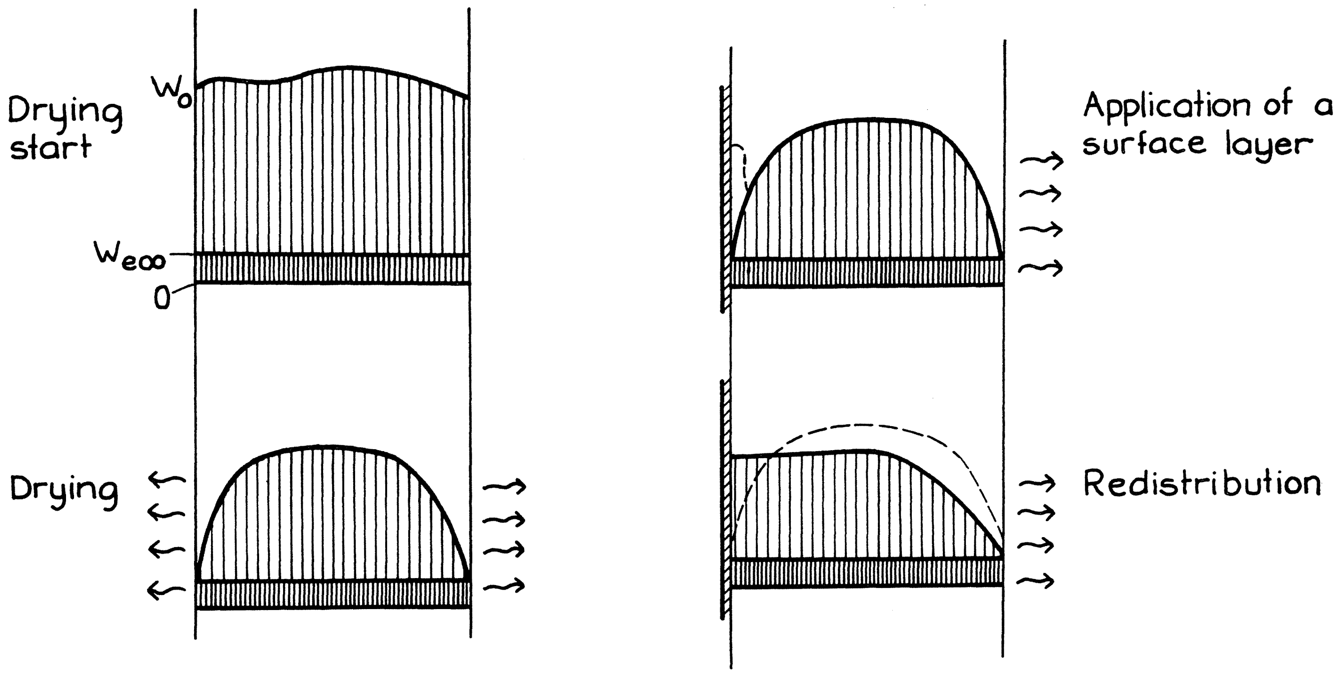


Fig. 1.2 Moisture distribution in a drying wall or slab before and after the application of a surface layer.

To describe moisture changes in a material, it is necessary to solve the so-called "law of mass conservation" which where concrete is concerned can be written, if carbonation is omitted, in one dimension as

$$\frac{\partial w_e}{\partial t} = - \frac{\partial F}{\partial x} - \frac{\partial w_n}{\partial t} \tag{1:1}$$

This equation is precise and contains no essential assumptions. The last term is rather simple. It describes the rate of hydration which depends on the type of cement, cement content, temperature, humidity etc.

The moisture flow F is however more difficult to express accurately and this is where assumptions and simplifications are needed as the mechanism of moisture flow in a porous material is extremely complicated. In the case of concrete it is, if possible, even more complicated as concrete is a heterogenous material with a highly variable composition. Furthermore the properties, at a given compostiton, change with the degree of hydration.

To solve the above equation boundary conditions have to be expressed. In order to do this the sorption isotherm is invaluable as it gives the equlibrium conditions towards which the material is striving. It is of course also a function of composition and age.

The material properties needed for the description of moisture in concrete are consequently:

- rate of hydration
- sorption isotherm
- moisture flow coefficients

expressed as functions of composition and age as well as of moisture and temperature conditions.

Many solutions to the equation (1:1) have been published with different degrees of simplification of the equation and the material properties e.g. excluding hydration, assuming the sorption isotherm is a straight line or using constant moisture flow coefficients.

However the main purpose of this work is to determine and estimate the most important constituents of the material properties and together with a computerized model of equation (1:1) compare the solutions to laboratory and field measurements of the drying of concrete and concrete structures. The effect of different variables can then be calculated and information intended for practical use put forward.

Because of the method chosen for describing the moisture flow only isothermal conditions are dealt with, but as the rapid heat transfer in concrete equalizes temperature differences very rapidly compared to moisture equalization, this limitation should not be too serious.

Another limitation is that generally only moisture changes within the hygroscopical range are dealt with, i.e. relative humidities below 98%.

2 COMPOSITION, STRUCTURE & POROSITY - A REVIEW

Concrete can, where moisture is concerned, be looked upon as a mixture of cement paste and an aggregate, as all the water is usually held in the cement paste and none in the aggregate at least this is the case when a non-porous aggregate is used. The air voids must however not be forgotten, even if their moisture content is definitely negligible.

The fixation of water in concrete is mainly a question of the composition and age of the cement paste only, but the migration of water is affected by the properties of the cement paste as well as the amount and distribution of the aggregate and air.

The cement paste is originally a mixture of water and cement in proportions w_o/C, the water-cement ratio, which is a measure of the space between the cement grains originally suspended in the water. If the grains are assumed to be spheres of equal size, cubic packed, the average distance between them is about 6% of the diameter for $w_o/C = 0.4$ and about 18% for $w_o/C = 0.7$, i.e. about three times greater for the higher water-cement ratio. This affects the properties of fresh and hardened cement paste and concrete to a great extent, see later.

When the cement is mixed with water, the different cement clinker components react to some of the water and the cement becomes hydrated. This water becomes chemically bound. The degree of hydration, α, is the ratio between hydrated cement and the original cement content. The maximum amount of chemically bound water is to the order of one quarter of the weight of the cement, according to Powers & Brownyard (1948), i.e.:

$$\frac{w_n}{C} \approx 0.25\alpha \qquad (2:1)$$

When the cement is hydrated the reaction products are growing as crystals from the cement grain creating the cement gel containing the gel pores, cf Fig. 2.1.

The amount of water in the gel pores, w_{gel}, at saturation is according to Powers & Brownyard (1948) shown as proportional to the non-evaporable water content with a proportionate constant, which depends on the type of cement and the method of determining w_n. The weight of the capillary water, w_{cap}, occupying the space outside the cement-gel was originally equal to the volume of w_o, but diminishes as the cement-gel grows even if the cementpaste is saturated.

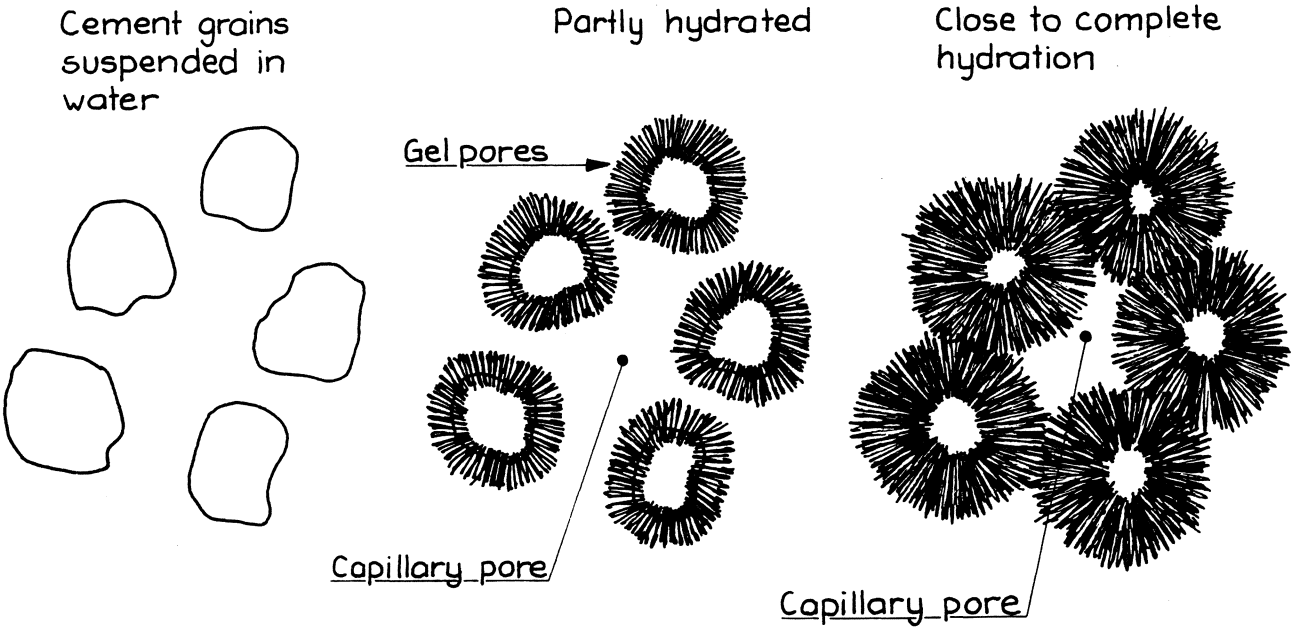


Fig. 2.1 Different phases of cement hydration in principle.

The total amount of evaporable water at saturation according to several authors, Powers & Brownyard (1948), Copeland & Hayes (1956), Czermin (1964), is approximately given by using the expression

$$\left(\frac{w_e}{C}\right)_{max} \approx \frac{w_o}{C} - 0.75\,\frac{w_n}{C} \approx \frac{w_o}{C} - 0.19\alpha \qquad (2:2)$$

This expression includes the amount of water, w_{contr}, absorbed in the pore volume originating from the contraction of the system cement + water during the hydration. This amount is given by Powers & Brownyard (1948) and is corrected by Powers (1960) to approximately

$$\frac{w_{contr}}{C} = 0.25\,\frac{w_n}{C} \approx 0.06\alpha \qquad (2:3)$$

If stored under water the cement paste will absorb this amount of water and if stored in air a part of the pore volume will be emptied by the weight of this water. This is known as selfdesiccation.

Dividing the evaporable water in cement paste into gel water respectively capillary water is not only a question of the above mentioned proportionate constant and whether the "contraction water" is a part of the gel water or the capillary water. The definitions of Powers & Brownyard (1948) and Powers (1960) use the origin and not the size of the pores as a basis. This means that the state of the pore water, and thereby its "mobility", is neglected. This is however a difficult task, especially when taking hysteresis phenomena into consideration, when water in a large pore with the shape of an "ink-bottle" can be inmobile at low humidities.

In Figure 2.2 the approximate distribution of the pore water at saturation is shown according to Powers (1960). The amount of water in the gel is then expressed by

$$\frac{w_{gel}}{C} = 0.21\alpha \qquad (2:4)$$

and contains the water absorbed by contraction.

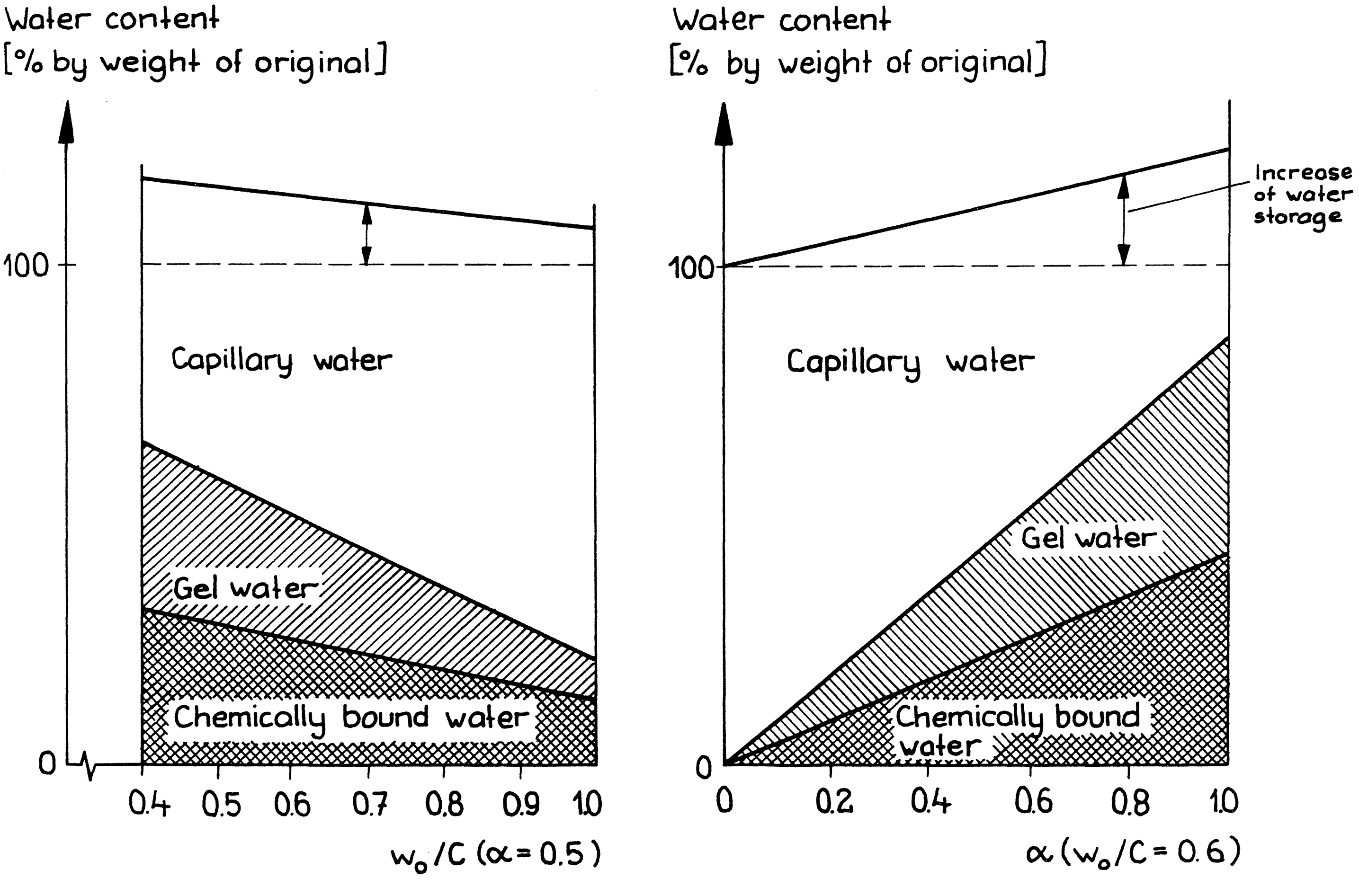


Fig. 2.2 Distribution of pore water in cement paste as a function of water-cement ratio at 50% degree of hydration and as a function of the degree of hydration at $w_o/C = 0.6$ respectively.

Consequently

$$\frac{w_{cap}}{C} \approx \frac{w_o}{C} - 0.40\,\alpha \qquad (2:5)$$

is an approximate expression for the amount of capillary water at saturation and corresponds to the frequently used capillary porosity.

When the hydration continues the capillary pore volume decreases. This occurs as a result of the growing cement-gel diminishing the size of the capillary pores. In Fig. 2.3, from Whiting & Kline (1977), this can be seen clearly.

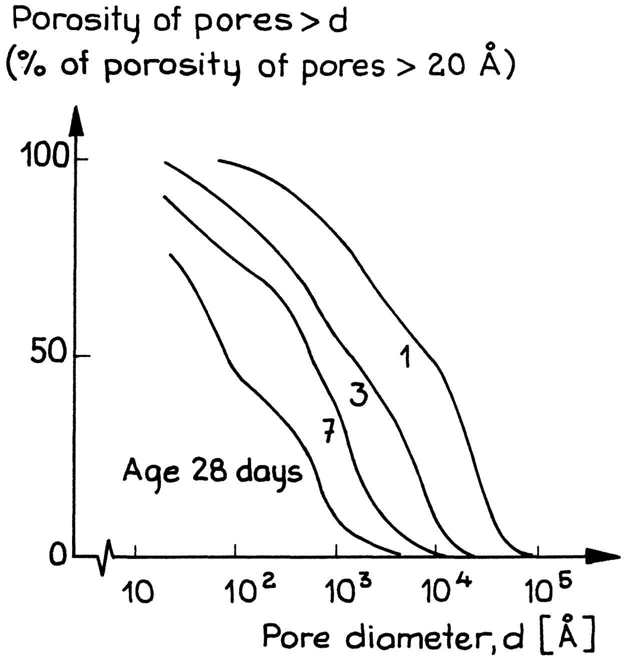


Fig. 2.3 Pore size distribution of cement paste, $w_0/C = 0.60$, of different ages, from Whiting & Kline (1977).

The pores in the capillary pore system gradually become smaller and smaller until the connection between the capillary pores no longer exists. If and when this happens is a function of the water-cement ratio and the degree of hydration. Powers et al (1959) give the following approximate figures:

$\frac{w_o}{C}$	Time required to close continuous capillaries
0.4	3 days
0.5	7
0.6	14
0.7	6 months
>0.7	never

This naturally affects the moisture flow and water permeability to a great extent.

Apart from gel pores and capillary pores, the majority with the size of d <50 Å and 50-2000 Å respectively, concrete contains pores of a much larger size. Microcracks, mainly in the interfaces, originate from the difference in shrinkage of the aggregate and cement paste but also from great shrinkage stresses at the surfaces. Voids, ~0.01-10 mm, originate from the natural air content entrapped during mixing and waterfilled pockets under the coarse grains of the aggregate due to bleeding. Entrained air bubbles, ~0.001-1 mm, are often consciously produced by using admixtures to change the properties of fresh and hardened concrete.

These large pores do not generally contain water and are difficult to, even deliberately, fill with water. Their effect on the moisture flow and water permeability can however be of crucial importance.

3 HYDRATION, SELF-DESICCATION & INITIAL CONDITIONS

3.1 Introduction

The fixation of the chemically bound water to the cement, i.e. the cement hydration, plays a significant role when dealing with moisture effects in concrete. It is of great importance to know the rate of hydration in different conditions because of the direct effect on the moisture content, according to eq. (1:1), and consequently on the moisture flow as well. The degree of hydration is however also an essential quality when describing different moisture properties of the material in question, e.g. sorption isotherm and moisture diffusivity.

The hydration taking place for instance before the drying begins, reduces the physical bound water and consequently the amount of water to be removed. The initial conditions, i.e. the moisture content at the start of drying, are given as follows:

$$w_{eo} = w_o + \Delta w - w_n \tag{3:1}$$

where Δw is any additional water during curing. The "internal drying" is known as self-desiccation and is naturally continuous during external drying as well. The decrease in evaporable water content according to eq. (3:1) is usually assumed to be equally distributed in a cross-section, but as additional water or air is supplied from the surface there should be a rise in the water or air content close to the surface. Studies regarding this matter have not been found in the literature and consequently the effect is difficult to quantify.

The progress of cement hydration is shown in principle in Fig. 3.1, according to e.g. Kondo & Ueda (1968).

The induction period is the first contact between cement and water with a short rapid reaction and a "dormant" period with a very low rate of hydration. During the acceleratory period the rate of hydration increases to a maximum when the decay period begins and the rate of hydration decreases. In practical applications it is the later period that is of interest as it begins in a few hours or days after mixing.

The progress and rate of hydration depend on the type and make of the cement used and has to be known or determined. The hydration of the cement is however affected by the concrete composition, mainly w_0/C as is well-known, the temperature and moisture conditions in each point of the concrete.

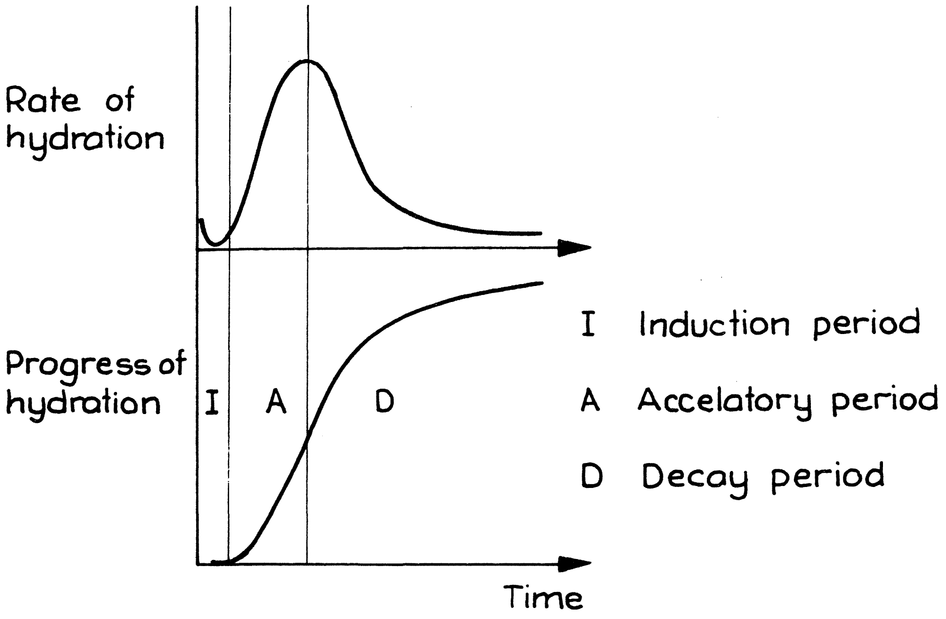


Fig. 3.1 Progress and rate of cement hydration in principle.

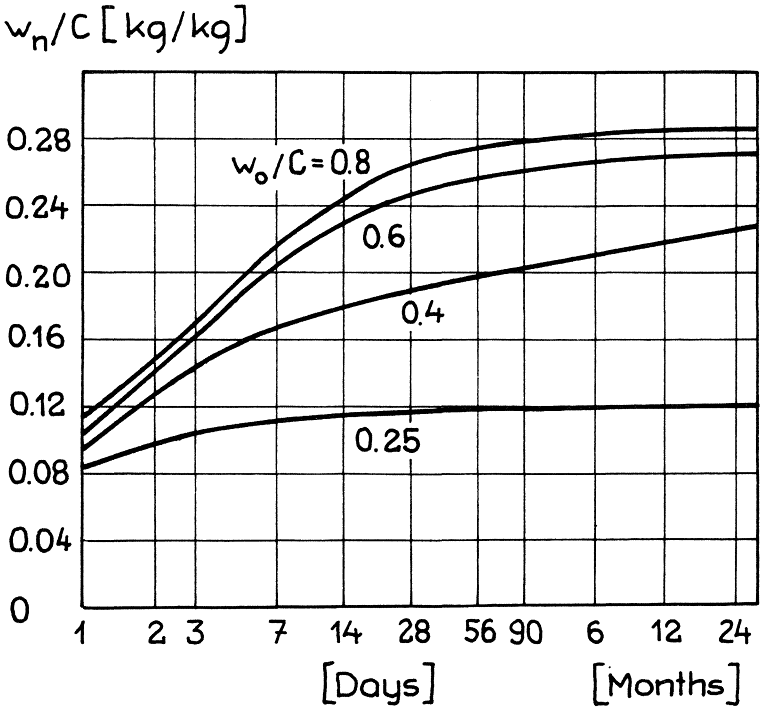


Fig. 3.2 Effect of the water-cement ratio on the progress of hydration. From contraction measurements by Czernin (1964), evaluated by eq. (2:3).

In Fig. 3.2 the effect of the water-cement ratio is shown with data from the contraction measurements by Czernin (1964).

The rate of hydration increases with an increase in w_0/C. For water-cement ratios less than 0.4 the hydration stops at degrees of hydration less than 1 when the capillary porosity is zero, cf. eq. (2:5), and there is no space left for additional hydration products.

The effect of temperature can be estimated approximately by using the maturity factor, Bergström (1953)

$$M = \int_0^t (\theta + 10)\, dt \quad (\text{days } ^0\text{C}) \tag{3:2}$$

where dt is the curing time at a curing temperature of θ ^{0}C. At a constant temperature θ the progress of hydration can be estimated from the hydration at +20 ^{0}C by

$$w_n(t_\theta) = w_n(t_{20}^{eq}) \tag{3:3}$$

where the equivalent curing time at +20 ^{0}C is given as follows

$$t_{20}^{eq} = t_\theta \frac{\theta+10}{30} = \frac{M}{30} \tag{3:4}$$

In Fig. 3.3 data from Danielsson (1966) are used together with t_{20}^{eq} as a parameter.

The agreement is rather good for temperatures between -2 ^{0}C and +40 ^{0}C, at least for equivalent ages of more than seven days. A more sophisticated and probably a more accurate way to express the effect of temperature is given by Hansen & Pedersen (1977).

The effect of the moisture conditions on the process of hydration is quantatively less known. Powers (1947) determined the progress of hydration of a dry cement stored in climates of different relative humidity with the result shown in Fig. 3.4.

This example shows that the hydration nearly stops at humidities below 80% relative humidity. The rate of hydration is very low for humidities below 0.80 but a progress is measured for humidities as low as 0.40. Measurements of the decrease in humidity under sealed conditions, i.e. self-desiccation, indicate also a negligible rate of hydration at a humidity of about 0.80 cf. Copeland & Bragg (1955) etc.

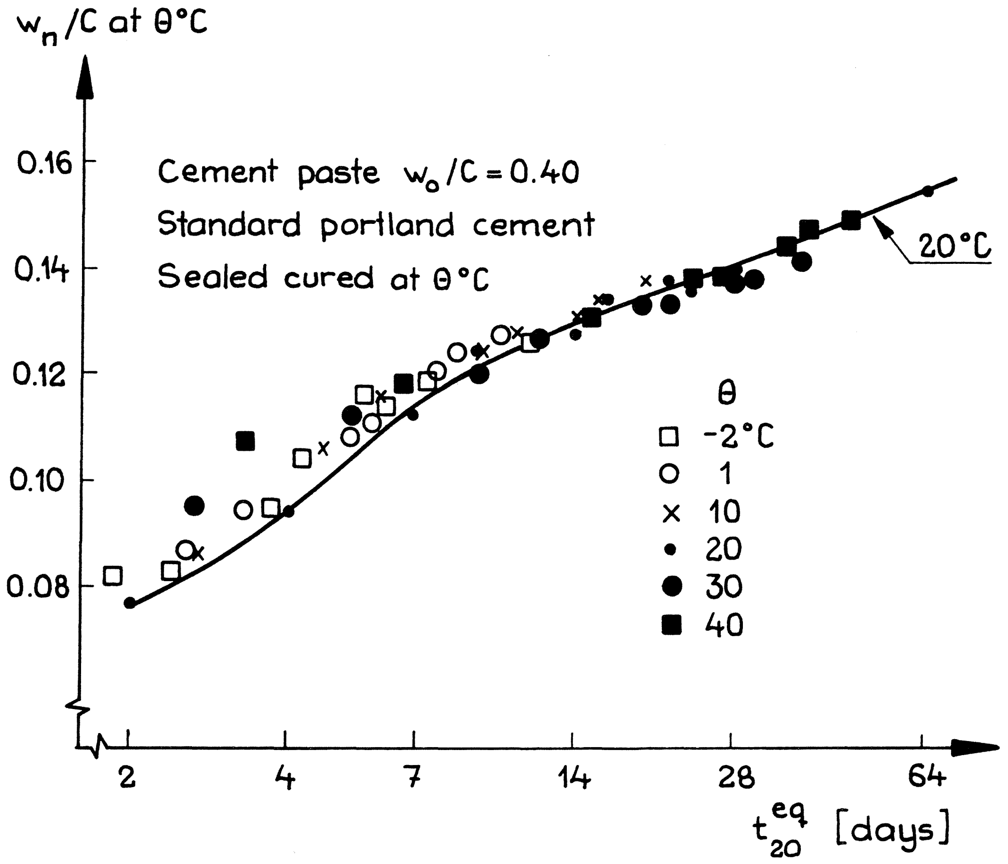


Fig. 3.3 Progress of hydration at different temperatures with "equivalent age at +20 ^{0}C" as a parameter. Data from Danielsson (1966).

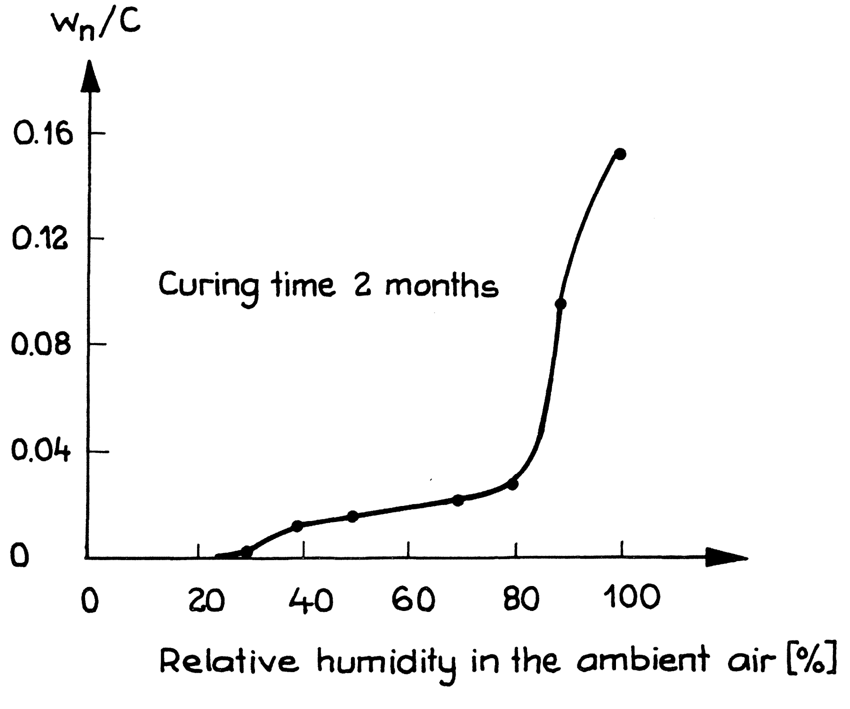


Fig. 3.4 Effect of storing climate on the progress of hydration for a dry cement, acc. to Powers (1947).

3.2 Definitions

The chemically bound water is fixated to different cement components as hydrate water and hydroxide. When determining the amount of bound water, the physically absorbed water has to be removed first of all. However no method exists for separating physically and chemically bound water but this is done, by definition, using a drying method. In this work drying in a ventilated oven with laboratory air at +105 °C has always been used and the water removed, the weight loss corrected for weight loss of cement and aggregate, is called the evaporable water

$$w_e = m - m_{105} = u \cdot m_{105} \tag{3:5}$$

The amount af water left after drying at 105 °C is called the non-evaporable water, w_n, and is treated as the amount of chemically bound water.

To determine the amount of non-evaporable water a sample is usually heated to a certain temperature where all of the water is supposed to have been liberated and the weight loss is measured. The temperature should be chosen so that all the bound water and nothing else is removed. This is however difficult to acquire if the sample contains carbon-dioxide as well. According to Englert, Wittmann & Nußbaum (1971), cf. Fig. 3.5, the main part of the hydrate water is liberated between 125 °C and 400 °C. At about 550 °C calcium-hydroxide is decomposed and between 700 °C and 800 °C carbon-dioxide is lost from the calcium-carbonate.

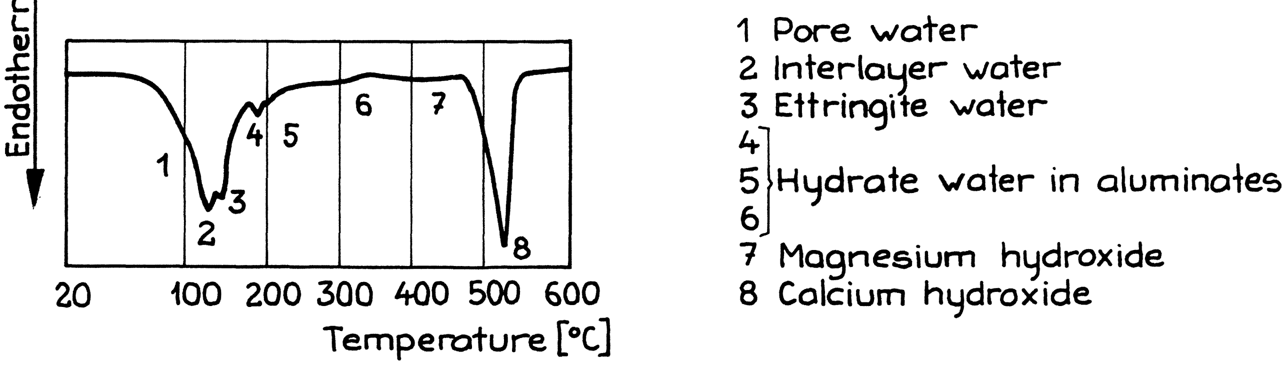


Fig. 3.5 Example of DTA record of hydrated Portland cement paste, Englert et al (1971).

Different temperatures have been used for quantitative measurements, cf. Danielsson (1966, 1974)and Pihlajavaara (1965), and the carbon-dioxide has either been neglected or corrected. The question remains however how to determine the true amount ot non-evaporable water. According to Fig. 3.5 and Englert et al (1971) 600 °C seems to be a suitable temperature for separating water and carbon-dioxide. This is further discussed in 3.4.2.

3.3 Experiments and results

In practical applications water-cement ratios of about 0.6 are of interest. As cement pastes of this high w_0/C are difficult to prepare without extensive separation, mortars have to be used.

The progress of hydration has been measured in two ways. A few simple experiments using eq. (2:3), i.e. the contraction of the system cement + water, have been carried out on mortars. The progress can be followed here on one sample, which means that the rate of hydration can be obtained in a better way than when using different mortar samples at different time ages. Experiments using thermal methods have been carried out in order to obtain a method for determining the "true" amount of w_n and to measure the progress of hydration for different cements used in drying experiments and in practice.

3.3.1 Contraction measurements

For the contraction measurements the volumenometer consisted of a glass bottle connected to a pipette with a rubber tube and another rubber tube from the bottle made it possible to fill it up with water and remove the air-bubbles. The volumenometers were placed in a heat insulated water bath where the temperature was measured.

Two mortars with w_0/C = 0.6 and 0.8 were made using a standard Portland cement; compositions see Table I. Directly after mixing several test tubes were filled with mortar and the test tubes were placed in the glass bottle. The volumenometer was filled with water and the first reading was made half an hour after mixing. The results are presented in Table I as contraction and rate of contraction in kg water/kg cement ($\rho_{H_2O} \approx 1000$ kg/m^3). Corrections have been made for temperature changes, 17.6 - 18.2 °C, and water leakage in joints and evaporation from the pipette of 0.01 cm^3/day.

3.3.2 Thermal methods

The thermal method normally used was to measure the weight loss of samples which had been heated to different temperatures; 105 °C for the evaporable water content and 600, 800, 1000 and/or 1050 °C for the non-evaporable water content in different series. The drying time at each temperature varied from days at 105 °C to hours at 600-1050 °C, to obtain a constant weight of samples with different sizes and shapes. Normally the weight was determined after cooling in a desiccator at room temperature.

The weight losses at different temperatures are always corrected for weight loss of the cement and aggregate used and given in relation to the original cement content of the sample. The weight loss of the original cement and aggregate at heating to θ °C, is defined by

$$C_\theta = (1 - a_\theta)\, C_{20} \tag{3:6}$$

$$A_\theta = (1 - b_\theta)\, A_{20} \tag{3:7}$$

In Tables II and III the values of a_θ and b_θ are given together with some data for the cements and aggregates used.

The original cement content of a sample is evaluated from the remaining weight after ignition at 1000-1050 °C assuming that this is cement and aggregate only, i.e. $C_{1000} + A_{1000}$, and that the proportion is the same in the sample as in the original mixture A/C. One obtains

$$C_{20} = \frac{m_{1000}}{1 - a_{1000} + \frac{A}{C}\,(1-b_{1000})} \tag{3:8}$$

with C_{20} as the weight of cement in the unheated sample.

In series A the effect of the temperature level for the heating has been determined for a cement paste with $w_0/C = 0.5$ sealed cured at +22 °C.

The paste was mixed from a standard Portland cement, Li 1, and deionized water and poured into test tubes with rubber stoppers. In spite of the test tubes being put on rotation rollers for one day, a certain degree of separation could not be avoided. After different times samples were taken from one test tube. The samples were crushed and sieved in order to obtain grains of 1 to 2 mm. All samples were dried at 105 °C and then the weight losses during heating up to 600, 800 and 1000 °C were determined. The results are presented in Table IV.

In series B mortar were prepared with $w_0/C = 0.6$ and different cements; Li 2, Li LH, Sk SH and Sl 2 according to Table II. The mortars were mixed using aggregate I with a cement/aggregate proportion of 1:4.4. Drying was prevented for one day and then the mortars were stored at +20 °C in water with an excess of calcium hydroxide. Three samples of each mortar taken at different times were divided into pieces not smaller than 1 cm^3 and dried at 105 °C. The weight losses during heating up to 600 and 1000 °C were then determined. The results are presented in Table V.

In series C an attempt was made to study the effect of humidity on the rate of hydration by rapidly drying crushed mortar samples to different levels of humidity and determining the progress of hydration thereafter. Samples stored continuously in water were intended as a comparison. The rapid drying was performed in a precision moisture chamber, according to Ahlgren (1972), and the humidity in question was maintained by means of saturated salt solutions in desiccators. The results shown in Table VI are highly affected by carbonation due to the use of crushed samples and a bad CO_2-filter in the precision moisture chamber. The determined weight losses of the mortar samples stored in water however give an estimation of the reproducibility since they originate from four different mixtures with the same composition and treatment.

In series D an attempt was made to check the exact amount of water from the original mixture throughout the heating procedure. This was carried out by mixing a mortar in the crucible and messuring the amount of water added. An inert thread was used for mixing and left in the crucible. The samples were cured for one week in a sealed pot and then the weight losses during the curing time and the subsequent heating procedure were determined. The results are shown in Table VII.

3.4 Analysis and evaluation

On the basis of the contraction measurements a mathematical description of the progress and rate of hydration is put forward. By analysing the results of the thermal methods, the progress of hydration of the different cements used can be evaluated.

3.4.1 Contraction measurements

The contraction measurements are few and not reproduced and the results are strange in many ways, e.g. they indicate a very rapid hydration of the standard Portland cement used and a greater than usual amount of chemically bound water.

The coefficient in eq. (2:3) is however found to be in the order of 0.25-0.28 and the results are similar to those of Czernin (1964) for higher water-cement ratios, with an amount of chemically bound water of approx. 0.30 kg/kg cement, cf. Fig 3.2. The correctness of this result is difficult to value because studies of the hydration at high w_0/C are rare.

The results have however led to a simple mathematical description of the rate of hydrations and consequently the progress of hydration. The results from Table I, shown in Figure 3.6, can be expressed fairly accurately by a straight line if the logarithm of the rate of contraction is treated as a function of the logarithm of time.

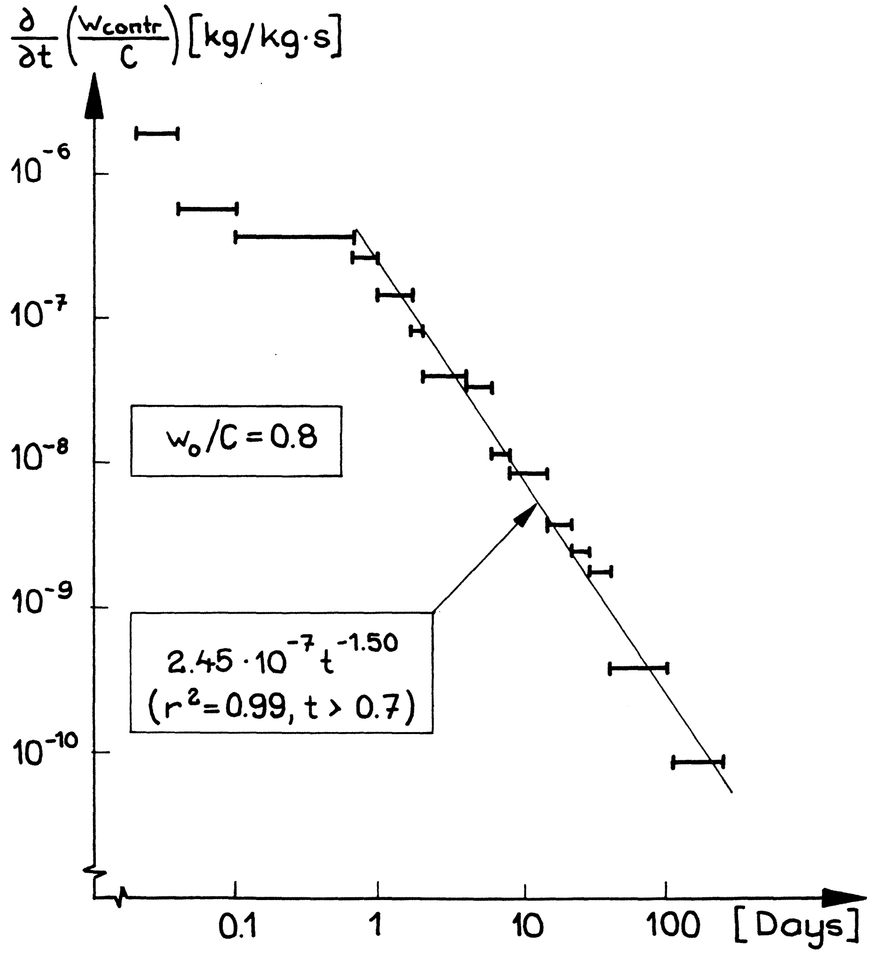


Fig. 3.6 The rate of contraction as a function of time for one of the experiments described in 3.3.1. (r^2 = correlation coefficient)

Then according to eq. (2:3) the rate of hydration should be expressed in the same way, after two to three days of hydration:

$$\frac{\partial w_n}{\partial t} = \text{const}\cdot C\cdot t^{b-1} \qquad (3:9)$$

with b < 0. By integration this equation one obtains the following for the progress of hydration:

$$\frac{w_n}{C} = \frac{w_{n\infty}}{C} - a\cdot t^b \quad ; \; b < 0 \qquad (3:10)$$

where $w_{n\infty}/C$ is usually given the value 0.25, cf. eq. (2:1) as other values do not necessarily give better correlations. This expression is used below and shown to be useful for this purpose.

3.4.2 Thermal methods

The loss during ignition at 1000-1050 °C is frequently used as a measure of the non-evaporable water. If the sample does not contain any carbon-dioxide and correction is made for the weight loss due to cement and aggregate it would be correct. The weight loss between 600 °C and 1000 °C is usually believed to be due to the liberation of carbon-dioxide and nothing else. Bozhenor et al (1960) report however weight losses due to water at about 700 °C, but further information on this subject has not been found.

In all the experiments carried out a weight loss between 600 °C and 1000 °C has been obtained that cannot be neglected. In series A it is shown that most of this weight loss is found between 600 °C and 800 °C, cf. Fig. 3.7, but as the samples are crushed and sieved, some carbon-dioxide could have been absorbed. This is also the case for the crushed samples in series C.

In the remaining experiments the samples have been stored in water and pieces have been used instead of crushed samples. A contribution of larger amounts of carbon-dioxide is therefore less probable. An exception is the later measurement in series B, where the samples have been stored in water with an excess of calcium-hydroxide. If this is not carefully removed from the samples, a rapid carbonation occurs which is probably what has happened and has resulted in greater weight losses between 600 °C and 1000 °C for these samples.

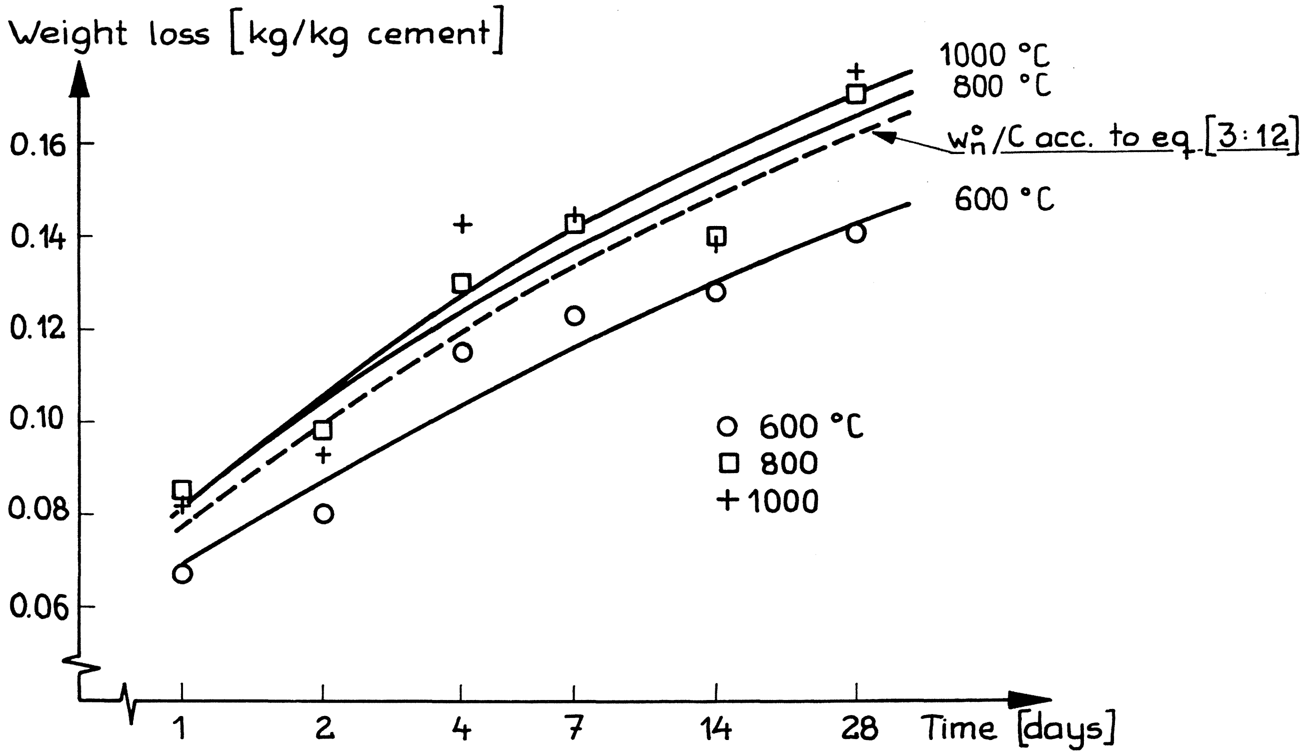


Fig. 3:7 Weight losses at heating to different temperatures, series A. Curves according to eq. (3:10) by regression analysis.

This has been dealt with in the following way. The non-evaporable water content can always be expressed, if the sample contains no CO_2, by:

$$w_n = f\,\Delta m_{105\to 600} \qquad \left(f = \frac{\Delta m_{105\to 1000}}{\Delta m_{105\to 600}}\right) \qquad (3:11)$$

where, of course, the weight losses are corrected for weight losses of the cement and aggregate. In Fig. 3.8 the experimental results, with the above mentioned exceptions but including the contraction experiments, are shown to estimate the factor f.

A reasonable way of evaluating w_n seems to be by using eq. (3:11) with the factor f as a constant with the value ~1.1. This is also indicated by the experimental series D, where the actual amount of water added to the mixture is liberated during heating in such a way that the factor f is 1.1. That the reason for f deviating from 1.0 should be carbonation is highly improbable as the same deviation is obtained for different sizes and shapes of the samples, except for crushed samples. Carbonation should produce a more variable f.

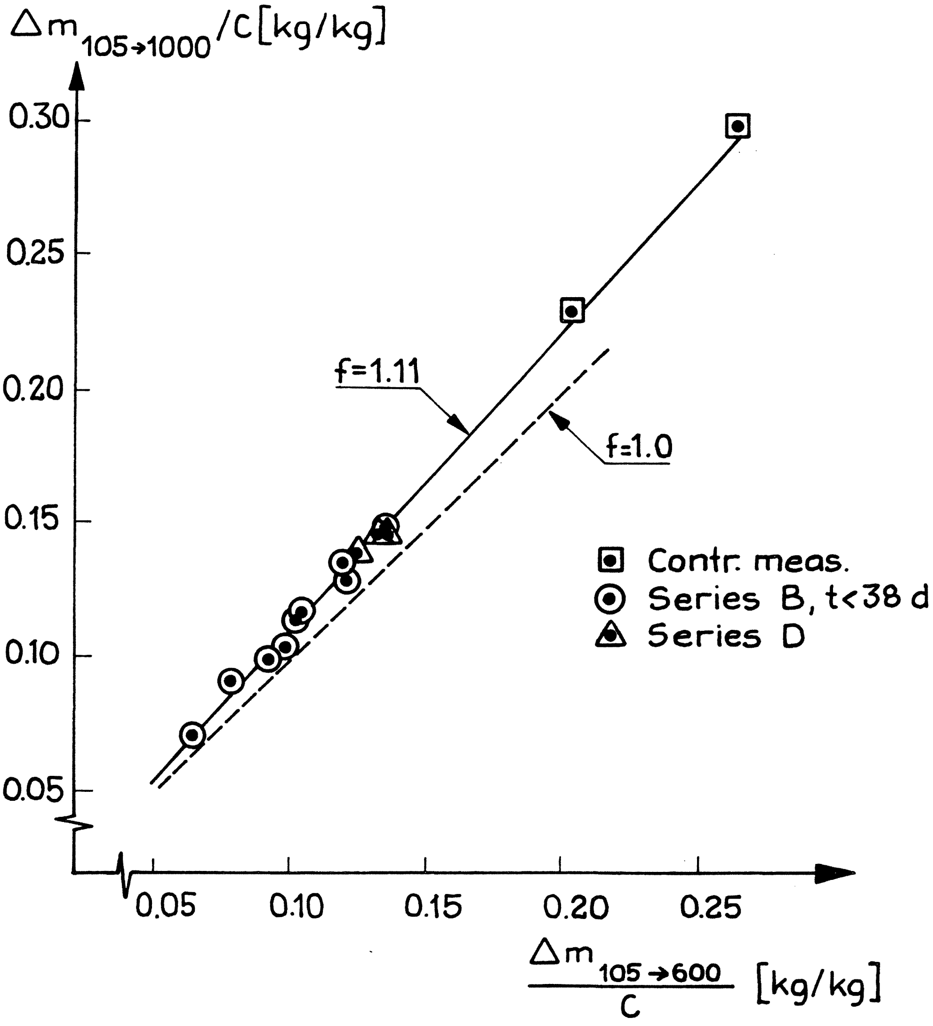


Fig. 3.8 Experimental results showing the connection between weight loss at 1000 °C and weight loss at 600 °C for the standard Portland cement used.

It is remarkable that the factor f seems to be almost independent of the degree of hydration. The amount of chemically bound water that is liberated after 600 °C should originate from one or two cement clinker components and as they hydrate at different rates the factor f should vary with time. It is probable that this happens, at least during the first days of hydration.

The weight losses between 600 °C and 1000 °C, in addition to the water expressed by the factor f, are carbon-dioxide liberated from carbonates of calcium and some magnesium and potassium. The carbonation has liberated some chemically bound water according to the formula

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Carbonation by one mole of CO_2 means that 18 grams of chemically bound water pass into the same amount of evaporable water and simultaneously 44 grams of carbondioxide are fixated. This means that the amount of non-evaporable water is decreased.

If all the carbon-dioxide is assumed to be liberated between 600 °C and 1000 °C and the non-evaporable water released by carbonation is assumed to originate from the calciumhydroxide from which all water is liberated below 600 °C, the <u>original amount of non-evaporable water</u> can be estimated by (deduction see Appendix I):

$$w_n^o = \frac{44f}{26+18f} \left(\Delta m_{105\rightarrow 600} + \frac{18}{44} \Delta m_{600\rightarrow 1000}\right) \qquad (3:12)$$

The experimental results for the different Portland cements used are evaluated by eq. (3:11) and (3:12) and the results are presented in Table VIII. In Fig. 3.9 an example is shown for the standard Portland cement used later.

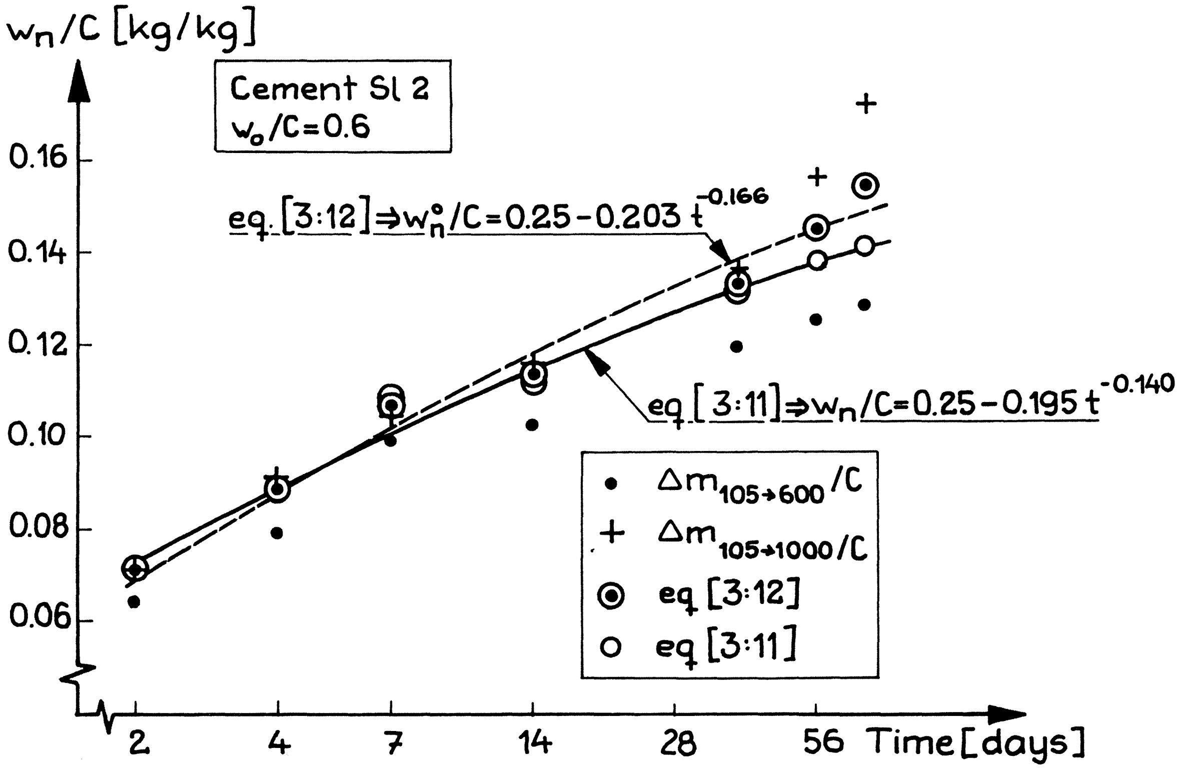


Fig. 3.9 Progress of hydration of standard Portland cement Sl 2 used later in the drying experiments. Evaluations by eq. (3:11) and (3:12).

The agreement between eq. (3:11) and eq. (3:12) is of course very good when no carbonation has occurred as during curing times shorter than 38 days, cf. the boundary in Table V. The carbonation that occurred later and caused great losses during heating over 600 °C is difficult to explain. The most probable explanation has been mentioned above. The calcium-hydroxide that has been carbonated originates from the storing water and not the sample and consequently eq. (3:11) should be used to evaluate the later measurements in series B. In Fig. 3.10 the results for the different cements, evaluated in this way, are shown.

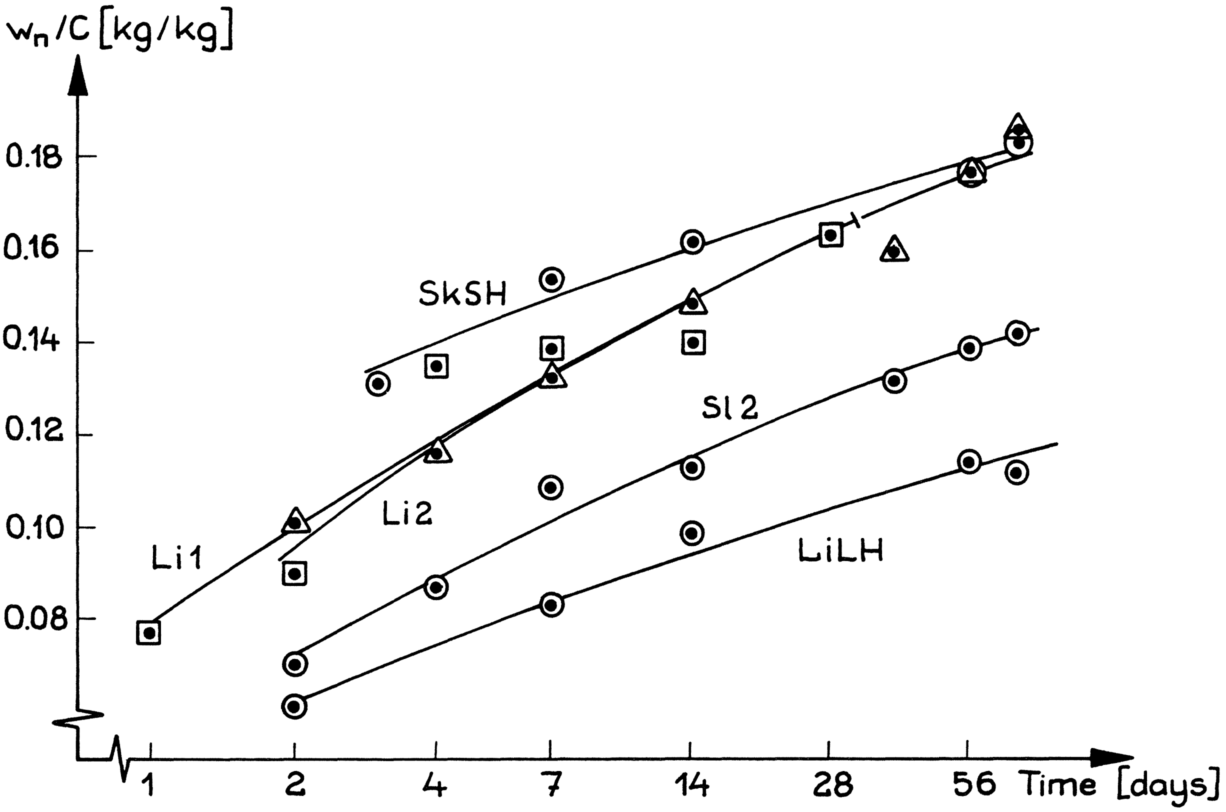


Fig. 3.10 Progress of hydration of the cements used in series A and B, evaluated by eq. (3:11) (B) and eq. (3:12) (A), cf. Table VIII.

There are several possible sources of error in the described way of determining the non-evaporable water content. The most important is of course the separation of carbon-dioxide and water. This has been carried out in a way that seems to be correct, but is not sufficiently proved. To do this the gases liberated during heating have to be analyzed and this has not been possible.

The precision of the method adopted is indicated by the results in Table VI to be about 0.005. Most of this error is assumed to originate from a bad representativeness of the samples, i.e. the aggregate-cement ratio A/C and water-cement ratio in the sample deviates from those of the original mixture. This is especially important for the cement-paste samples as all the samples used at one time step are taken from one test tube. Danielsson (1974) states that this fault means an error of about 0.3 times the change in w_o/C, i.e. an error in w_n/C greater than 0.01 if an inhomogeneous mixture and separation changes the water-cement ratio from 0.50 to 0.45. If the aggregate-cement ratio in a mortar sample is five percent wrong, it could mean an error in w_n/C to the order of 0.005 according to eq. (3:8).

The effect of changes in climate when drying at 105 °C is small compared to the above mentioned. Danielsson (1974) results indicate errors less than 0.002 in w_n/C due to changes in temperature and humidity of the laboratory air and temperature changes in the oven. Greater faults can arise, and may have done so, if a moist specimen of greater size is dried together with the samples in the oven. This is probably what has happened for the measurements excluded in Table VIII.

The cements Sl 1 - Sl 4 come from the same manufacturer and should be the same cement but show quite different rates of progress of hydration. However the cements have been delivered at different times during a period of four years and differences are not unprobable especially as the cement factory has changed its manufacturing process. The cement Sl 2 has been stored in the laboratory at least two years and some changes might have occurred as the cement has been stored in sealed plastic bags.

3.5 Summary

Simple mathematical expressions for the progress and rate of hydration as a result of water contraction measurements have been put forward in this chapter. By thermal methods the hydration of different cements is determined and evaluated by means of equations expressing the actual amount of non-evaporable water cement. It has been found that approximately 10% of this water is liberated during heating above 600 °C and that it is not carbon-dioxide that causes this weight loss. The effect on the hydration of water-cement ratio, temperature and humidity is indicated by showing results from literature.

4 MOISTURE FIXATION, EQUILIBRIUM CONDITIONS

4.1 Introduction

Knowing the way in which the evaporable water in concrete is fixated under different conditions is essential for several reasons. The sorption isotherm gives information regarding the moisture content at the surface of a material and thereby the moisture content towards which the concrete strives. The sorption isotherm is also necessary to judge the moisture load arising at a tight surface layer applied when the concrete has a certain moisture content. Furthermore the sorption isotherm is a great help when translating moisture flow coefficients from one way of description to another.

In a porous material the water is fixated at different energy levels. The chemically bound water has reacted with the material and is present as hydroxide or crystal water, when the water has kept its original molecular shape and is fixated with covalent bounds or hydrogen bounds as hydrate.

Physically bound water can be fixated in several ways. Zeolitic or interlayer water is firmly bound between different layers in the crystal structure but is not chemically bound. Dependent on the drying method used, some of it might however be included in the non-evaporable water, w_n.

Adsorbed water is fixated by van der Waal-forces to the surface of the pores and the force depends on the distance to the surface, i.e. the first molecular layer is the most firmly bound. The thickness of the adsorbed water layer increases with an increasing pore humidity and is approximately 10 Å at 90% RH, Hillerborg (1979). As the adsorbed water is fixated to the walls of the pores, the amount of adsorbed water is proportional to their total surface, that is the specific surface when expressed per weight unit.

Capillary condensed water is fixated by curved surfaces of water, meniscus, arising in the pores due to the surface tension. Over these water surfaces the water vapour pressure at saturation is lower than on a plane surface, i.e. the vapour pressure at saturation is reached and condensation occurs at a pore humidity ϕ less than 1. The connection between the pore humidity and the radius of the curvature, r, is given in the Kelvin-equation. For a partly filled cylindrical pore this is as follows:

$$\ln \phi = - \frac{2\sigma V_m}{r RT} \qquad (4:1)$$

where the surface tension of water is $\sigma \approx 0.074$ N/m and the molar volume of water is $V_m \approx 0.018$ m^3/k mole. The radius is generally assumed to be equal to the radius of the pore reduced by the thickness of the adsorbate. The Kelvin equation with this assumption is shown in Fig. 4.1.

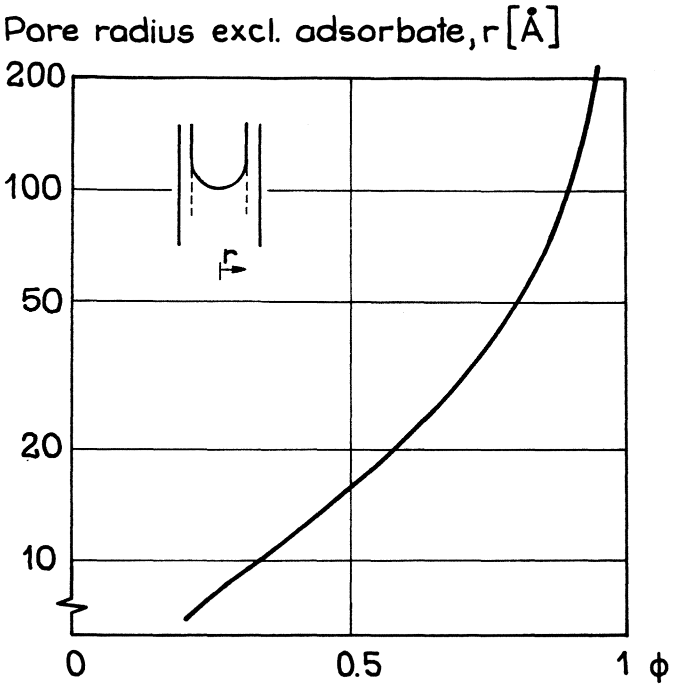


Fig. 4.1 Size of water-filled pores as a function of pore humidity at desorption, Kelvin equation at 293 K.

For a material with known porosity and pore-size distribution, the amount of fixated water at a certain humidity can be calculated by using eq. (4:1).

In this case the amount of physically bound water is treated as the evaporable water when drying at 105 ^oC, cf. 3.2, and usually determined as the moisture ratio u but expressed as moisture content per unit volume

$$w_e = \frac{\text{weight of water evaporable at 105 } ^oC}{\text{total volume of the material}} \quad (kg/m^3) \qquad (4:2)$$

The connection between moisture content or moisture ratio and relative humidity or pore humidity at equlibrium is called the sorption isotherm. In Fig. 4.2 a sorption isotherm is shown in principle with hysteresis between the absorption and desorption isotherms, i.e. the difference in equilibrium moisture content during drying and wetting respectively.

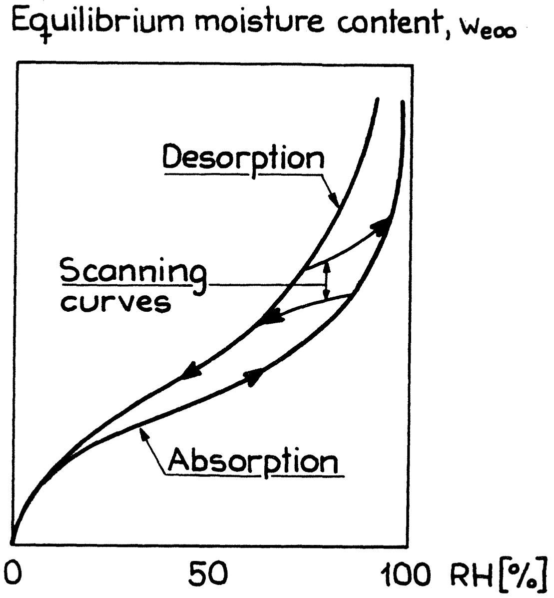


Fig. 4.2 Sorption isotherm in principle.

The moisture capacity is defined as the slope of the sorption isotherm for the moisture content in question, i.e. $(\partial w_{e\infty}/\partial\phi)_w$.

The hygro-thermal coefficient is defined as the slope of a curve with the humidity as a function of temperature at constant moisture content, i.e. $(\partial\phi/\partial T)_w$.

4.2 Sorption isotherms for concrete

As concrete is used with highly variable compositions and hardens continuously, its properties are changed with composition and age. This is also valid for the sorption isotherm. As the sorption isotherm has a upper limit of about 98% RH and the pores that become filled with water are very small, cf. Fig. 4.1, only the changes in composition of the cement paste in concrete are to be considered. The pores added when making concrete, e.g. separation voids, are of far greater size and contain no water at 98% RH. By knowing the sorption isotherm as a function of water-cement ratio and degree of hydration for cement paste it should be possible to calculate the sorption isotherm for any concrete with non-porous aggregate. Information from literature and some experiments are presented below and evaluated in order to obtain some knowledge regarding this matter.

4.2.1 Literature survey

Moisture fixation in concrete has been studied among others by Powers & Brownyard (1948), Sereda, Feldman & Swenson (1966), Ahlgren (1972) and Pihlajavaara (1965, 1974). The absorption isotherm is carefully determined and the agreement between results reached by different authors is very good. The effect of age and composition has been determined by Ahlgren (1972) and in Fig. 4.3 his results are assembled.

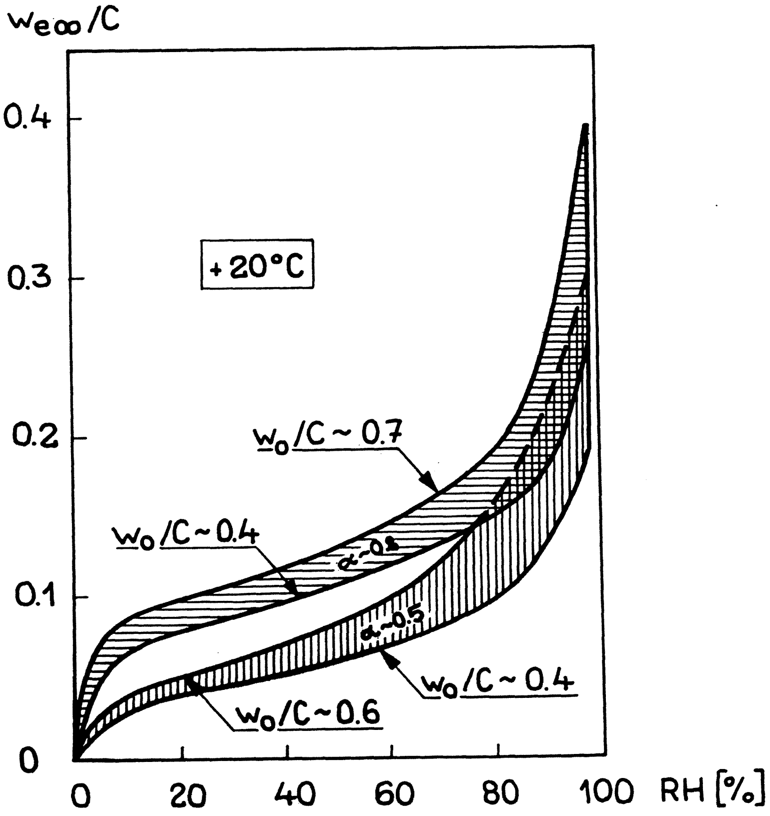


Fig. 4.3 Absorption isotherms for concrete assembled from results by Ahlgren (1972).

The results in Fig. 4.3 agree well with the results stated by Powers & Brownyard (1948) and Ahlgren (1972) has developed a method of calculating the absorption isotherm for any composition of concrete by using the so called "gel-isotherm", Powers & Brownyard (1948), i.e. an isotherm for a cement paste containing no capillary water. The gel-isotherm is shown to be valid for any composition of concrete in humidities less than 45% RH with an equilibrium moisture content at 45% RH of

$$\frac{w_e}{C}\ (\phi = 0.45) \approx 0.11\ \alpha \qquad (4:3)$$

and at RH = 100% eq. (2:2) is valid. Between 45% and 98% RH an empirical expression is used.

In most applications it is the desorption isotherm that is of interest. However, the results presented by different authors concerning this material property are very divergent. An attempt to compare different results is shown in Fig. 4.4. As the shown isotherms are valid for different degrees of hydration, the absolute values are of secondary importance. Instead the shape and slope of the curves should be compared.

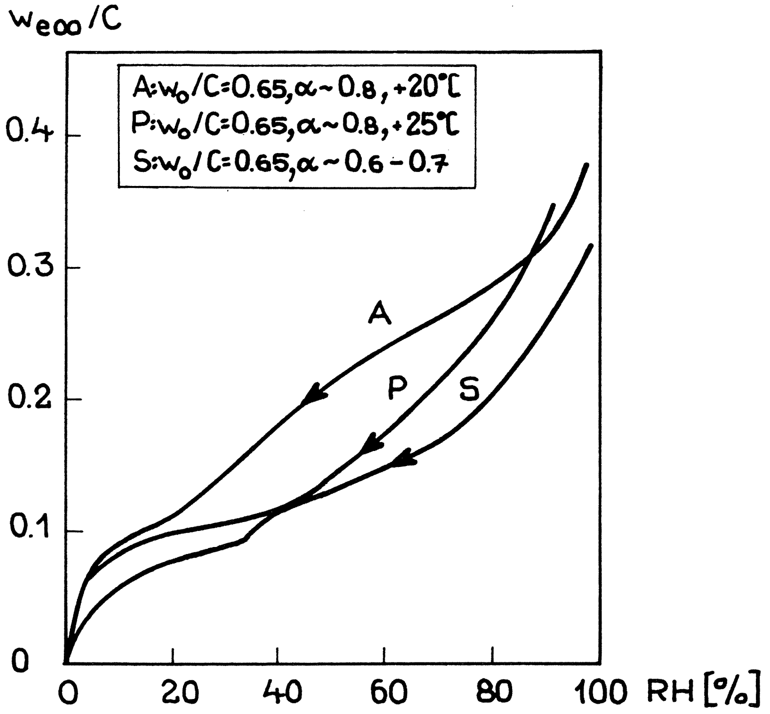


Fig. 4.4 Desorption isotherms according to different authors. Observe the difference in the degree of hydration.

The great difference is in the interval 30-80% RH, where Ahlgren and Sereda et al show approximately the same shape of the curves with a flat slope over 40% RH and a sudden "drop" down to the value at 30% RH. Pihlajavaara however shows a very flat curve where the others show a drop and a much greater slope in the interval 50-80% RH.

This great difference between various desorption isotherms is quite unsatisfactory when calculating the drying of concrete, as the equilibrium moisture content in a normal drying climate can vary by up to 60 per cent depending on which curve is used. It is difficult to explain with certainty the cause of these great discrepancies, as accurate information from the experiments is not available. This matter will however be discussed below.

Information regarding the effect of temperature on the sorption isotherm is rare. However, preliminary results by Pihlajavaara are presented in Fig. 4.5.

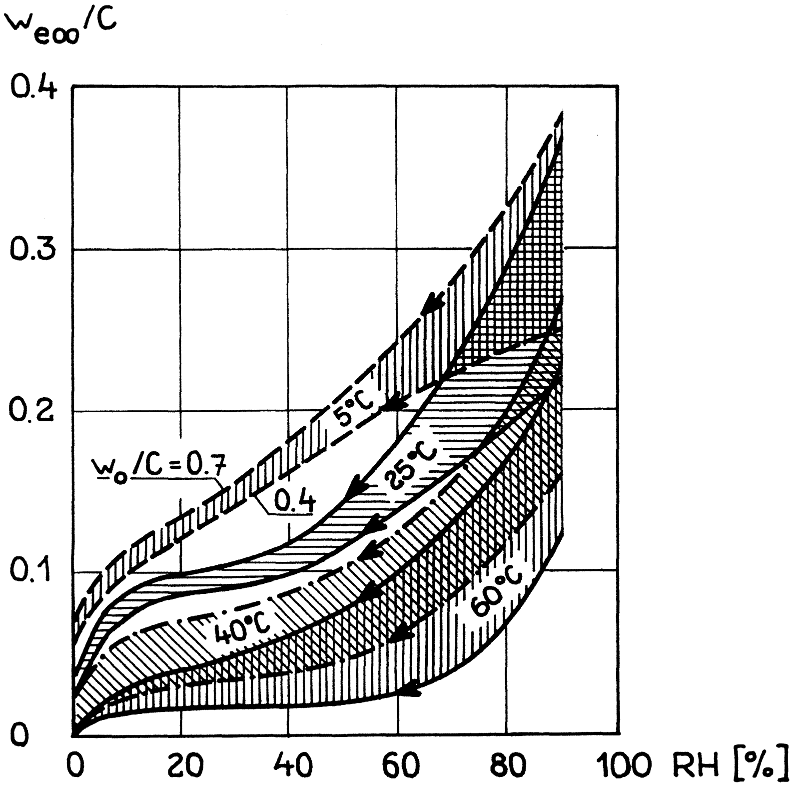


Fig. 4.5 Desorption isotherms at different temperatures according to preliminary results by Pihlajavaara (1974).

4.2.2 Experiments and results

To experimentally determine the desorption isotherm of low ages, short-time measurements have to be carried out when the intended degree of hydration has been reached.

An attempt has been made to do this by using crushed mortar samples, $w_0/C = 0.6$, containing grains smaller than 0.5 mm. The samples have then been dried in a precision moisture chamber, according to Ahlgren (1972), producing a very stable climate by humidifying an air stream at a high pressure and then lowering the pressure at a constant temperature. The air stream passes through a CO_2-filter before entering the climate chamber.

The weight change of the sample was followed during the drying and the constant weight was reached in one day only, in many cases due to weight gain by carbonation. After one day of drying the evaporable water content was determined by drying at 105 ^{o}C and then the loss on ignition was measured. Weight losses during handing and weighting were considered as well as the weight losses of the original cement and aggregate. The results are presented in Table IX and by using the previously determined progress of hydration for the cement in question the results can be expressed as functions of non-evaporable water content, as in Fig. 4.6. This is done because the loss on ignition contains large amounts of carbon-dioxide.

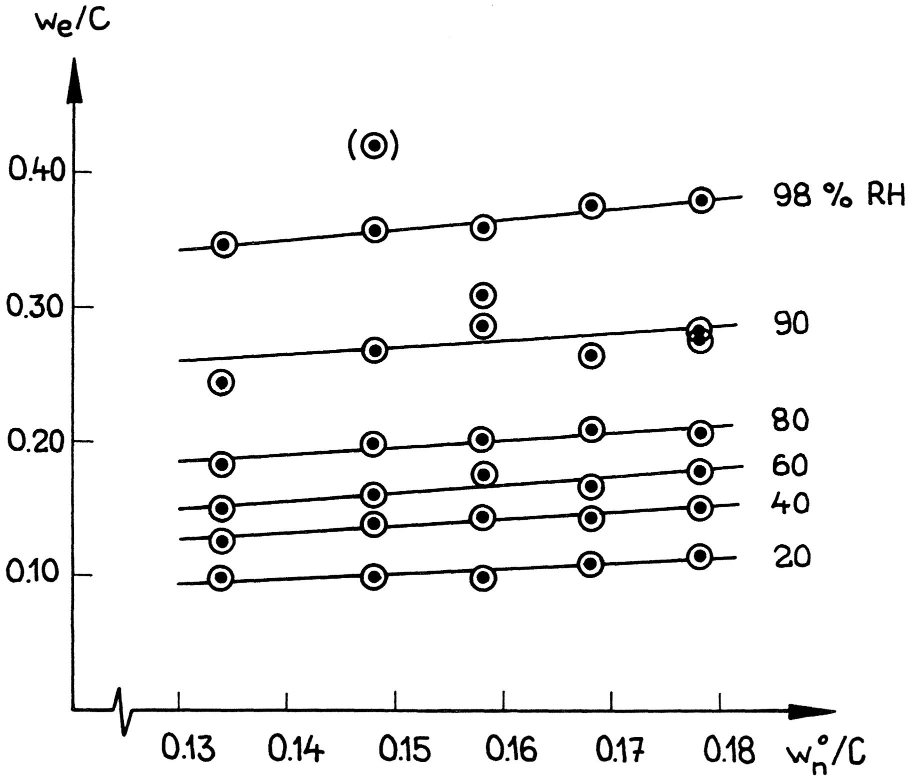


Fig. 4.6 Evaporable moisture content of crushed mortar samples of different ages after one day of drying in various humidities. No equilibrium at lower humidities, see text.

The first two measurements were carried out in CO_2-free air but the filter did not function properly. The weight gain due to carbon-dioxide was giving a constant weight before drying in the lower humidities, <80% RH, had reached equilibrium.

At lower humidities the equilibrium moisture content was evaluated from the drying experiments presented in the next chapter. Mortar specimens with a water-cement ratio of 0.6 and a thickness of 20 mm, drying on both surfaces, were dried in climate rooms for a year and a half and then the evaporable and non-evaporable water content were determined. The specimens were carbonated to a depth of approximately 2 mm at the end of the experiment. The results are presented in Table X together with the above results in Fig. 4.7.

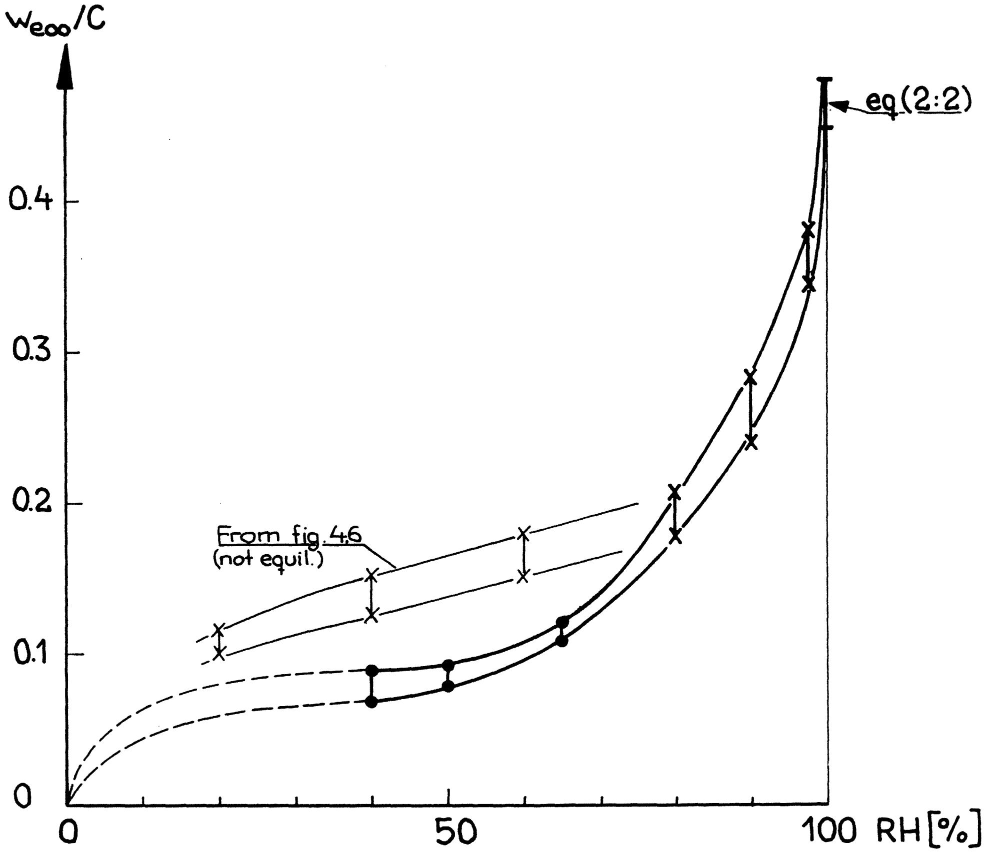


Fig. 4.7 Desorption isotherms for partly carbonated cement mortar with $w_0/C = 0.6$ & $w_n^0/C = 0.15-0.20$

● climate room, 1.5 year
● 20 mm specimens

x precision moisture chamber
x crushed samples, 1 day, cf. Fig.4.6

A smaller experimental series has been carried out to estimate the hygro-thermal coefficient, i.e. the temperature dependence of the sorption isotherm. This has been carried out by using a method quite different from the above. The relative humidity was measured on concrete samples dried in an oven to different remaining moisture contents by using the method presented in chapter 10, with the samples enclosed in test tubes together with the RH-sensor. The relative humidity of the sample was measured at equilibrium at different temperatures without separating the sample and the sensor, i.e. at a constant moisture content. The results are presented in Table XI and Fig. 4.8.

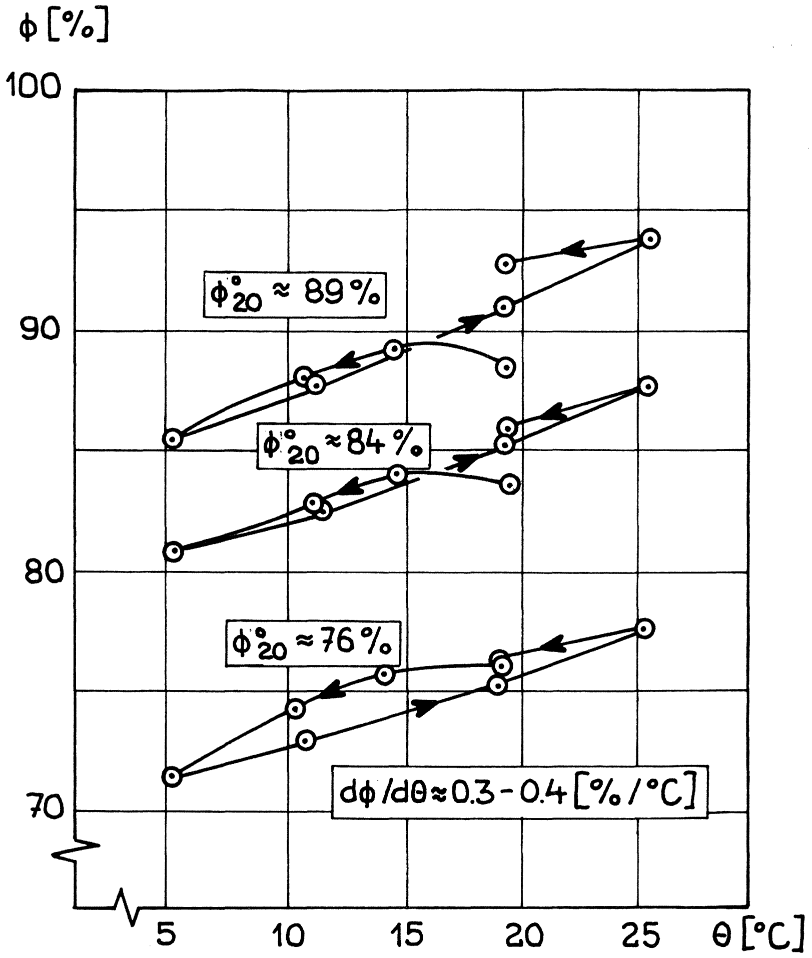


Fig. 4.8 Relative humidity as a function of temperature at a constant moisture content. (The temperature dependence of the sorption isotherm) $w_0/C \approx 0.3$.

4.2.3 Analysis and discussion

The determined desorption isotherms,cf. Fig. 4.7, show a great similarity with the sorption isotherms of Pihlajavaara (1974), cf. Fig. 4.4, even if the absolute values are smaller due to deterioration by carbon-dioxide and a somewhat lesser degree of hydration. The discrepancy between these and the other desorption isotherms in Fig. 4.4 is obvious. The most probable cause of this difference is that the drying times were too short to reach equilibrium in the later cases.

The time needed to reach equilibrium is very long, especially during the interval 30-80% RH, cf. Fig. 4.7. This can be seen clearly in Fig. 4.9, which presents the results by Grudemo (1976), even if they are valid for C_3S-paste and not for

Portland cement. In the case of a disc of 1 mm thickness equilibrium was not reached after two weeks of drying, ten times the time is required.

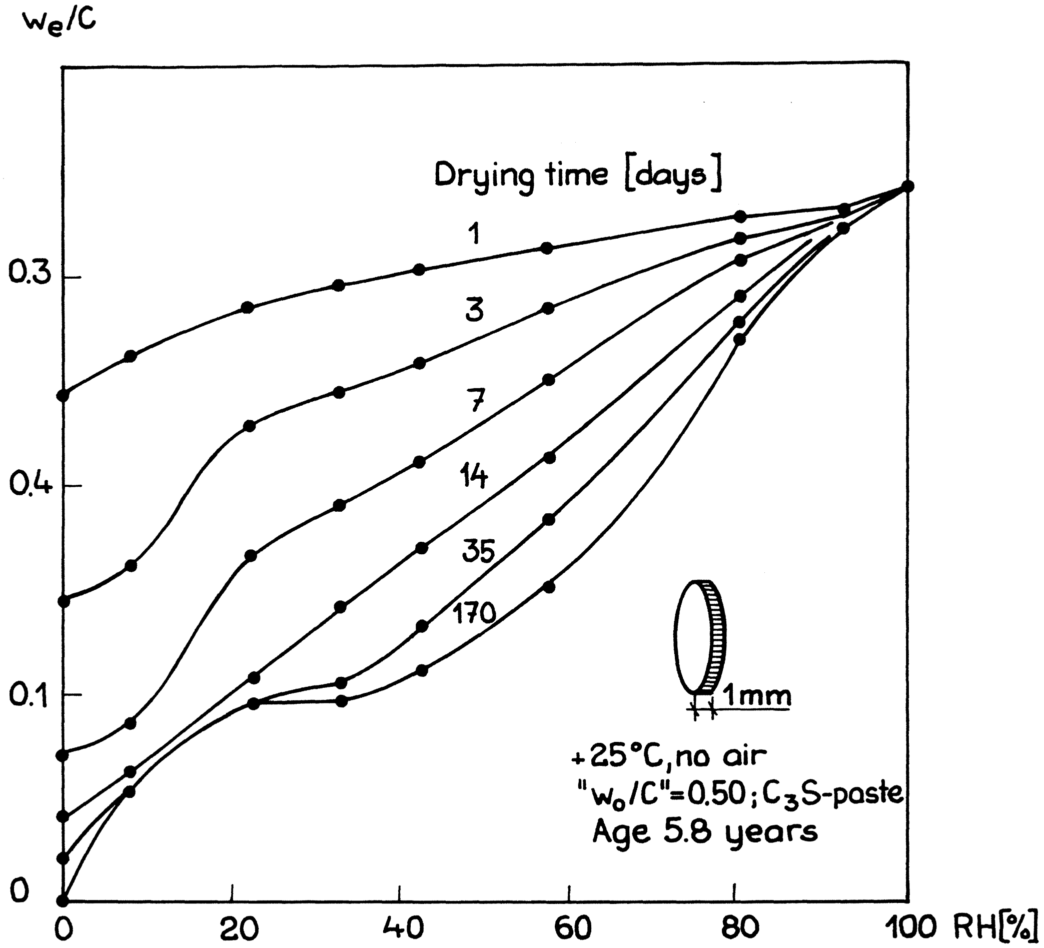


Fig. 4.9 Time course at determining the desorption isotherm for C_3S-paste, Grudemo (1976).

The shape of the equilibrium curve by Grudemo is similar to the results of Pihlajavaara and the experimental results presented above. The curve after seven days of drying looks very much like the desorption isotherms by Ahlgren (1972) and Sereda et al (1966). A possible explanation is that these isotherms were determined by using only one sample in order to obtain the whole curve and then allowing it to gradually dry in a decreasing humidity; there is a great risk of interrupting the drying too soon. The other isotherms were determined on separate samples in different humidities.

The normal method of deciding when equilibrium has been reached, by weighing until the weigh is constant, can result in too high a moisture content if the sample is subjected to carbon-dioxide during drying. The gain in weigh can spoil the possibility of determining when equilibrium has been reached. This might have happened in the experiments by Ahlgren (1972). The temperature also has a certain significance but the difference is much smaller than the deviation shown in Fig. 4.4, where the temperatures are +20 ^{o}C and +25 ^{o}C respectively.

The type of cement could affect the pore-size distribution in same way and consequently also the sorption isotherm. No such information has however been available and a significant effect is improbable at least where the lower humidities are concerned.

Since the experimental results agree with the results of Pihlajavaara, his desorption isotherms will be used in the future. They are however uncertain over 90-95% RH as Pihlajavaara separates 100% RH and storage in water. By using eq. (2:2) and the shape of the desorption isotherms by Ahlgren at higher humidities the most accurate desorption isotherms available are obtained. The result is shown in Fig. 4.10 where the degree of hydration has been calculated by eq. (2:2) applied to the results from water storage, Pihlajavaara (1974).

Knowledge concerning the desorption isotherms at lower ages is still far from complete. A reasonable estimation for practical applications can however be achieved by interpolating in Fig. 4.10 at humidities less than or equal to 45% RH, i.e. using a "gel-isotherm" at desorption, independent of w_o/C, with an equilibrium moisture content at 45% RH of

$$\frac{w_e}{C}\ (\phi = 0.45) \approx 0.15\ \alpha \qquad (4:4)$$

With eq. (2:2) the equilibrium moisture content at 100% RH is obtained between 45 and 98% RH the desorption isotherm can be drawn with the aid of Fig. 4.7 and 4.10.

By using the desorption isotherms in Fig. 4.10 the moisture capacity was evaluated graphically. The result is presented in Fig. 4.11 as the inverse of the moisture capacity expressed in terms of vapour pressure instead of relative humidity.

The measurements of the temperature dependence of the sorption isotherm, cf. Fig. 4.8, indicate that the temperature changes result in a drying-wetting phenomena with a certain hysteresis. Powers & Brownyard (1948) suggested an effect of an increase in temperature by an expansion of the pore water. This would mean that the moisture occupied a greater volume, i.e. acted as in wetting. The resulting change in humidity would then be proportional to the temperature change, moisture content, inverse of moisture capacity and the coefficient of volume expansion of water. However, a rough estimation results in too small an effect with only this explanation.

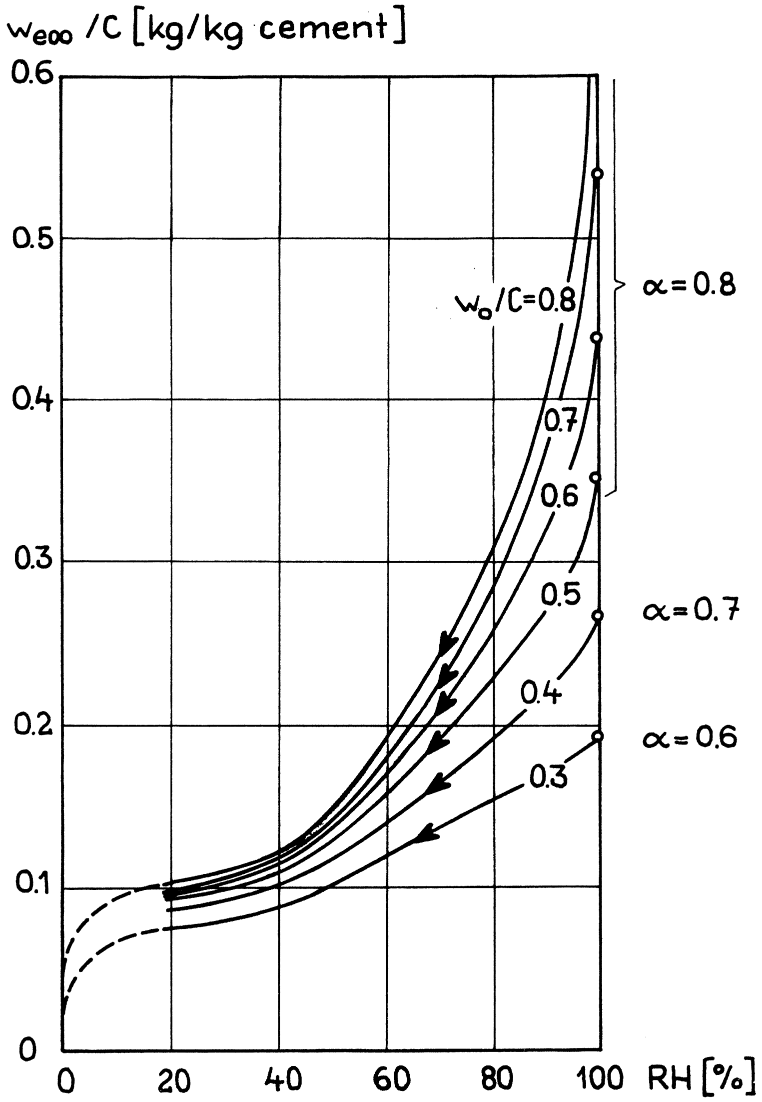


Fig. 4.10 Desorption isotherms for different water-cement ratios. Degrees of hydration 0.6 - 0.8. Based on results by Pihlajavaara (1974), Ahlgren (1972) and eq. (2:2).

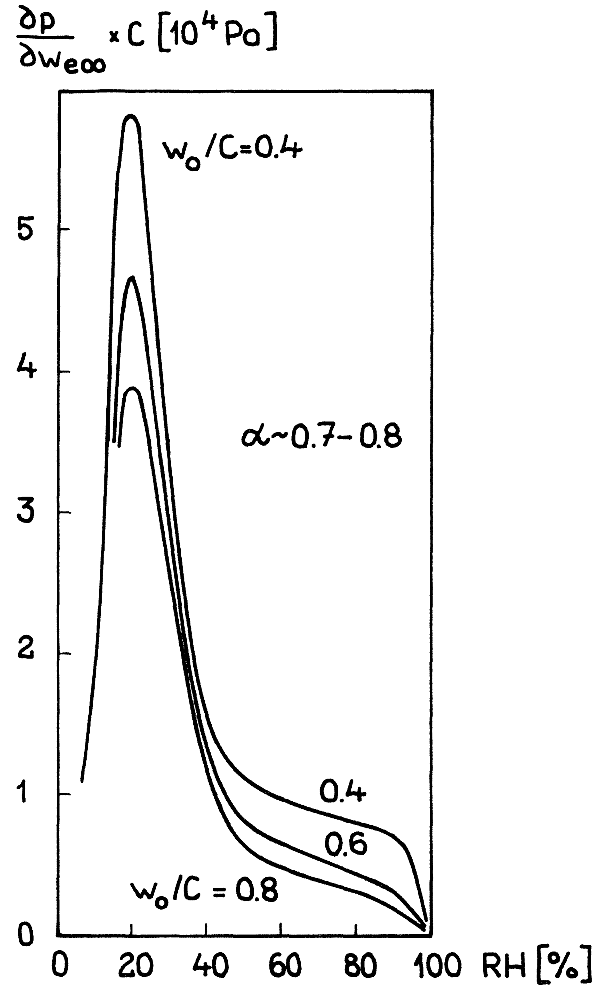


Fig. 4.11 Inverse moisture capacity at different humidities for some water-cement ratios. Evaluated from Fig. 4.10.

4.3 Excess moisture

The amount of excess moisture in concrete is mainly a function of concrete composition, curing conditions and the future climate surrounding the concrete structure. For instance the amounts differ considerably in an indoor wall and a concrete floor on the ground because the climatic conditions are quite different.

In a concrete cured under sealed conditions, i.e. with no water added, the amount of excess moisture is simply

$$\Delta w_{exc} = w_o - w_n - w_{e\infty}(\phi) \qquad (4:5)$$

where ϕ is the relative humidity of ambient air or the critical moisture condition that should not be exceeded.

If the concrete is water cured instead the excess moisture increases. If continuously stored in water the additional amount of water corresponds to that absorbed by contraction during curing. This amount is given in eq. (2:3).

The effect of composition and climate on some common concrete qualities is illustrated in an example calculated for α = 0.8 by using eq. (2:1) (2:3) (4:5) and Fig. 4.10.

Concrete quality *	$\frac{w_o}{C}$	w_o	w_n	40% RH		90% RH		Added if stored in water
				$w_{e\infty}$	Δw_{exc}	$w_{e\infty}$	Δw_{exc}	
K150 II	0.86	180	42	25	113	92	46	10
K250 II	0.63	180	57	33	90	96	27	14
K400 I	0.51	180	71	39	70	99	10	17

* K150 with compressive strength of 15 MPa, etc. All figures in (kg/m^3)

It is clear that the best concrete quality, with a greater cement content, contains a considerably smaller amount of excess moisture if cured at sealed conditions. Especially when the concrete has to be dried to an average moisture content corresponding to a rather high relative humidity, the difference is very great, one third and one fifth respectively. This is shown later to be of vital importance where required drying times are concerned.

If there is access to water during curing this favourable effect can however be completely ruined. The amount of excess moisture for the best quality can become nearly trebbled and if this type of concrete is used to reduce the amount of excess moisture, it must be cured under sealed condition.

4.4 Summary

On the basis of literary information, which in some cases is contradictory, and some experimental results, the desorption and absorption isotherms for concrete are estimated and the effect of composition and age elucidated.

Some examples of the moisture capacity are evaluated and the temperature dependence of the sorption isotherm is dealt with to a lesser degree. The amount of excess moisture affected by the composition is calculated in a few examples and the significance of a high cement content is shown.

5 MOISTURE FLOW

5.1 Introduction

Due to the large amounts of excess moisture usually to be found in concrete and the extremely long times needed to reach equilibrium, it is seldom sufficient to know only the equilibrium conditions in order to judge the effect a concrete structure has on the surrounding material. The time-course, i.e. the rate of the change in moisture condition, is of crucial importance in most cases.

This means that the magnitude of the flow coefficients that rule the moisture transport and the effect of different factors on these coefficients have to be known. This is where the lack of knowledge is greatest, concerning moisture in concrete. A number of mathematical models for moisture transport in concrete are presented in literature, but very little has been done regarding the material properties required for the calculation methods to be applied practically. In this project most of the work has been concentrated on determining some of these material properties.

5.1.1 Mechanisms & descriptions

In a porous material moisture is transported from the wetter part to the drier part. This transport takes place either in the vapour phase or in the liquid phase or a combination of the two. The direction of the moisture flow is determined by the state of the water at the different points, cf. Moore (1972).

Many ways of describing the state of moisture have been used and are being used, the most common being the temperature in combination with the water vapour content, vapour pressure, moisture content, moisture ratio or pore humidity. In rare cases the pressure of the water in the pores is used. This pressure which is usually negative, is given as follows, cf. eq. (4:1)

$$P_w = P_a + \frac{RT}{V_m} \ln \phi \qquad (5:1)$$

where P_a is the air pressure in the pores and ϕ the pore humidity.

The moisture flow under isothermal conditions can be described in one dimension by

$$F = - k \cdot \frac{\partial \psi}{\partial x} \quad (kg/m^2 \cdot s) \qquad (5:2)$$

i.e. with a gradient in some of the above quantities, ψ, multiplied by a coefficient that rules the magnitude of the flow. Of course the coefficient k has different values depending on the quantity ψ to be used. In some cases different descriptions are used in different humidity intervals to separate the vapour flow from the liquid flow, but since it is usually a combination, such a separation is very difficult, and completely unnecessary under isothermal conditions. The coefficient used in one method of describing the moisture flow can easily be converted to another. The connections required for this are summarized in Appendix II. From this information, moisture transport coefficients expressed in most ways can be translated to the desired one.

Moisture transport in concrete, as in other porous materials, takes place mainly as the diffusion of water vapour in airfilled pores with the vapour pressure or content as the driving force and as capillary suction in water-filled pores with the pore-water pressure as the driving force. Due to the pore structure, it is practically always a combination of these two, and only one gradient is usually used to describe the moisture transport under isothermal conditions, as the vapour flow can be expressed in the same way as the liquid flow and vice versa, cf. Appendix II.

At the moment when it is not possible to measure the pore-water pressure and sorption isotherms expressed in this quantity do not exist, capillary suction is usually described with the evaporable moisture content w_e as the driving force. In one dimension the description of the total flow becomes

$$F = - D \frac{\partial w_e}{\partial x} \qquad (kg/m^2 \cdot s) \qquad (5:3)$$

where the coefficient D (m^2/s) is called the diffusivity, which is certainly not a constant but a function of the local climatic conditions, composition and age etc.

This way of expressing moisture transport has chiefly two limitations. It cannot be used accurately for a combination of drying and wetting with hysteresis as moisture might flow from a lower to a higher moisture content in such a case. Under a temperature gradient vapour flow and capillary suction can take place in different directions and a way of separating them becomes necessary. It is however only in very special cases that greater temperature differences occur within the type of concrete structures dealt with here.

The description by eq. (5:3) has among other things one very favourable advantage. The law of mass-conservation, eq. (1:1), becomes an equation expressed only in moisture contents w resulting in a simple and rapid computer program for its solution.

5.1.2 Literature survey

The diffusivity D according to eq. (5:3) is not a constant but a function of several factors, mainly the moisture condition and the concrete composition. In literature the conceivable dependence of moisture content is described for a few compositions, but the examples are few and often contradictory. In Fig. 5.1 examples of the variation by the moisture condition are shown according to different authors. They are however valid for quite different concrete qualities, sometimes only cement paste, and are determined in different ways.

Pihlajavaara (1963) estimated the diffusivity from drying experiments on cement mortar with $w_0/C = 0.56$ and maximum size of "stones" 1.4 mm. The results are shown in Fig. 5.1a for two different drying climates.

Pihlajavaara (1965), by measuring the distribution of moisture at different time steps, calculated the dependence of the diffusivity on the moisture content, cf. Fig. 5.1b. The results are valid for sealed cured cement mortar and consequently the maximum moisture content is much lower than in Fig. 5.1a. The downward trend at higher moisture contents in Fig. 5.1a have therefore not been obtained.

Bray (1969) performed diffusion measurements on cement paste with low water-cement ratios and cured at very high temperatures, resulting in pore-size distributions different to those obtained when curing at normal temperatures. The results are principally shown in Fig. 5.1c and are valid for very much lower moisture conditions than previously shown. They indicate a maximum in diffusivity at lower moisture contents.

Bazant & Najjar (1972) adapted a calculation model with certain parameters to a few measurements of the distribution of pore humidity during drying of the concrete. They described it in terms of humidity, but as the sorption isotherm was approximized with a straight line and the law of mass conservation, eq. (1:1), rewritten, their moisture flow coefficient became the same as the diffusivity. The best correlation was obtained by a variation of the diffusivity as in Fig. 5.1d, when the diffusivity increased very rigorously at humidities about 75% RH to a maximum of approximately $D_1 \approx 30 \cdot 10^{-11}$ m^2/s.

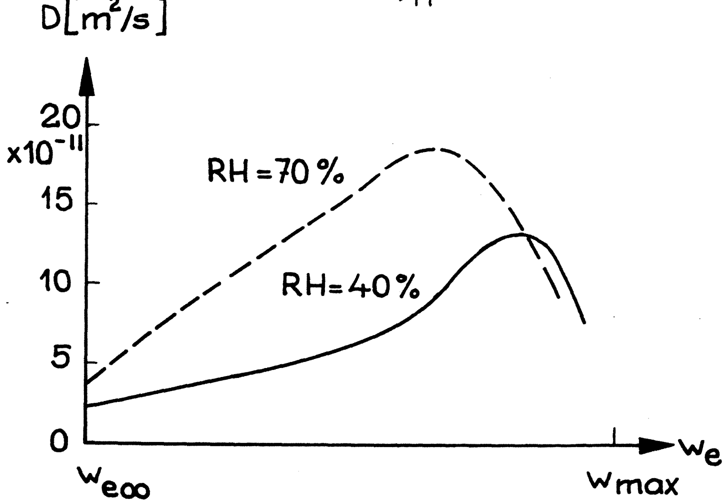


Fig. 5.1a Diffusivity acc. to Pihlajavaara (1963). Cement mortar $w_0/C = 0.56$, 28 days water curing. Drying climate 40 & 70% RH.

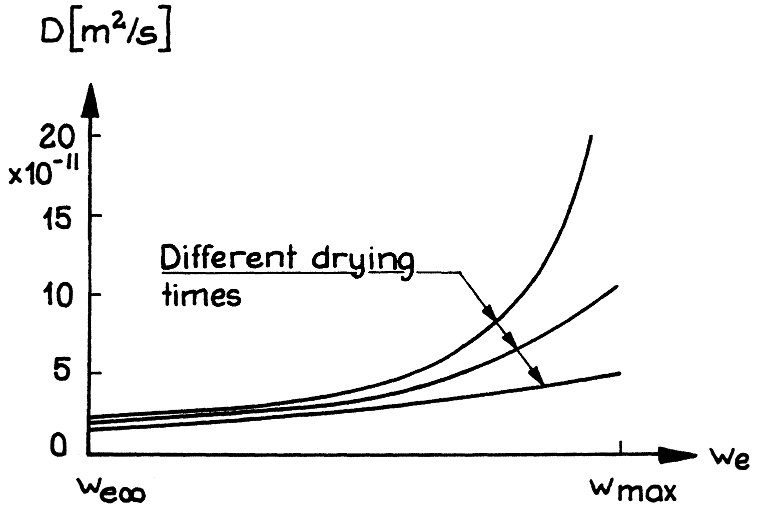


Fig. 5.1b Diffusivity acc. to Pihlajavaara (1965). Cement mortar, 7½ months of sealed curing. Drying climate 40 & 70% RH.

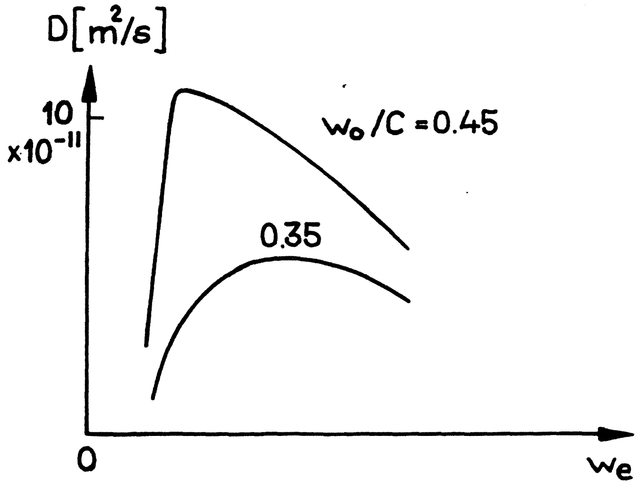


Fig. 5.1c Variation of the diffusivity by moisture content acc. to Bray (1969). Cement paste with low w_0/C. Cured at high temperature.

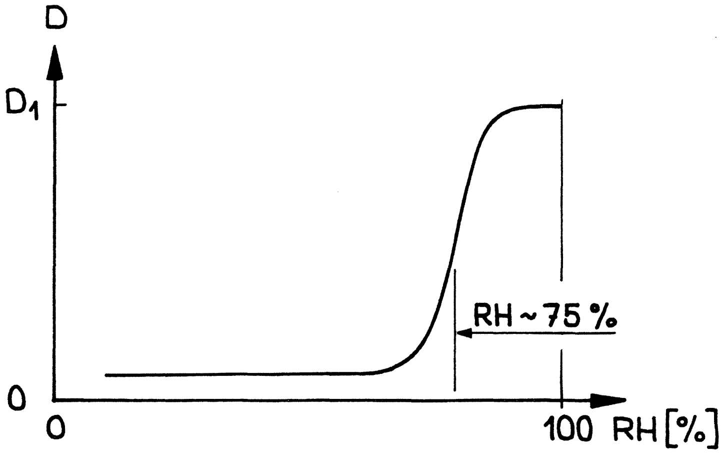


Fig. 5.1d Variation of diffusivity by relative humidity acc. to Bazant & Najjar (1972).

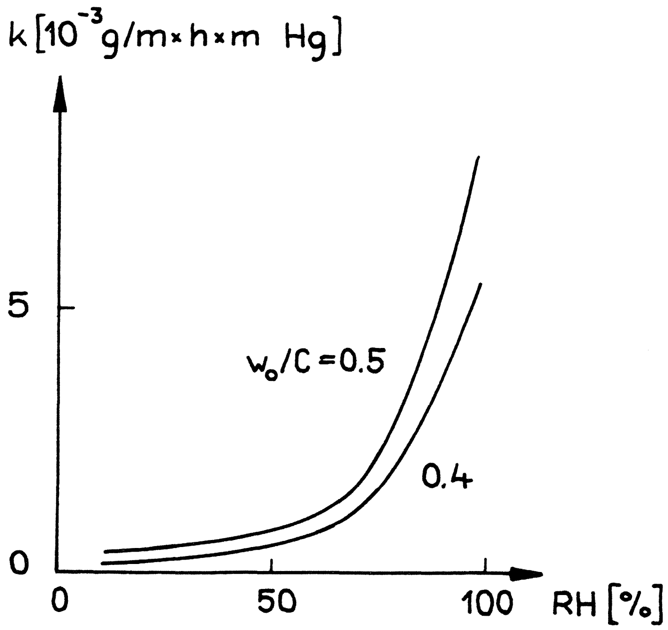


Fig. 5.1e Variation of water vapour permeability by relative humidity acc. to Sørensen & Radjy (1976). Cement paste, dried and rewetted.

Sørensen & Radjy (1976) determined the water vapour permeability for cement paste by diffusion measurements. Examples of their results are shown in Fig. 5.1e. A comparison with the diffusivity above is difficult as the sorption isotherms are unknown.

Nielsen (1976) carried out a few measurements of the moisture distribution by gamma-ray attenuation and obtained diffusivities with a time dependence similar to that of Pihlajavaara.

The effect of the temperature was measured by Yuan, Hilsdorf & Kesler (1968) and estimated by Bazant & Najjar (1972) by means of the Arrhenius equation. Their results are compared in Fig. 5.2.

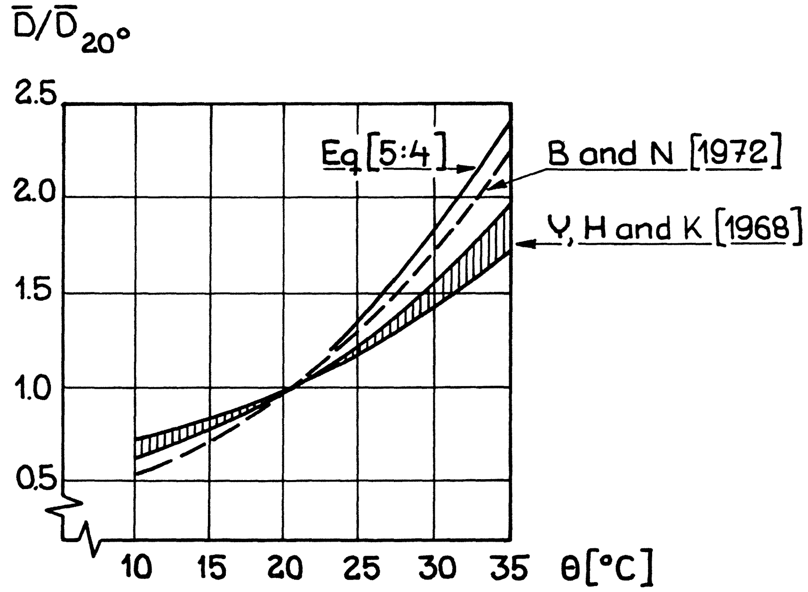


Fig. 5.2 Effect of the temperature on the average diffusivity of concrete. Data from different authors and eq. (5:4).

The effect of the temperature agrees rather well with the dependence on the temperature by the water vapour pressure at saturation. This is what one obtains if the sorption isotherm, or at least the slope of it, and the water vapour permeability k_p are assumed to be independent of the temperature:

$$\frac{D(\theta)}{D(\theta_0)} = \frac{k_p(\theta)\,(\frac{\partial p}{\partial w})_\theta}{k_p(\theta_0)\,(\frac{\partial p}{\partial w})_{\theta_0}} = \frac{p_s(\theta)}{p_s(\theta_0)} \qquad (5:4)$$

This expression is compared with the above in Fig. 5.2. The agreement is rather good and indicates that the moisture flow in concrete can be described as a diffusion process.

The above examples, representing the main part of the information available in literature, give a rough conception of the effect of moisture and temperature on the diffusivity of concrete. For a practical application measurements on normally used concrete compositions are required and knowledge of the effect of different changes in the composition is needed. The work carried out in order to achieve some information regarding this is described below.

5.2 Experiments & results

To make direct measurements of the effect of all essential variables on the diffusivity of concrete is of course quite preposterous. To gain as much knowledge as possible by reasonable means, simple methods and nosophisticated equipment available, two types of measurements have been carried out. The most important variables have been studied more accurately with flow measurements while the rest of the interesting factors have been estimated in a more simple way by means of a large number of drying experiments.

5.2.1 Flow measurements

By using a certain method of performing flow measurements, the effect of the moisture conditions on the moisture flow coefficients has been determined in a few cement mortars with different water-cement ratios. The usual cup method has been used in this case, but has been exploited in a special way, mentioned by e.g. Bazant & Wajjar (1972).

The moisture flow through a disc of a material is attained by placing a cup, with the disc as a lid and containing a saturated salt solution giving a vapour pressure p_1, in a climate room with the vapour pressure p_2, see Fig. 5.3.

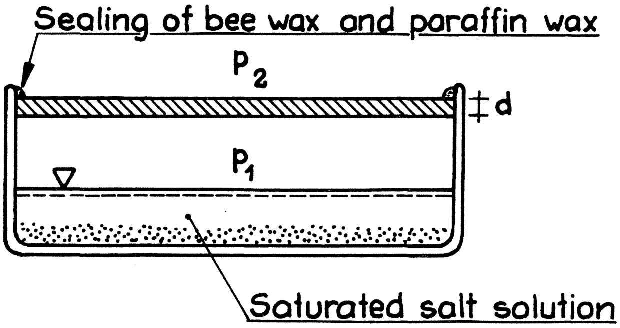


Fig. 5.3 Principle of diffusion measurements using the cup method.

The moisture flow through the disc is determined by weighing until the stationary flow is obtained. The average flow coefficient, in the interval between the two climates, is estimated by one measurement. Much more information can however be obtained by using a series of measurements.

If the moisture flow through a disc as in Fig. 5.3 is described by the water vapour permeability

$$F = - k \frac{\partial p}{\partial x}$$

one obtains if this is integrated between $x = 0$ and $x = d$

$$F \cdot d = \int_{x=0}^{x=d} - k(p) \frac{\partial p}{\partial x} \, dx$$

Derivation with respect to the vapour pressure p_1 is as follows after simplification

$$k(p=p_{1i}) = d \frac{\partial F}{\partial p_1} (p_1=p_{1i}) \tag{5:5}$$

A complete deduction is given in Appendix III.

Eq. (5:5) means that by a series of measurements with a constant climate at one side and a gradually higher vapour pressure p_{1i} at the other, the effect of moisture on the water vapour permeability can be measured at discrete vapour pressure and not only the mean value during an interval.

In this way flow measurements have been carried out on thin discs of cement mortars with water-cement ratios 0.4, 0.6 and 0.8 and containing an aggregate with the maximum size of "stones" of 1 mm. The specimens have been cured at +20 ^{0}C in water for one month and then the thickness of the disc and the wet density have been measured by weighing in air and water. The discs were then put in a glass cup and the edges were sealed resulting in a free specimen surface with a diameter of 170 mm. The weight change was followed for half a year in order to reach a steady flow. The results are presented in Table XII.

As can be seen in Fig. 5.4 the difference in vapour pressure over the specimen will be somewhat smaller than that corresponding to the ambient climates.

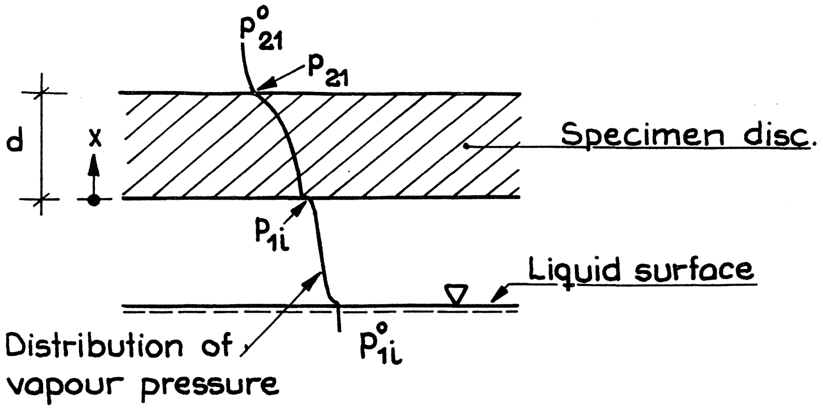


Fig. 5.4 Detail of Fig. 5.3 showing the distribution of vapour pressure for measurement No. i in principle.

The surface resistances are negligible but the vapour resistance of the air between the liquid surface and the specimen has to be considered. This is done by calculating a new vapour pressure p_{1i} from the one given by the saturated salt solution p^o_{1i}. With a thickness of the air layer of 4-5 cm and a water vapour permeability of air of 0.085 g/m·h·mm Hg ($1.77 \cdot 10^{-10}$ kg m/Ns) one obtains a correction in vapour pressure of

$$p_{1i} \approx p^o_{1i} - \frac{F}{1.9} \quad \text{(mm Hg) if F in } (g/m^2 \cdot h)$$

Additionally the variation in thickness from specimen to specimen has been corrected by using the flow equation above.

With these corrections the flows, vapour pressures and water vapour permeabilities obtained are shown in Table XIII.

5.2.2 Drying experiments on cement mortars

To determine the effect of different factors in the concrete composition on the diffusivity, several series of drying experiments have been carried out by measuring weight changes. Most variables can easily be studied in this way without expensive equipment and without waiting a long time to reach steady-state conditions.

The drying course of concrete with a certain composition and thereby a certain diffusivity, can principally be described as shown in Fig. 5.5 using the Fourier number F_o as a parameter, cf. for instance Pihlajavaara (1963)

$$F_o = \frac{D \cdot t}{L^2}$$

The diffusivity coefficient D is the diffusivity at a certain moisture content, t is the time and L a characteristic dimension corresponding to the slab thickness for one-sided onedimensional drying of a slab.

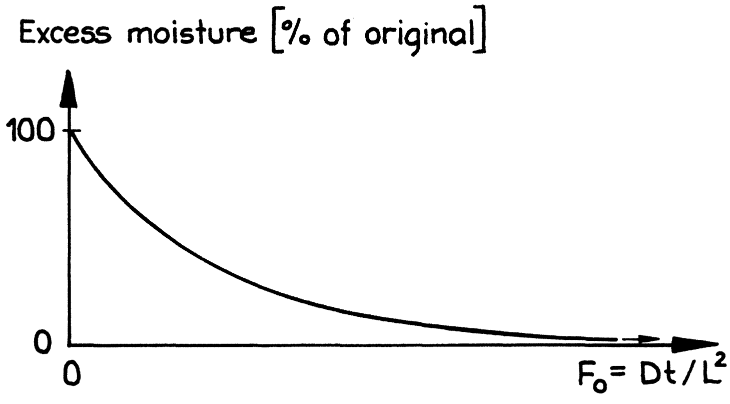


Fig. 5.5 Drying course for concrete of a certain composition.

If the concrete composition is altered in such a way that the moisture dependence of the diffusivity is the same, proportionally, but the diffusivity of another magnitude, the drying course for this concrete can also be described by Fig. 5.5 if the diffusivity coefficient D is changed to correspond to the change in magnitude of the diffusivity. Additionally the moisture content at the surface must be assumed to be in equilibrium to the ambient air during the drying, cf. Pihlajavaara (1963).

This means that if the coefficient D_1 for <u>one</u> composition is known, the corresponding coefficient D_2 for another composition can be determined in a drying experiment by fitting the drying curves to one another, to obtain the same Fourier number when the same degree of drying has been reached. The coefficient D_2 is then obtained from

$$D_2 = D_1 \cdot \frac{t_1\ (y)}{t_2\ (y)} \qquad (5:6)$$

where t_1 and t_2 are the drying times required to reach the same degree y of drying. The procedure is shown in Fig. 5.6.

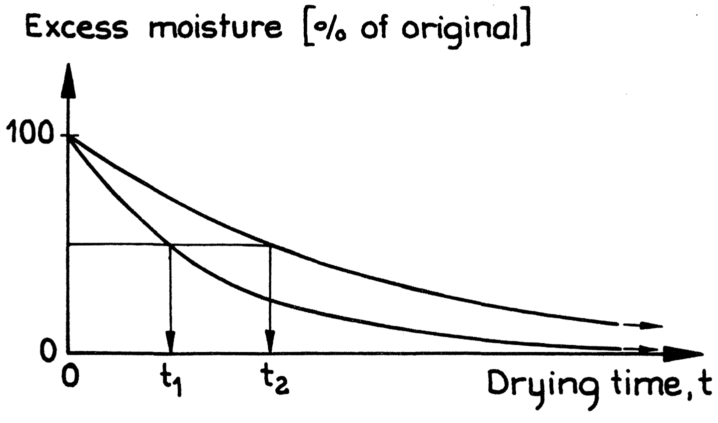


Fig. 5.6 Drying course for two different concretes.

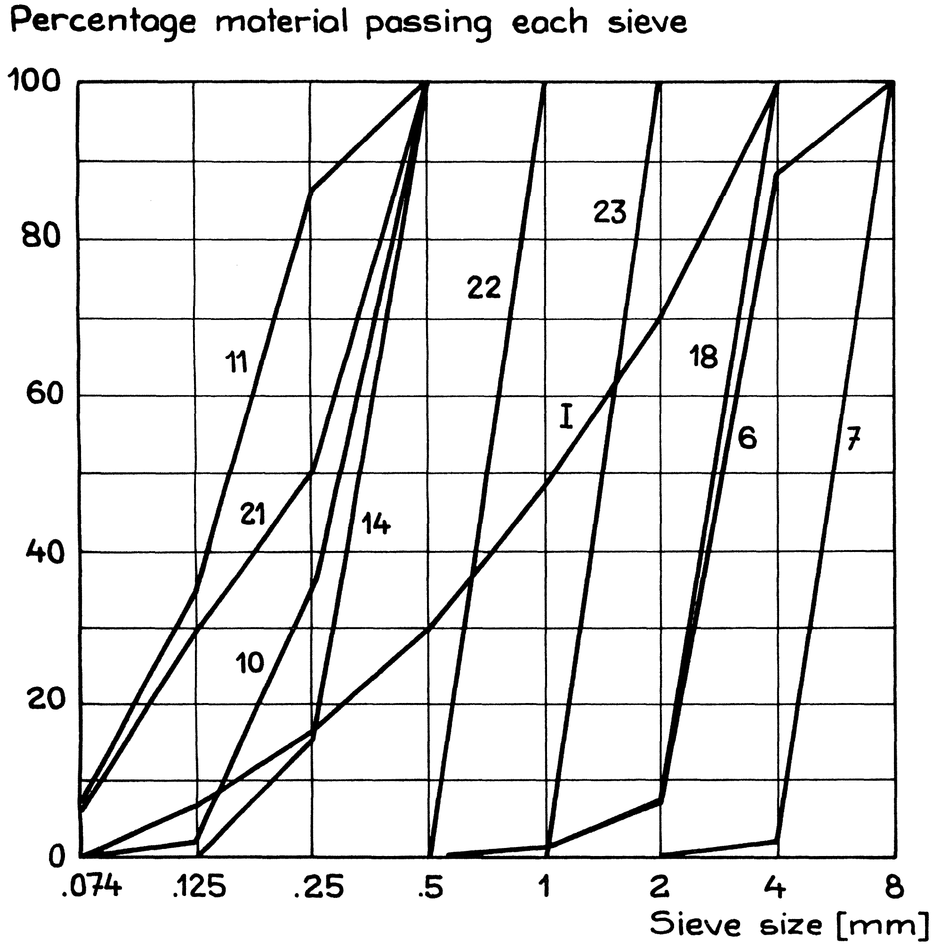
Theoretically speaking any degree of drying can be used, for example when one half of the excess moisture has dried up. The procedure for concrete and cement mortar is however complicated by a simultaneous weight gain due to carbonation. For this reason the times, required to obtain 1/10 (y=0.1) or 1/4 (y=0.25) of the excess moisture dried up, have been used to determine the effect of different factors on the composition. During these short drying times the effect of carbonation is less than during longer times, e.g. the halftime, where carbonation gives misleading results for small specimens.

Drying experiments using some 300 specimens have been carried out with a cement mortar of "standard composition" as a basis:

Original water content, w_o	~218 kg/m^3	$w_o/C = 0.60$
Cement content, C	~364 kg/m^3	(Cement Sl 2)
Air content	4.5-5.2 %	A/C = 4.40
Aggregate content, A	~1600 kg/m^3	(aggregate I)

In Fig. 5.7 the gradation curves for aggregate I and fractions of other aggregates used are shown together with the composition of the different aggregates.

With the standard composition as a basis different factors in the composition have been varied in a systematic way. The variables in the different series are given in the table below.



Aggr	Sand/gravel No.	Proportions (%)	Modulus of Fineness
I	10/22/23/18	30/20/20/30	2.87
II	11/14/22/23	28/20/26/26/	1.96
III	10/22/23/6/7	15/13/15/26/31	3.90
IV	10/22/23/18	15/37/38/10	2.87
V	10/22/23/18	25/12/53/18	2.88
VI	11/22/23/18	31/10/14/45	2.87
VII	10/11/22/23/18	21/20/2/2/55	2.88
VIII	11/22/23/18	30/20/20/30	2.66
IX	21/22/23/18	30/20/20/30	2.78
X	14/22/23/18	30/20/20/30	2.93

Fig. 5.7 Gradation curves for aggregate I and fractions of sand and gravel. The table shows the mix proportions of aggregates I - X.

series	variable	constant
01	w_0/C & curing time	aggregate content = 1600 kg/m^3
03	aggregate content	$w_0/C = 0.6$
04	filler proportion	grading >0.5 mm, aggregate content=1600 kg/m^3
05	modulus of fineness	aggregate content = 1600 kg/m^3
06	grading	modulus of fineness=2.9, aggr.cont.=1600 kg/m^3
07	air entrainment	aggregate content = 1600 kg/m^3
08	stone proportion	aggregate content = 1700 kg/m^3
09	max size of stones	aggregate content = 1700 kg/m^3
10	carbon-dioxide in air	composition
12	drying climate	composition
13	direction of drying	composition

The different aggregate gradings have been achieved by mixing fractions of sand and gravel, cf. Fig. 5.7.

The specimens were casted to a thickness of usually 2L = 20 mm in a battery mould of PMMA, see Fig. 5.8, sparingly oiled, and vibrated on a vibrating table. The air content of the mortar mass was determined with a small air content device. The separation of water was determined on the standard composition as ~5%, corresponding to a reduction in water-cement ratio to 0.57. The specimens were removed from the mould the next day and then usually cured for another 27 days at +20 °C.

Each variable in each series was represented by eight specimens, of which four were cured in well sealed double plastic bags of polyethen and four stored in water with an excess of calcium-hydroxide. After determining the initial weight the edges were sealed with bee and paraffin wax mechanically protected by a rubber ring. The drying experiments took place in climate rooms at +20 °C (±1-2 °C) and 40, 50 and 65% RH (±2% RH). The weight changes of the specimens were determined after gradually increasing the time intervals, the shortest being ~20 minutes at start of drying and the weighing was continued for more than a year.

To determine the effect of carbonation the drying took place in a climate box, see Fig. 5.9. An attempt to get a CO_2-free atmosphere by using a CO_2-filter failed; the filter lasted only a few hours. Instead the air was circulated through a dehumidifier, based on the condensation principle, and the small amounts of

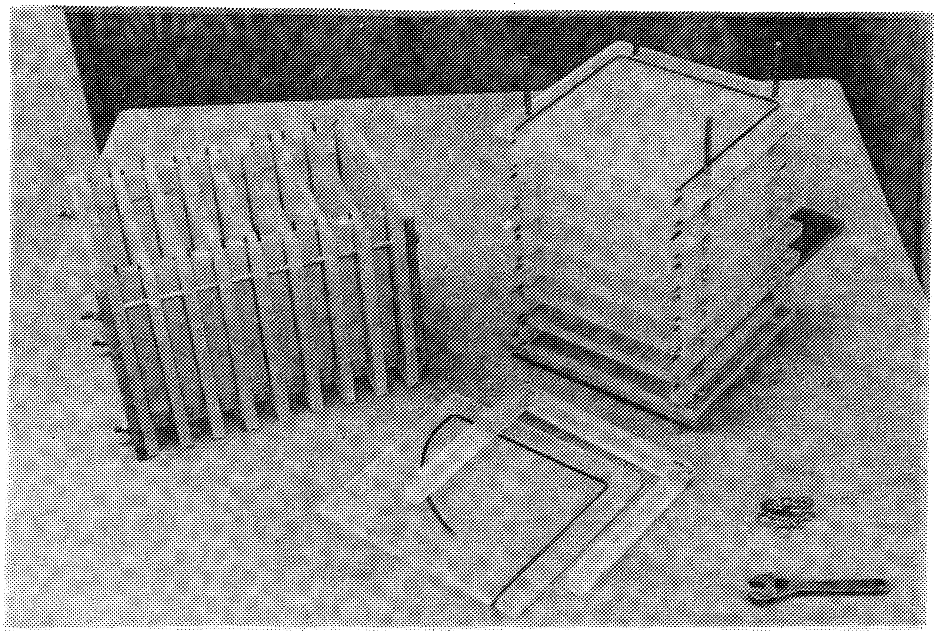


Fig. 5.8 Battery mould of PMMA with O-ring packing.

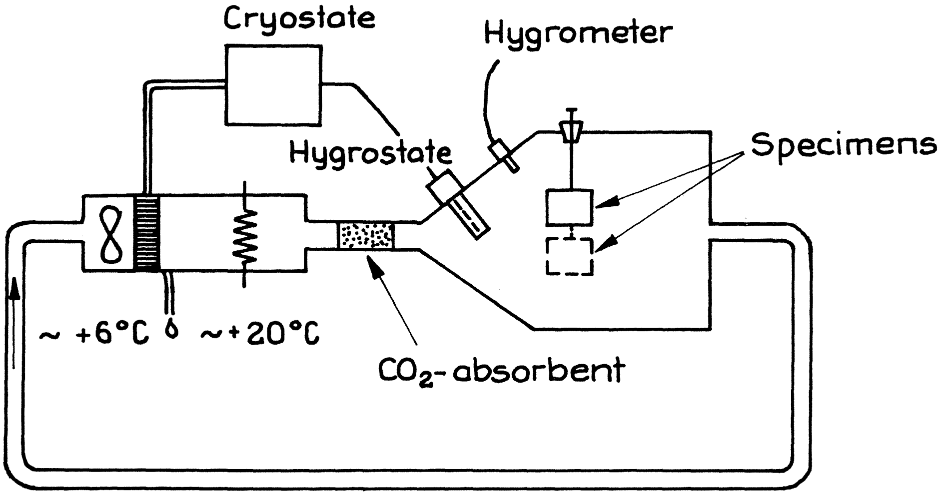


Fig. 5.9 Climate box for CO_2-free atmosphere.

carbon-dioxide that leaked into the box during weighing were taken care of by a CO_2-filter. The specimens still in plastic bags were hung up in the climate box, then the plastic bags were removed for one specimen at a time and the first weight immediately determined. The same procedure as for CO_2-free air was used to produce a very low humidity, ~10% RH, but with a dehumidifier based on the sorption principle.

The drying experiments have resulted in a large number of weight changes as a function of time more or less affected by carbonation. Some measurements of the depth of carbonation by means of phenolphtalein show good agreement with the difference between the maximum determined weight loss and the weight calculated by means of the desorption isotherm. The amount of excess water at the start of the drying was calculated by eq. (4:5) using the progress of hydration and desorption isotherm evaluated in 3.4 and 4.3 respectively. The results are presented as drying times t(0.1) and t(0.25), interpolated from the weight changes, in Tables XIV - XXIII. The air content is presented as air content of "paste", i.e. in per centage of the volume of cement, water and air. In Appendix IV the complete results are shown as weight changes as a function of time for each series.

5.2.3 Drying experiments on cement pastes

In order to study the effect of age on the drying a series of experiments has been carried out on cement pastes with $w_0/C = 0.5$ and during different curing times under sealed conditions. The weight changes in +20 °C and 50% RH have been determined continuously by means of automatic balances, cf. Anon (1971), with the results shown in Fig. 5.10.

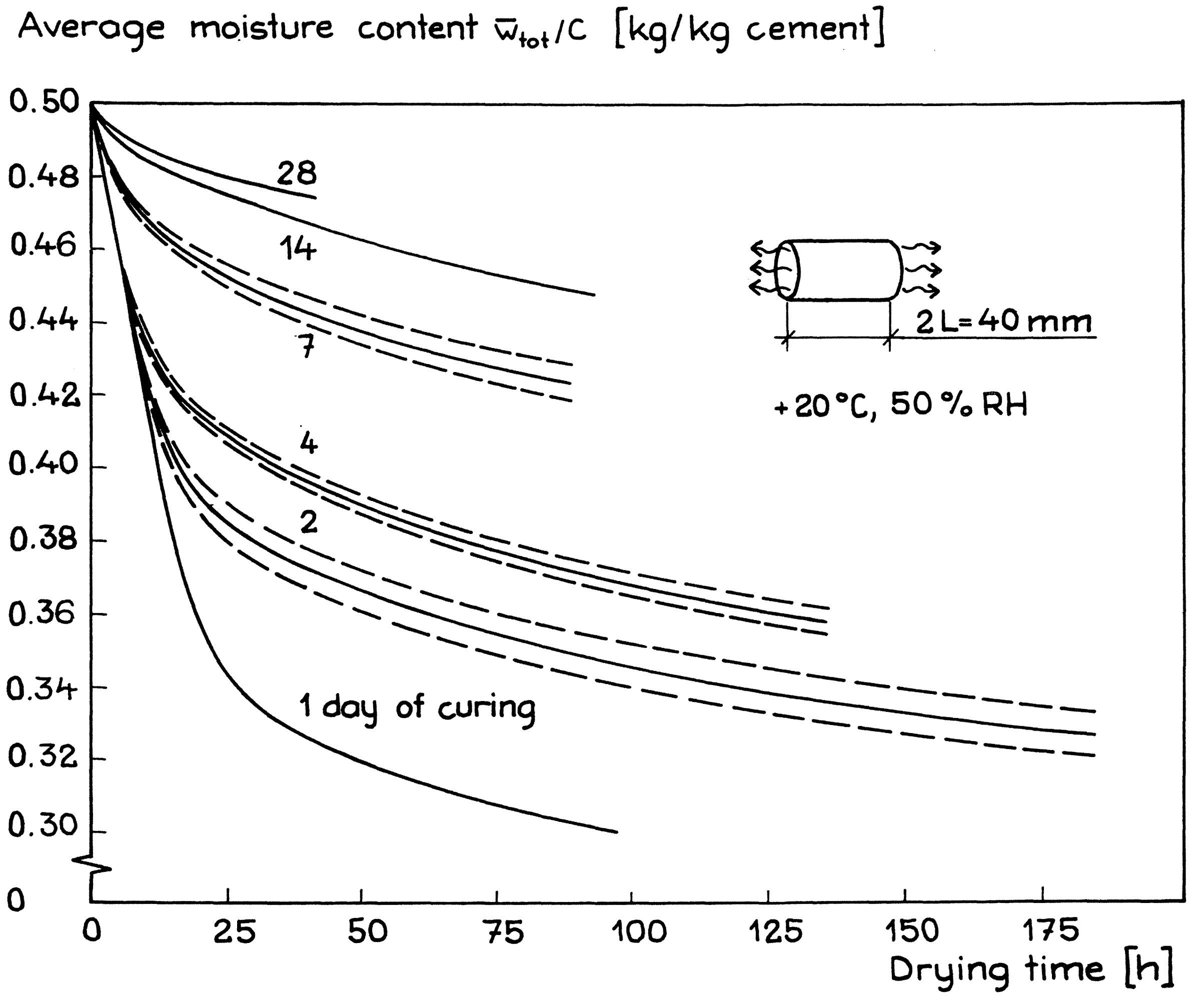


Fig. 5.10 Drying courses for cement pastes with $w_0/C = 0.5$ and varying curing times under sealed conditions. Mean values of 3 to 4 specimens. Broken curves show the standard deviation.

5.3 Analysis and evaluation

5.3.1 Flow measurements; moisture dependence

An estimation of the possible errors, arising when the water vapour permeability is evaluated according to eq. (5.5) from the measurements described above, gives an estimated error of not more than 10 to 15% of measured values, at least for the lower humidities, if the differences in thickness of the specimen and air layer are corrected and the specimens are equal in other respects. Some of the specimens used have however a deviating wet density indicating differences in air content and compactness. A single specimen in a series with this deviation has been excluded from the evaluation. Such differences between two series, cf. mixtures I - III in Tables XII & XIII, produce however a deviating result. This is a possible explanation for the somewhat different results of the three series with the same cement mortar composition. However the reproductiveness is not too poor as can be seen in Fig. 5.11, where the evaluated water vapour permeabilities are shown.

The results can be interpreted in the following way. As the capillary pores are smaller at low water-cement ratios, a continuous liquid phase is present at lower humidities. The moisture flow between the capillary pores must however pass through very narrow gel pores and the water vapour permeability is consequently still rather low even at higher humidities. At higher water-cement ratios the communication between the capillary pores is better. This of course leads to increasing permeability by increasing w_0/C at low humidities, where the moisture flow mainly takes place in a vapour phase. At higher humidities the capillary flow becomes dominating and the permeability increases very rapidly at a high w_0/C once a continuous liquid phase has been formed.

When expressing the moisture transport with a gradient in moisture content, according to eq. (5:3), the moisture dependence of the diffusivity can be obtained from the water vapour permeability by dividing this by the moisture capacity, cf. Appendix II. By using the moisture capacities in Fig. 4.11, valid for a somewhat higher degree of hydration however, the diffusivities corresponding to the vapour permeabilities in Fig. 5.11 are obtained with results as shown in Fig. 5.12.

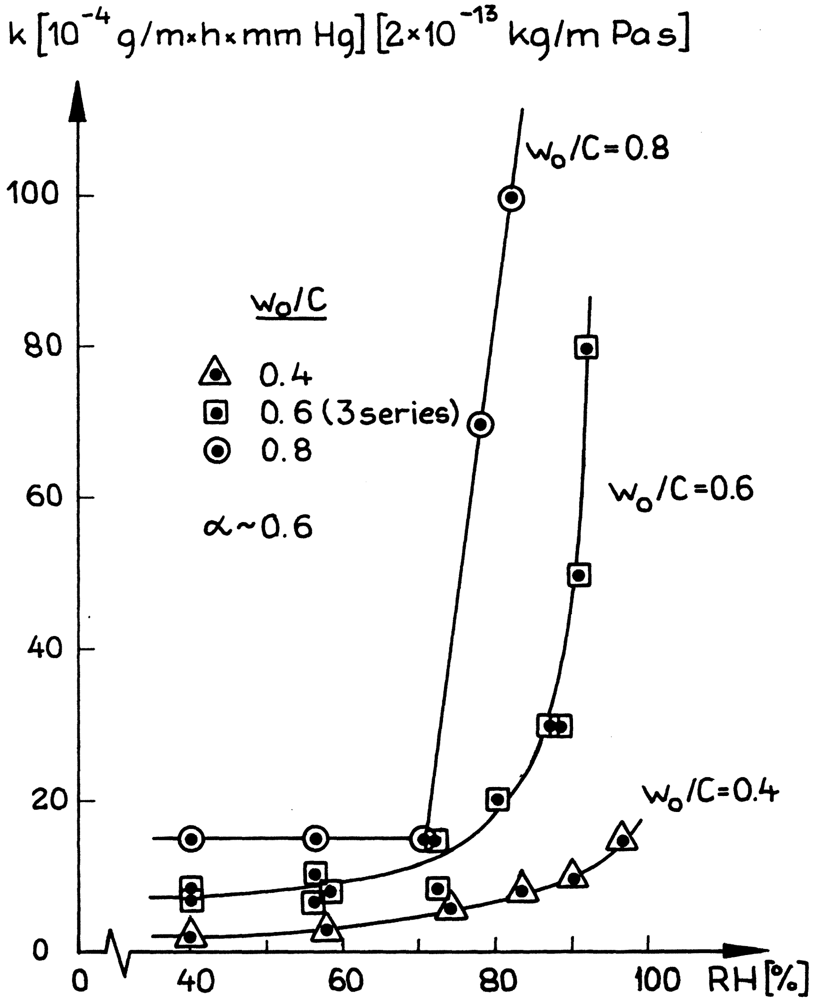


Fig. 5.11 Water vapour permeabilities as functions of pore humidity for cement mortars of different water-cement ratios, measured by the modified cup-method, cf. Table XIII.

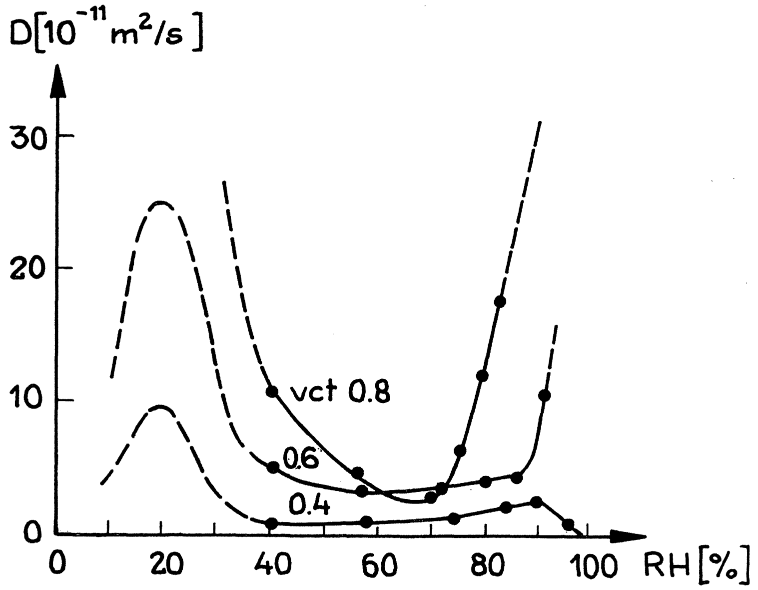


Fig. 5.12 Diffusivities as functions of humidity for the cement mortars in Fig. 5.11.

The characteristic for these diffusivities is a maximum at about 20% RH due to the slope of the desorption isotherms, low diffusivities in an intermediate interval and a new maximum at higher humidities, more pronounced at high water cement ratios.

With the method used it has not been possible to determine the diffusivities at very high humidities for $w_0/C = 0.6$ and 0.8, mainly depending on the desired thickness of the air layers in the cups and the specimens. Quite another method of measurement, not available in this project, should be utilized in order to obtain this information, see for example Nielsen (1976).

A comparison with the diffusivities in Fig. 5.1 from the literature show some similarities, even if these do not always correspond to each other. The absolute values in Fig. 5.1a & b agree rather well with the obtained results and so does the diffusivity at low w_0/C in Fig. 5.1c. The slope of the curve in Fig. 5.1d is similar to those of higher water-cement ratios in Fig. 5.12. At lower humidities there is a very little agreement, resulting from the deviation in desorption isotherms used.

5.3.2 Drying experiments; composition & age

With the "standard mortar" as a basis different factors in the composition was varied. The effect of different variables is always related to the standard mortar having a diffusivity coefficient marked D_0. If, for instance, in the case of D/D_0 equals 2 the drying for this composition is twice as fast and the absolute level of the diffusivity is twice that of the standard mortar.

To reduce the number of specimens, the standard mortar has not been used in every experimental series, but only reproduced three times with the same thickness and drying climate, namely series 016:1 & 2, 033 and 052. Some of the results of these three series are presented for comparison in the table below.

	t(y) (days) ($\bar{t}$ = average; s = standard deviation)								
	016:1		033:1		052:1		016+033+052		Coeff. of variation
	$\bar{t}$	s	$\bar{t}$	s	$\bar{t}$	s	$\bar{t}$	s	
t(0.1)	0.70	0.040	0.83	0.014	0.61	0.016	0.71	0.097	14%
t(0.25)	4.8	0.22	5.3	0.18	4.5	0.06	4.8	0.40	8%
t(0.5)	28	1.5	34	1.4	26	0.3	29	3.9	13%

The precision of the obtained times t(y) is very good but the reproductiveness between the different series is bad, which means that by leaving out the standard mortar in some of the series, it is difficult to compare these accurately with the standard composition.

A possible explanation for this rather bad reproductiveness is that there are some differences in temperature during curing and in the carbon-dioxide content of the air during drying. There is an indication that there is a decreasing amount of absorbed water during curing in water with increasing series number, possibly due to the lower temperature of the water bath or a change in the properties of the cement. The carbon-dioxide content of the air in the climate rooms (and - boxes) is unknown as no equipment has been available for measuring such small amounts of carbon-dioxide.

A reasonable way to solve these problems is to use the series, which is closest in time to a series that does not include a standard mortar.

The accuracy of the drying times t(y) is rather bad mainly due to the effect of carboration, but other factors are also involved. The error due to carbonation increases with time so that the half-time t(0.5) becomes two to three times greater than the true one, cf. series 10. The evaluation of the drying times has also produced some errors. By using a linear interpolation the drying times have become too long. For times between ~0.2 and 1 day the errors can be rather large as no weighing has been carried out during this interval. For times of about one or two days further errors are possible due to the fact that the weights have not always been determined at the same time of the day for each series. Where the thicker specimens are concerned hydration also has an effect during longer drying times and the shorter times should be used for the comparison.

The rather bad accuracy of the drying times is greatly improved by evaluating the effect on the diffusivity by dividing the drying times, according to eq. (5:6), as the errors mentioned above act in the same direction in different series. The accuracy of the diffusivity coefficient D is much better than the accuracy of the drying time. Theoretically a total elimination of the errors is possible if the errors have an equal proportional effect, but even if this is not so the accuracy is greatly increased.

5.3.2.1 Water-cement ratio

The effect of w_0/C has, to some extent, been dealt with in the flow measurements. The results of the drying experiments, series 01, have produced more information regarding this subject, which is presented in Fig. 5.13.

Naturally the water-cement ratio is found to have a crucial effect on the rate of the moisture transport, even if a gradient in the evaporable water content does not represent the same driving of different w_0/C. No other factor investigated is of equivalent importance.

A somewhat different result is obtained when using different drying times t(y) for the calculation of D/D_0. This is quite natural and does not necessarily originate from faster carbonation at higher water-cement ratios. The moisture dependence of the diffusivity is different for different w_0/C, as was seen previously, which means that the drying courses deviate and the requirements in 5.2.2 are not fulfilled. Theoretically only one point at a time can be fitted together and of course this leads to different results for different points.

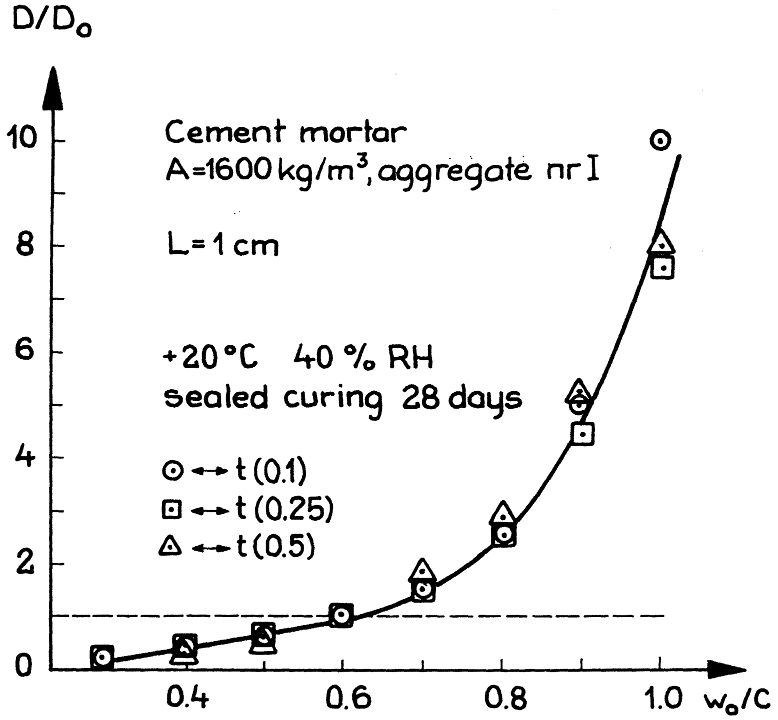


Fig. 5.13 Effect of water-cement ratio on the diffusivity for cement mortars (t(y) = drying time needed to reach a degree of drying when a proportion y of the excess water has evaporated). Each point represents the mean value of four specimens, cured under sealed conditions for 28 days.

At higher w_0/C the required boundary condition of equilibrium with the ambient air at the surface may not be fulfilled either, at least for shorter curing times. This also causes different deviations for different w_0/C.

5.3.2.2 Air content

The air content of the cement mortars has proved to be of great importance to the rate of drying. In many cases the differences in the air content of mixtures in a series have consealed the effect of other factors in the composition and it has been necessary to correct for the air content; see below.

A simple composite model can explain the great effect of the air content. A mathematical model, see e.g. Hillerborg (1979), expressed in terms of the water vapour permeability k for cement "paste", i.e. cement + water + air, can be written as follows:

$$k^n = \delta k_1^n + (1-\delta)\, k_2^n = k_2^n \left[\delta\left(\frac{k_1}{k_2}\right)^n + 1 - \delta\right]$$

where k_1 = water vapour permeability of air
k_2 = do. of paste excluding air
δ = air content of "paste"
n = a constant; $-1 < n < 0$ in this case

As the vapour permeability of air is much higher than that of the paste, approximately 100 times greater, the expression is simplified to

$$\frac{k}{k_2} \approx \left[1 - \delta(1-100^n)\right]^{1/n}$$

A translation to a description in terms of diffusivities is obtained from, cf. Appendix II,

$$\frac{D}{D_2} = \frac{k}{k_2} \cdot \frac{\partial w_2}{\partial w} = \frac{k}{k_2} \cdot \frac{1}{1-\delta}$$

since the moisture content is less in a paste containing air than in a paste without any air, at the same moisture condition.

In terms of diffusivities the effect of air content can then be written as follows:

$$\frac{D}{D_2} = \frac{\left[1 - \delta(1-100^n)\right]^{1/n}}{1 - \delta} \qquad (5:7)$$

which is valid for both mortar and concrete, as their diffusivities are proportional to the diffusivity of the paste, if the aggregate is non-porous.

Eq. (5:7) can be seen in Fig. 5.14 with $n = -1/3$, cf. Hillerborg (1979), together with some of the results from cement mortars with a composition near to the "standard".

The agreement is obviously rather good and the effect of air may be interpreted entirely as a volume effect with the moisture flow finding its way through air voids where the resistance is much less than in the rest of the paste.

For the rest of the experimental series a correction for derivating air content has been carried out in a more simplified way. The corresponding drying time for an air content of 10% has been calculated with a constant correction factor of 0.02 days/% change for $y = 0.25$, obtained by means of series 07. The latter can be seen in Fig. 5.15.

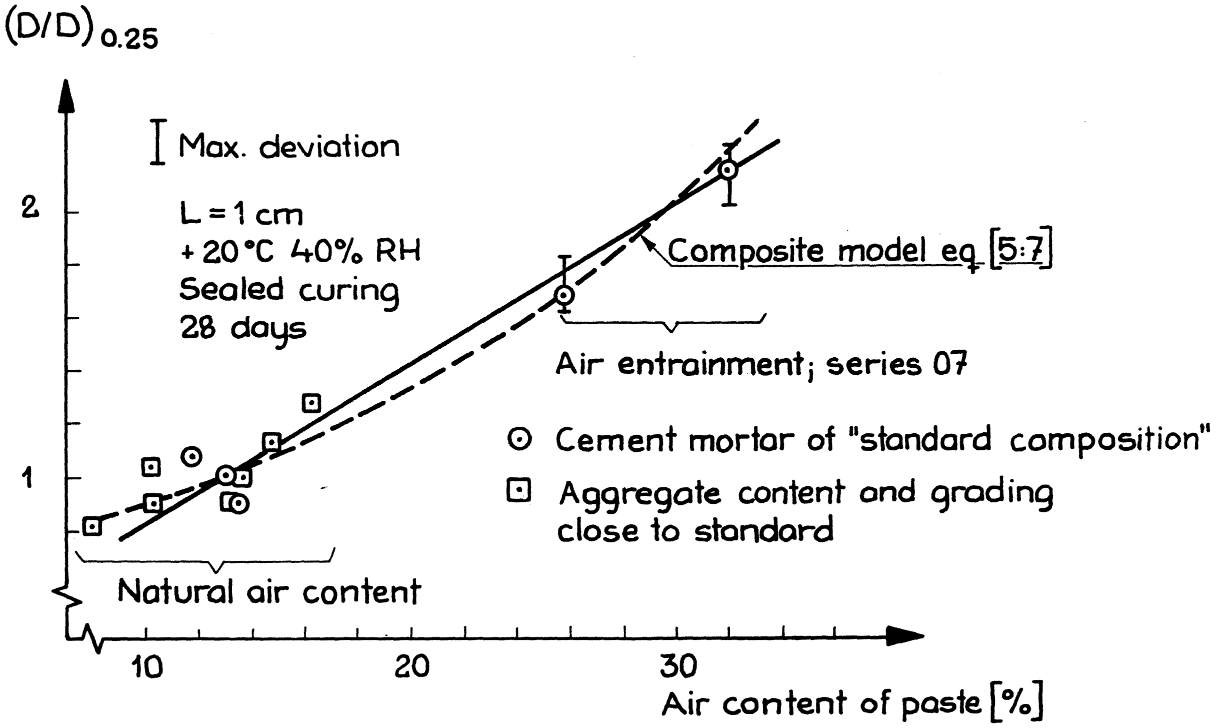


Fig. 5.14 Effect of air content of the "paste" on the diffusivity of cement mortars. Mean values of four specimens.

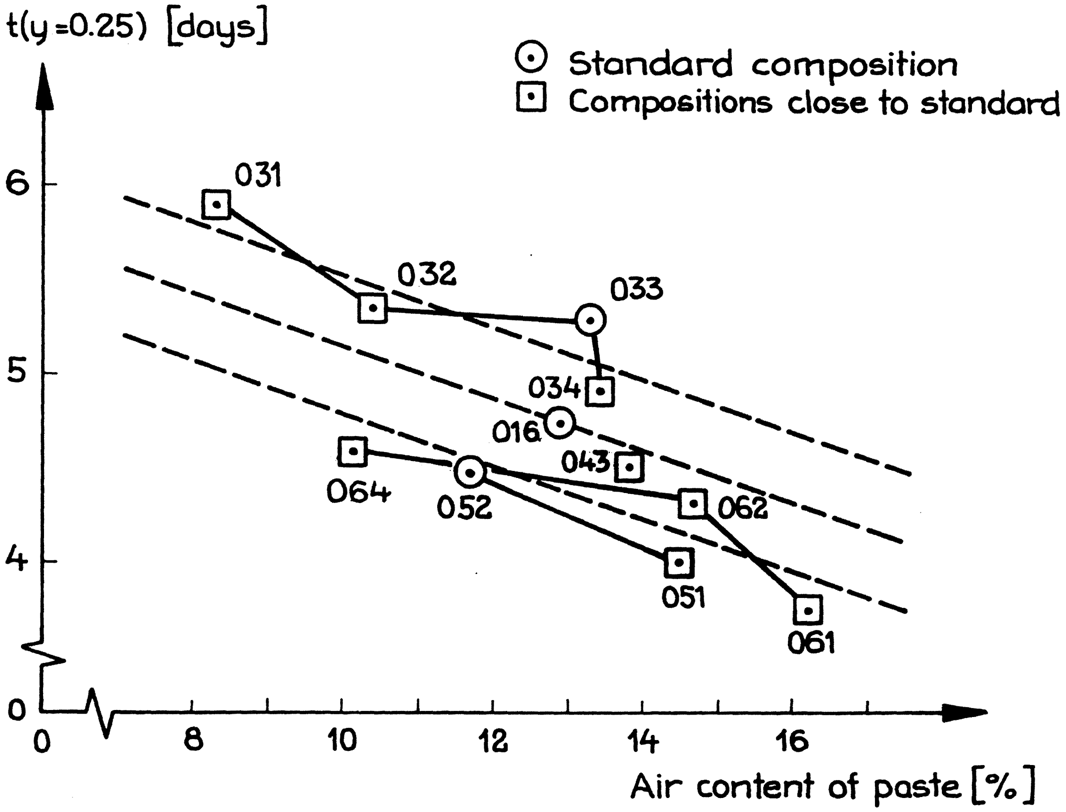


Fig. 5.15 Drying times as a function of air content for cement mortars near to the standard composition. Lines of short dashes have a slope of - 0.14 days/% air.

This correction is not quite accurate as it does not entirely agree with eq. (5:7). Using the slope of the straight line in Fig. 5.14 is an approximation as well as it neglects the fact that the correction factor should be proportional to the drying time and not a constant.

5.3.2.3 Aggregate content and gradation

The effect of the water-cement ratio and air content has been studied at a constant aggregate content and gradation and by varying the composition of the volume not being aggregate. The effect of the aggregate has consequently been studied at a constant w_0/C but the air content has varied simultaneously with the changes in the aggregate composition and has been corrected for as mentioned above.

The aggregate content is varied in experimental series 03 with the results presented in Fig. 5.16, where the corrections for air content are shown.

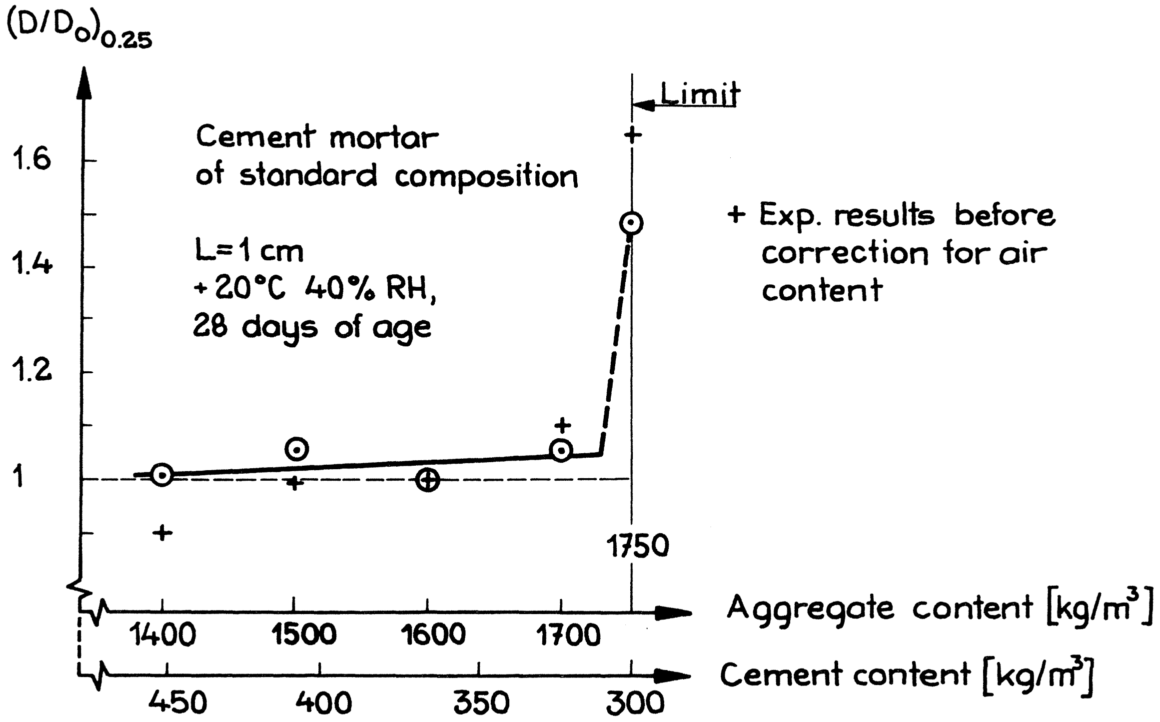


Fig. 5.16 Effect of the aggregate content on the diffusivity. Mean values of four specimens, series 03:1.

A higher aggregate content should cause a volume effect similar to the effect of air as the permeability of the aggregate is zero, meaning a decreasing moisture flow with an increasing aggregate content. A calculation with a composite model gives a decrease in diffusivity of 5% when the aggregate content increases from

1400 to 1750 kg/m^3. As is seen from the result such a composite model is preposterous in this case. An increasing aggregate content might cause more microcracks and separation voids with an increasing moisture transport capability instead. The diffusivity increases very rapidly close to the possible maximum aggregate content, determined by the gradation, when the filling of the space between the aggregate grains is more difficult and cracks due to shrinkage and separation voids arise.

The proportion of filler <0.25 mm has been studied in series 04 and the result should be compared to series 052. If this comparison is carried out no significant effect will be found, the greatest difference being 13%, even though the proportion of filler is usually increased to reduce the permeability to water. Quite surprisingly the effect on moisture is negligible.

The gradation of aggregate at a constant modulus of fineness has been studied in series 06 completed with 052 for comparison. The greatest effect is found on the obtained air content. The effect on the diffusivity is insignificant except for the aggregate with a gap-grading in the interval 0.5 - 2 mm with about 20% higher diffusivity.

The modulus of fineness has been studied in series 05 and to some extent in series 08 and 09, where the proportions and maximum sizes of the stones have varied. The results of these series are summarized in Fig. 5.17.

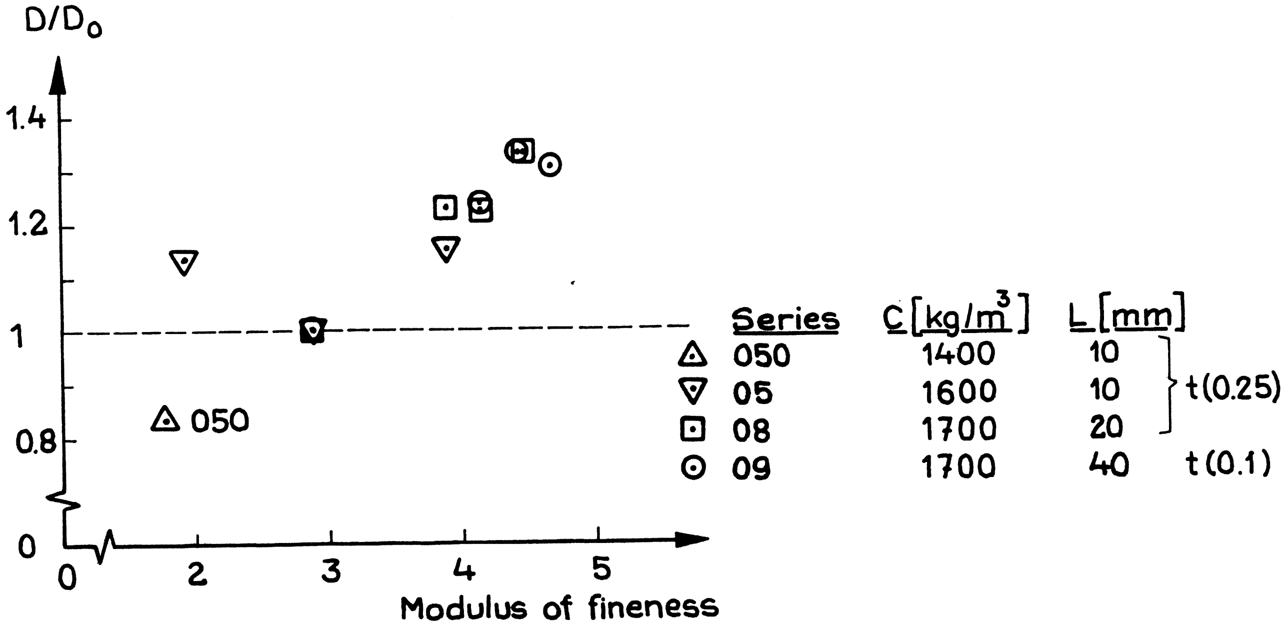


Fig. 5.17 Effect of modulus of fineness on the diffusivity. Different aggregate contents, proportions and maximum sizes of stones. Corrections for air content have not been made.

The results are difficult to value and compare as the aggregate contents, specimen thickness and drying times are different in the different series. There is however a tendency to an increasing diffusivity with an increasing modulus of fineness. Compared to the diffusivity D_0 of the standard composition the composition (050) used in the flow measurements above has a diffusivity of about 0.8 D_0 and the compositions containing stones greater than 4 mm have a diffusivity in the order of 1.2-1.3 D_0. The higher diffusivity of series 051 is due to a higher air content.

The main cause of the effect of increasing amounts of larger grains is probably the separation voids which appear under the stones, perhaps together with cracks, acting to some extent in the same way as entrained air. The concrete compositions which have been used are not very representative for normal concrete used in practice due to the wish to use a constant volume of larger grains, i.e. approximately a constant water content, at a different modulus of fineness. This resulted in a workability deviating to a certain extent from the one used in practice and consequently the diffusivities determined may be too small.

The direction of the moisture flow versus the direction of casting should have some significance due to the effect of the larger grains of the aggregate. The separation means an uneven distribution of larger grains in the concrete with an increasing concentration at an increasing depth. Additionally the separation voids under the stones have a greater extension horizontally than vertically and consequently the resistance to the moisture flow should be less for a horizontal direction of flow. The drying experiments in series 13, see Table XXIII, are however carried out with cement mortar with a maximum size of "stones" of 4 mm and no greater effect of direction of flow was found. This question consequently remains unanswered quantitatively.

5.3.2.4 Age

The effects of the curing time have been studied in series 01 and the experiments on cement paste. Since the drying progresses rapidly at the beginning, the hydration soon almost ceases to continue during a drying experiment with these specimens. At low ages the boundary conditions will be incorrect and the method of evaluation may be inaccurate. However an estimation of the effect of the age on the diffusivity should be obtained. The result evaluated in the usual way is presented in Fig. 5.18, where the age at t(0.25), the approximate "middle age", has been used as a parameter instead of the curing time.

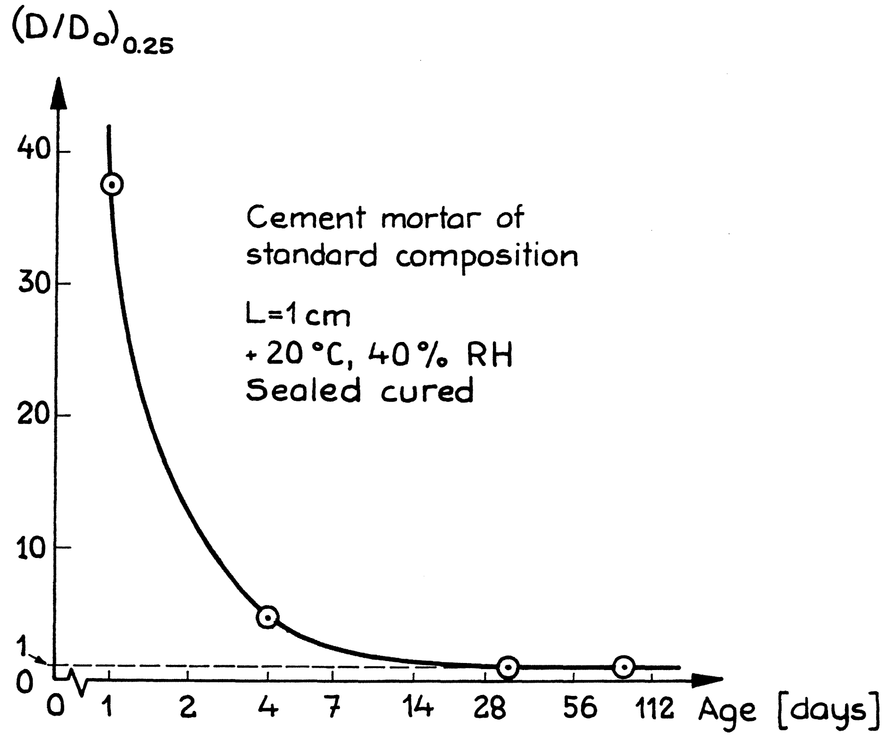


Fig. 5.18 The effect of age on the diffusivity. Mean values of four specimens.

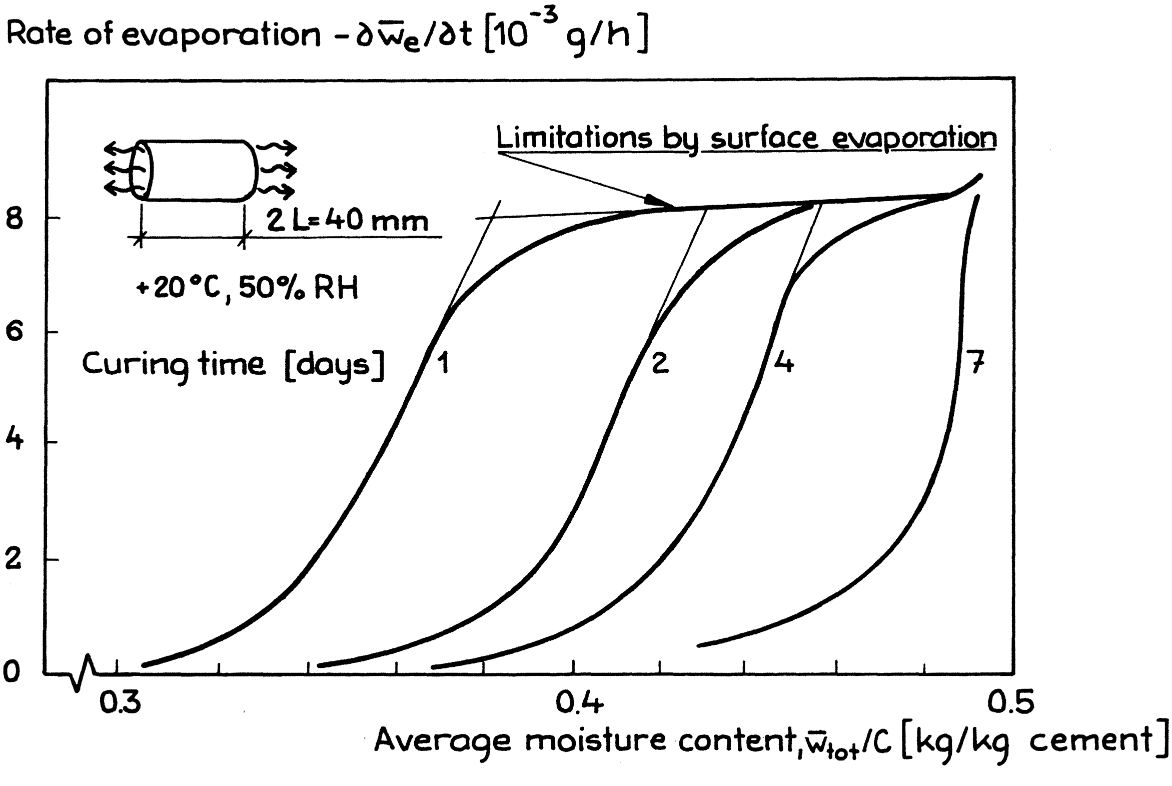


Fig. 5.19 The drying rates of cement pastes with different curing times. Mean values of 3-4 specimens.

As expected the diffusivity decreases considerably with an increasing degree of hydration and densification. The obtained result is probably an underestimation of the diffusivity at very low ages, as the moisture transport during the drying is limited by the evaporation from the surface, which is clearly seen in Fig. 5.19, presenting the results of the drying experiments on cement pastes of different ages.

A small increase in diffusivity is indicated between one and three months age. This could be correct to some extent and a result of an increase in evaporable water content at a constant state of moisture.

5.4 Summary

By using the flow measurements the moisture dependence of the diffusivity is determined for three cement mortars with different water-cement ratios. At very high humidities the measurements are however incomplete and in this case the diffusivity must be estimated from literature information or comparison with experiments.

An extensive series of drying experiments has been carried out in order to determine the effect of various factors in the composition, climate and curing on the diffusivity. The water-cement ratio, air content, modulus of fineness and age have been found to be of essential importance. The obtained information is useful for estimating the diffusivity of concrete and cement mortar of various compositions and ages with the mortar in the flow measurements as the starting point.

6 BOUNDARY CONDITIONS, SURFACE LAYERS

6.1 Introduction

Apart from the material properties concerning the phenomena inside the structure the properties affecting the evaporation of moisture at the surface have to be dealt with. When describing the moisture changes these properties are the boundary conditions needed to solve eq. (1:1). The conditions for evaporation from a certain surface are analysed and discussed below and the effect of various surface layers normally applied to concrete structures is elucidated to some extent.

6.2 Untreated concrete surface

A boundary condition is a way of describing the conditions at the surface of the concrete from information regarding the ambient air or material.

The moisture condition at the surface is determined by the connection between the evaporation from the surface and the moisture transport up to the surface. However the evaporation from the surface has an upper limit and as long as the moisture transport up to the surface in greater the moisture condition at the surface should not change, if so, only very slowly. This upper limit is usually expressed as an evaporation from a free surface of water at a rate given by

$$g = \beta(v_s - v) \quad (\mathrm{kg/m^2 \cdot s}) \qquad (6:1)$$

where

β = surface coefficient of moisture transfer, $\approx 0.3 - 3$ (10^{-2} m/s)
v_s = vapour content at saturation at the surface temperature (kg/m^3)
v = vapour content of ambient air (kg/m^3)

At the previously described drying experiments on cement mortars the climate was +20 ^{0}C and 40% RH which means that $\beta \approx 0.7 \cdot 10^{-2}$ m/s according to Adamson et al (1970). If the surface temperature is assumed to be equal to that of the air, the rate of evaporation then becomes $g \approx 0.26$ kg/m^{2}h. In Fig. 6.1 the rates of drying of these cement mortars of different water-cement ratios, curing conditions and ages are presented, evaluated as weight losses during the first twenty minutes of drying.

It can be seen that the upper limit is not reached for concrete even if it is water cured, unless the concrete is very immature and then only for high water-cement ratios and water storages, cf. also Fig. 5.19. Usually the moisture condition at a concrete surface obviously decrease immediately after exposure to dry air provided there is no free water at the surface.

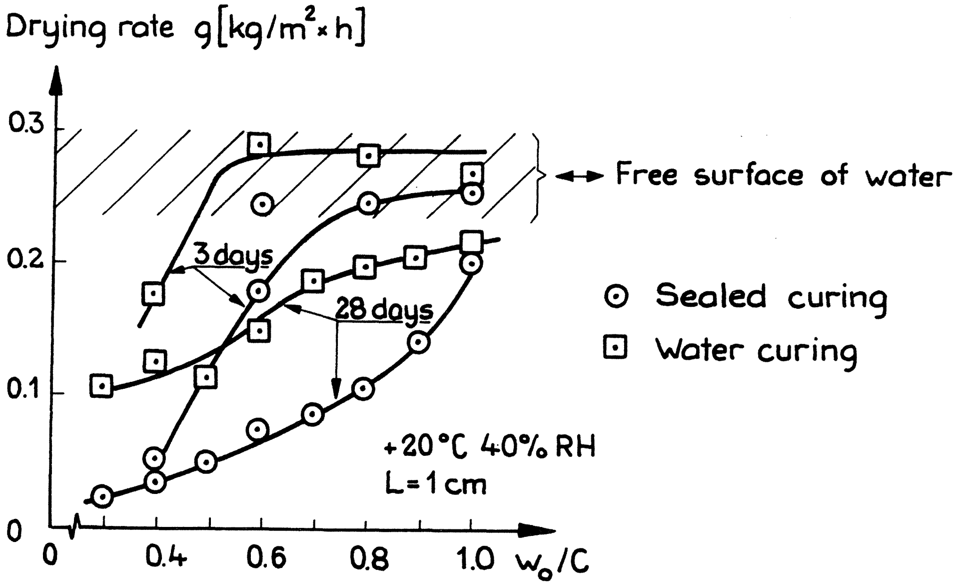


Fig. 6.1 Drying rates of cement mortars of different composition, curing and age during the first 20 minutes of drying. From experiments described in 5.3.2. Mean values of four specimens.

Picket (1946) and Bergström & Wastesson (1954) described the reduction in the moisture content at the surface with an expression similar to eq. (6:1) in terms of drying rate or moisture flow through a ficticous surface layer with a proportionality factor B:

$$g = B\left[w_e(x=0) - w_{e\infty}(\phi_{air})\right] \quad (kg/m^2 \cdot s) \tag{6:2}$$

The coefficient B has been evaluated by fitting total weight or shrinkage changes to linear solutions of eq. (1:1) with a moisture independent diffusivity.

Pihlajavaara (1963, 1965) and Bazant & Najjar (1972) have on the other hand assumed the concrete surface to be in equilibrium with the ambient air, i.e.

$$w_e\ (x=0,\ t>0) = w_{e\infty}(\phi_{air}) \tag{6:3}$$

If this assumption is correct, according to Bouche (1975) and Claesson (1979) the total weight change $\Delta\bar{w}_e$ during drying follows the expression

$$\Delta\bar{w}_e = c_1\sqrt{t} \tag{6:4}$$

as long as the moisture content is constant furthest in the material, i.e. in the centre if the slab is dried from both sides. Eq. (6:4) is equal to the one used to describe capillary suction from a free surface of water and is then, apart from this case, valid for any moisture dependence of the moisture flow. After logaritmation eq. (6:4) is a straight line with the slope 1/2. In Fig. 6.2 some of the drying experiments in 5.3.2.1 are presented in this way. Note that a description of eq. (6:1) gives a slope of 1.0.

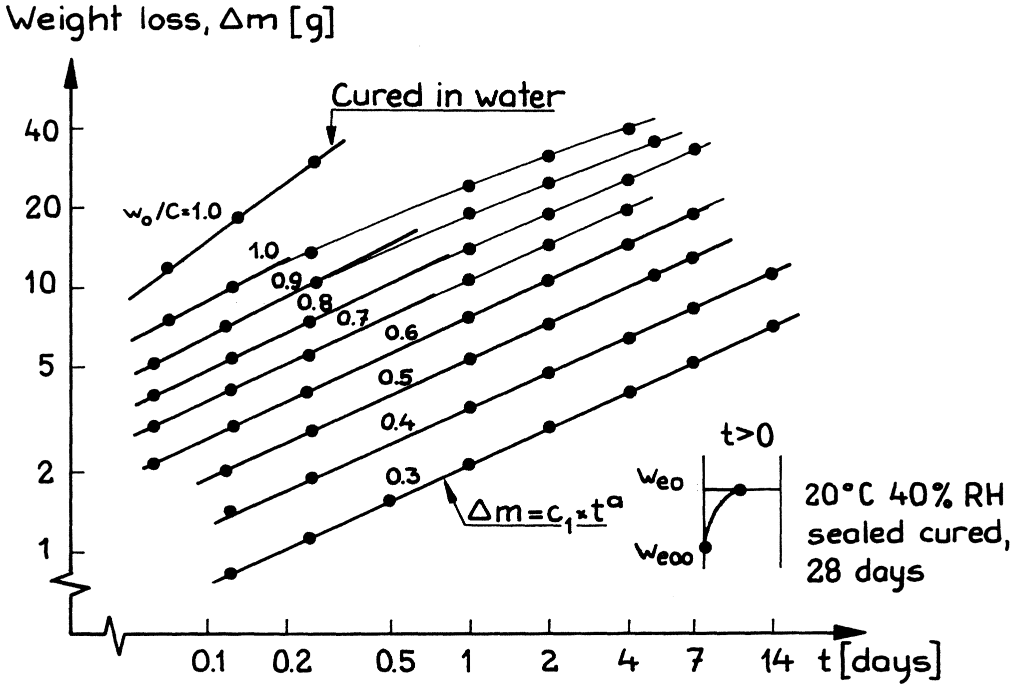


Fig. 6.2 The start of drying. Experimental data compared to eq. (6:4). Thick lines have a slope of 0.46-0.50.

The results shown comply fairly well with eq. (6:4). Some of the straight lines in Fig. 6.2 have a slope a little less than 0.5 and one greater than 0.5 is only found at a very high w_0/C cured in water. The accuracy of the slopes of the lines is however not good for very short times and a possible slope of 0.50 in the very beginning cannot be shown. With the exception of very high water-cement ratios, water cured, the obtained results do not contradict the assumption of equilibrium at the surface with the ambient air.

The evaporation at the surface results in a reduction of the surface temperature, due to the heat required, which is usually neglected in the case of concrete. The moisture transport up to the surface and the following evaporation are very slow and the temperature difference that arises is small and has no great effect on the moisture changes. An isothermal approach in this respect is therefore quite reasonable.

The above descriptions do not consider that concrete is a heterogenous material containing large stones. Close to the surface, to an approximate depth equal to the maximum size of stones, the concrete lacks stones and is more or less a mortar. In principle the concrete should be divided into two or three parts with deviating properties. In 5.3.2.3 this effect is quantified to some extent and an omission should not be too influential for normal concrete structures with a size many times that of the stones.

6.3 Surface layers

Generally surface layers combined with moist concrete have little effect on the behaviour of the concrete. Only if the surface layer is vapour-tight does its effect have to be considered. In this case mostly materials combined with concrete floors have been dealt with and the water vapour permeabilities of some of these materials has been measured in the same way as described in 5.2.1. Measurements have been made on several synthetic carpets and since no real connection with the composition has been found the results can be summarized in a few figures:

Water vapour permeabilities k/d of synthetic carpets ($kg/m^2 \cdot Pas$)	
PVC-carpets	$0.004\text{-}0.02 \cdot 10^{-9}$
Latex backed pile carpets	$\sim 1 \cdot 10^{-9}$
Felt carpets	$\sim 10 \cdot 10^{-9}$

If these figures are compared to concrete, cf. Fig. 5.11, it is clearly seen that PVC-carpets have a crucial effect on the moisture in the concrete on to which they are applied and act almost as a seal. A PVC-carpet has a vapour permeability equal to concrete with a thickness of about 1-5 m. The other carpets correspond to less than 1 cm of concrete.

Plastic foils of polyethene have a tightness equal to or greater than the PVC-carpets and are consequently also used as vapour-barriers in concrete structures. Heat insulation materials usually combined with concrete slabs have a water-vapour permeability according to Hedén (1977) of:

Water vapour permeabilities $\frac{k}{d}$ of heat insulation materials (kg/m^2 Pas)	
Expanded polystyrene, γ = 20 kg/m^3, 5 cm	0.05-0.2 · 10^{-9}
Expanded clay, cement stabilised, 15 cm	~ 1 · 10^{-9}
Mineral wool, γ = 150 kg/m^3, 5 cm	1.5-2.5 · 10^{-9}

The effect of a combined heat insulation of expanded polystyrene on, e.g. the drying of concrete, is quite different from the effect of the other materials due to their greater permeability. This effect is discussed below.

6.4 Summary

The boundary conditions, when having an untreated concrete surface, are found to be expressed rather accurately simply by assuming the concrete surface to be in equilibrium with the ambient air and consequently the moisture content at the surface is equal to the equilibrium moisture content. As indicated by drying experiments, this is valid in most cases with the exception of a very inmature concrete with a high water-cement ratio and cured with access to water.

The effect of surface layers combined with concrete floors is discussed and PVC-carpets found to act as a seal. Many other materials have a much greater permeability to water vapour than concrete and their influence is small.

7 CRITICAL MOISTURE CONDITIONS - A REVIEW

7.1 Introduction

Most materials are affected by moisture in one way or another. The moisture in concrete affects the concrete itself as well as materials in contact with it. This moisture dependence of different phenomena must be known if calculations or measurements of moisture are to be of any great importance. The actual moisture content or condition should then be compared to a limiting value where the effect of moisture becomes too crucial. This limiting value is called the critical moisture condition, cf. Fig. 1.1. The significance of moisture for some different phenomena is presented below.

Damage to materials sensitive to moisture is in most cases a result of moisture induced dimensional changes and/or a deterioration of the material where moisture can act in different ways. The resulting effect as a moisture dependence can vary to a great extent. Good examples of extreme cases are the freezing of a moist porous material and the swelling of a material due to moisture absorption. Both can be seen as more or less a volume effect of the moisture but in completely different ways, cf. Fig. 7.1.

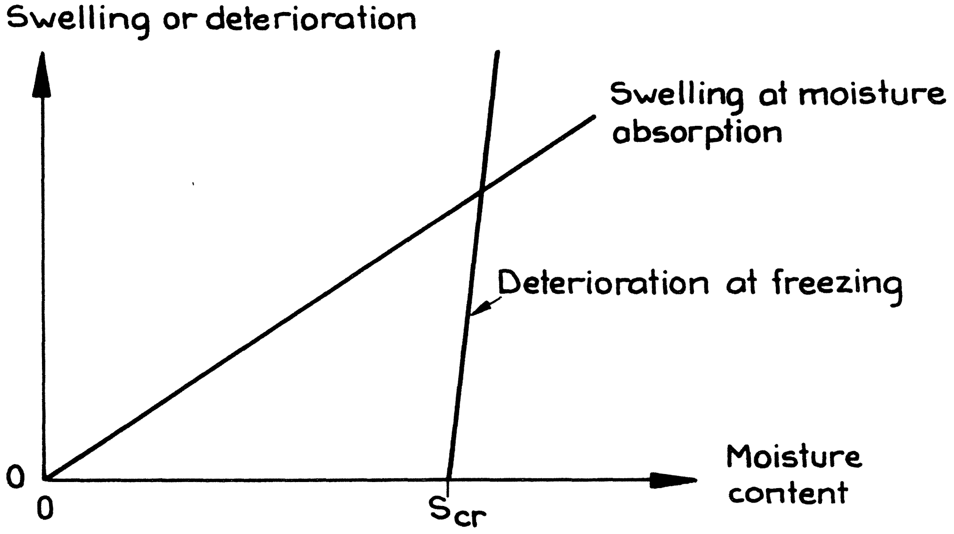


Fig. 7.1 Moisture dependence in principle at freezing and swelling respektively. (S_{cr}=critical degree of saturation at freezing, Fagerlund (1972))

Freezing will cause no damage whatsoever as long as the moisture content is too small, but if the critical moisture condition is exceeded, the deterioration begins. The mechanism is a hydraulic pressure originating from the sudden expansion of the water when it freezes and with too great a moisture content this pressure will damage the material. Frost damage usually occurs beyond the hygroscopic range and is therefore not dealt with again.

Swelling due to moisture absorption takes place in quite a different way. Each increase in moisture content, with some exceptions, causes an additional swelling in many cases proportional to the amount of water absorbed. To be able to define a critical moisture condition at swelling, the size of the acceptable swelling has to be limited by, for example, available space, maximum allowed moisture gradient etc. As a function of relative humidity the moisture dependence is somewhat different, cf. Fig. 7.2.

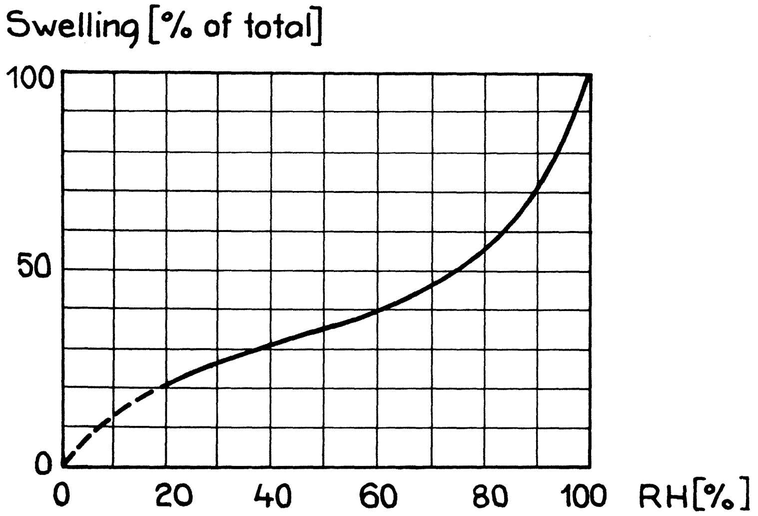


Fig. 7.2 Swelling of wooden-based materials as a function of RH in ambient air; from Hillerborg (1977).

The swelling increases rapidly at higher moisture conditions and half of it takes place at humidities over 75% RH. Manufacturers of wooden-based materials mention critical moisture conditions of 60-75% RH in this respect.

The critical moisture conditions should generally be described in terms of the state of moisture instead of the amount, as different materials or substances are usually involved and affect one another by exchanging moisture. At equal temperature such an exchange can be described by the relative humidity of the material, i.e. the pore humidity.

7.2 The participation of moisture in principle

Water participates in many phenomena that leads to a deteriaration in some way or other. The participation of water can vary considerably. As seen above a change in the moisture content can act to a certain extent as a volume effect by simply occupying space, but generally the absorption of water means an increase in pressure, the pore water pressure, cf. eq. (5:1). This naturally influences the dimensional changes.

Water is also a solvent for the gases and ions taking part in a deterioration. In some chemical attacks the reactants have to be dissolved in water. The ability of adsorbed water to act as a solvent is questionable as it has a thickness of just a few molecule layers. The capillary condensed water usually with a negative pressure can however act as a solvent. The direct effect of the moisture condition on the properties of such a solution is not known. Water also has a great effect as a transport media of dissolved ions and gases and of course the water flow itself is important in many cases. The flow of water is affected by the moisture condition, cf. Fig. 5.11, in a way that indicates a very slow moisture transport by diffusion at lower humidities and an increasing flow rate with increasing humidity due to an increasing capillary flow in the liquid phase. This means a time effect on a deterioration where water is needed. The flow of water of course causes an increasing transport of dissolved substances but where ions are concerned the moisture flow as diffusion at lower humidities is a "capillary break", i.e. an obstacle to such a transport. That is also what happens when no moisture flow takes place and the flow of ions as diffusion in water is prevented at lower humidities when no contionuous liquid phase is present. Increasing humidity means an increasing number of paths for such a flow.

The effect of humidity on the flow of gases in a moist material is the reverse. If no continuous gas phase exists the flow rate is drastically decreased due to the much slower rate of diffusion in water than in air, about 10^4 to 10^5 times less. Tuutti (1977), for example, has made measurements of the flow of oxygen through concrete and indicated this moisture dependence.

These different ways of moisture affecting various processes, as shown above, act singly or together in many cases of deterioration of concrete or materials combined with concrete. The moisture dependence of a total process can possibly be explained and estimated by dividing the mechanism into parts as those above and determine their effect. To some extent this has been done below for some examples with connection to concrete and concrete floors. A quantitative estimate is however difficult to make as a critical moisture condition is not only a matter of mechanism but in principle also a material property, that should be measured.

7.3 Examples of critical moisture conditions

Some examples of critical moisture conditions that are of interest to concrete and concrete structures are presented and discussed below. In most cases the mechanisms are not completely understood and critical moisture conditions determined for a single material quality or a single condition should not be generalised without further notice.

Hydration of cement has been dealt with in Chapter 3 and was found to have a critical moisture condition at about 80% RH, cf. Fig. 3.4. It is a chemical reaction with water as one of the reactants. The humidity affects the amount of adsorbed and capillary condensed water and the pore water pressure, but the mechanism of the resulting moisture dependence is not fully known and very few measurements exist.

In the carbonation of concrete moisture participates in different ways. The penetration of carbon-dioxide is delayed by moisture blocking the pores and the rate of carbonation decreases with increasing humidity, at least this is the case at higher humidities. On the other hand a high humidity means a greater amount of capillary condensed water containing dissolved calcium-hydroxide. To reduce lime efflorescences the carbonation nearest to the surface should be as complete as possible, i.e no calcium-hydroxide should be left. Samuelsson (1977) found a critical moisture condition of the curing climate, i.e the pore humidity close to the surface, of about 80% RH. Some of his results are presented in Fig. 7.3.

Most of the calcium-hydroxide is assumed to be dissolved at pore humidities over 80% RH and thus available for the CO_2 to carbonate.

Reinforcement corrosion is also affected by the moisture condition, cf. Tuutti (1977). Unembedded polished steel has a critical moisture condition regarding corrosion of about 80% RH, but when embedded in concrete the steel is protected by the alkaline environment. Carbonation can however neutralize this protection and reinforcement corrosion then proceeds at humidities over 80% RH. Initiation by clorides has an even lower critical moisture condition.

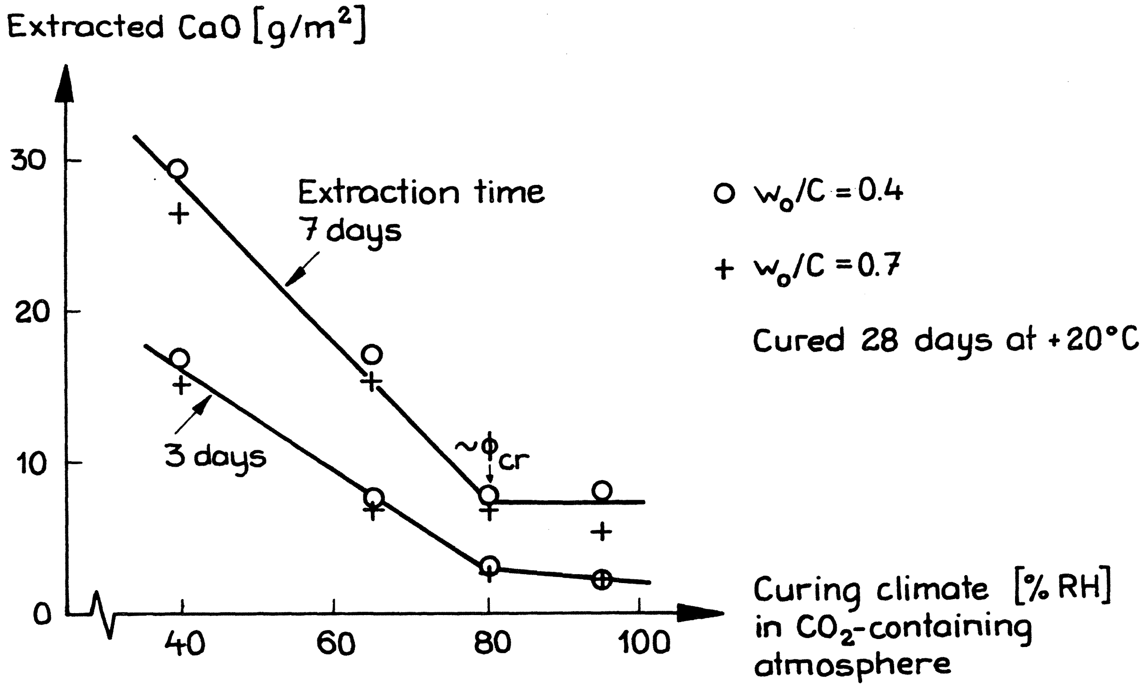


Fig. 7.3 Amount of lime extracted by water for cement mortars carbonated in different climates; data from Samuelsson (1977).

Alkali-silica reactions are greatly affected by moisture in many ways. For the reaction to take place water acts as a solvent and transport media of alkalies. The swelling of the gel is affected by the surrounding pore humidity. Krogh (1974) measured the absorption of water by synthetic gels and indicated a critical moisture condition in this respect of about 80% RH. The gels act similarly to a hygroscopic salt.

The mechanism of the swelling of the gel is still not fully explained, but both an osmotic pressure and the fixation of water, physically or chemically, should produce a faster swelling if a continuous liquid phase is present and the water can consequently be more rapidly moved to the gel.

The damage caused by the swelling of the gel is also affected by moisture as it affects the viscosity of the gel, Moore (1978). The resulting moisture dependence is determined in one case by Lenzner & Ludwig (1978) and their results are shown in Fig. 7.4, indicating a critical moisture condition of about 85% RH.

Alkali and moisture attack on polymer based floor adhesives is influenced by moisture in different ways. The deteriorative reaction requires water and calciumhydroxide. The diffusion of alkali to the adhesive requires a continuous liquid phase and this is probably where the decisive moisture dependence originates. Moisture also causes a swelling of a PVC-carpet attached to the concrete surface by the adhesive. This swelling means a strain on the adhesive and if this is too deteriorated damage will occur. Some experimental investigations have been carried out to determine a critical moisture condition of floor adhesives, cf. Bengtsson & Lundberg (1975) and Petersson (1974), but usually the time it takes for the adhesive to be affected by the alkali has been too short to cause the real deterioration. Nilsson (1977) has however suggested about 90% RH as a critical moisture condition for floor adhesives. This suggestion is based on the results of several damage investigations.

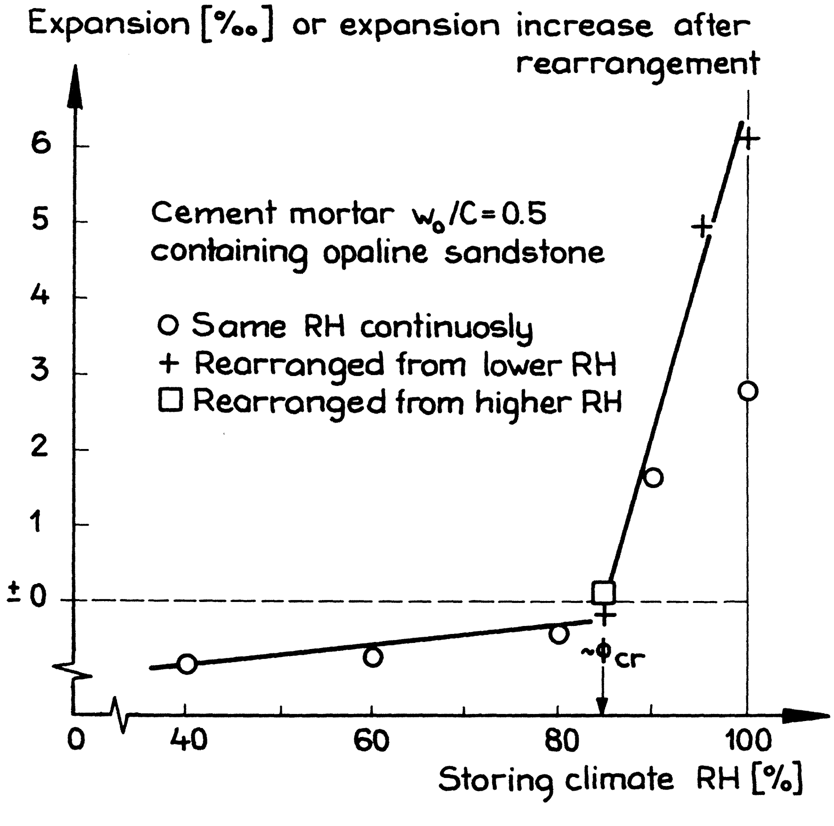


Fig. 7.4 Effect of atmospheric humidity on the alkali-silica reaction; data from Lenzner & Ludwig (1978).

Biological attack on wooden-based and other organic materials causing decay and bad odour requires water to be initiated and to propagate. The critical moisture conditions are different for different fungis but usually close to 100% RH. Some fungis however can continue to grow at much lower humidities. For instance *Merulius lacrymans* , causing decay, has a critical moisture condition of about 80% RH, cf. Björkman (1946). Some moulds of the type *Aspergillus* which cause bad odour, can develop at humidities as low as 75% RH, see e.g. Mislivec et al

(1975). The mechanism behind this moisture dependence is not explained. The fungis must have the ability to make use of the water having a pressure of great negative values.

7.4 Summary

Moisture participates in phenomena in concrete in many ways, in some cases as a plain volume effect or by its pressure. Water is also a solvent and transport media for gases and ions taking part in deterioration. The moisture dependence is mainly due to a time effect but is sometimes also an obstacle to a certain flow.

In the Table below approximate critical moisture conditions for some phenomena in concrete and materials sometimes combined with concrete are summarized. The values are very approximate, for instance the effect of the concrete composition is neglected.

Material & phenomenon			$\sim\phi_{cr}$ (%)
Concrete	Cement hydration		80
	Lime efflorescence *		80
	Reinforcement corrosion, CO_2-initiated		80
	Cl^--initiated		<80
	Alkali-silica reactions		85
Combined materials	Floor adhesives	- alkali attack	90
	Wooden-based	- swelling	60-75
		- decay	80
	Organic	- mould	75

* ϕ_{cr} should be exceeded to avoid efflorescence

8 COMPUTERIZED CALCULATION MODEL

8.1 Introduction

To describe moisture changes in non-steady conditions, e.g. drying, means solving eq. (1:1) with certain initial and boundary conditions. When using moisture and time dependent material properties and taking hydration into consideration, analytical solutions are very difficult to obtain. Instead a numeric method in a computer program has to be used. The method of solving the "law of mass conservation" in the present work by using, to a certain extent, simplified and approximate material properties, is described below and a comparison is made with linear analytic solutions.

8.2 Method of solution

A computer program for the solution of eq. (1:1) using a method of forward finite differences has been worked out in co-operation with the Department of Mathematical Physics at the University of Lund. The original program was published by Carlsson & Claesson (1975). This computer program was modified and completed in order to be adapted to non-steady moisture transport in concrete of different composition and with possibilities of considering hydration and various surface layers and combined materials.

In finite differences eq. (1:1) in one dimension is expressed by

$$\Delta w_e(i) = \frac{\Delta t}{\Delta x}\left[F(i) - F(i+1)\right] - \Delta w_n(i) \qquad (8:1)$$

where i is the number of the cell, cf. Fig. 8.1.

The moisture <u>flow</u> F(i) is described in terms of evaporable moisture content w_e, cf. eq. (5:3). This is an assumption meaning that a gradient in w_n at a zero-gradient in w_e produces no moisture transport. This is not quite correct but probably negligible in most cases. This description has however one essential advantage. The eq. (8:1) becomes an equation expressed only in moisture content and by similarly describing the material properties the necessary computer program for its solution becomes simple and quick. The principle of the program is shown in Fig. 8.2.

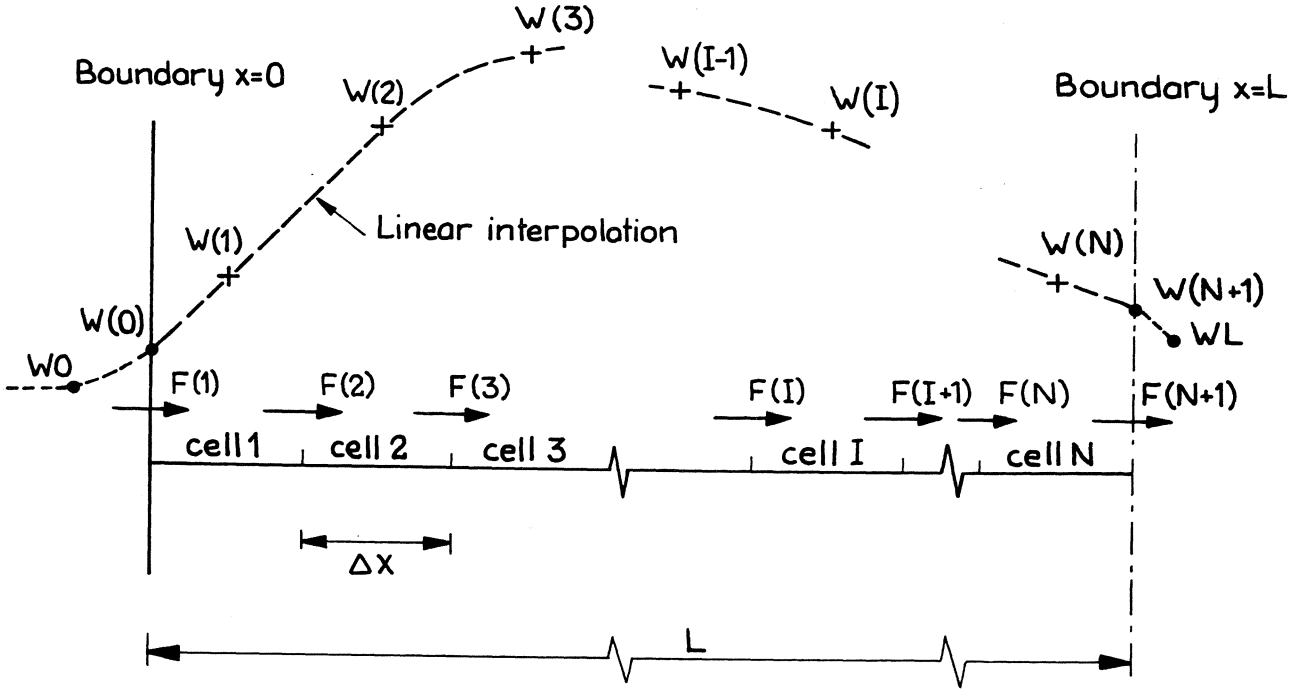


Fig. 8.1 The division of a concrete slab into N cells with a thickness of Δx. The numbering of the moisture flows F(i) between the cells is shown. Carlsson & Claesson (1975).

At each time-step the moisture flows F(i) are calculated using the resistance R2 to moisture flow of each cell-half and the resistances at the boundaries. A new time-step is then determined by considering the stability condition. At this new time-step the additions of non-evaporable water content are calculated and together with the moisture flows previously calculated the new amounts of evaporable moisture content are obtained by eq. (8:1).

The boundary conditions used are that there is an equilibrium with the ambient air at the surface and a resistance to moisture flow of zero for a concrete surface. A surface layer or combined material is described by its resistance to moisture flow. In order to simplify the program this is carried out in terms of the moisture content of the concrete. The initial conditions chosen are optional, but for drying an uniform distribution of evaporable and non-evaporable moisture content has been used in general.

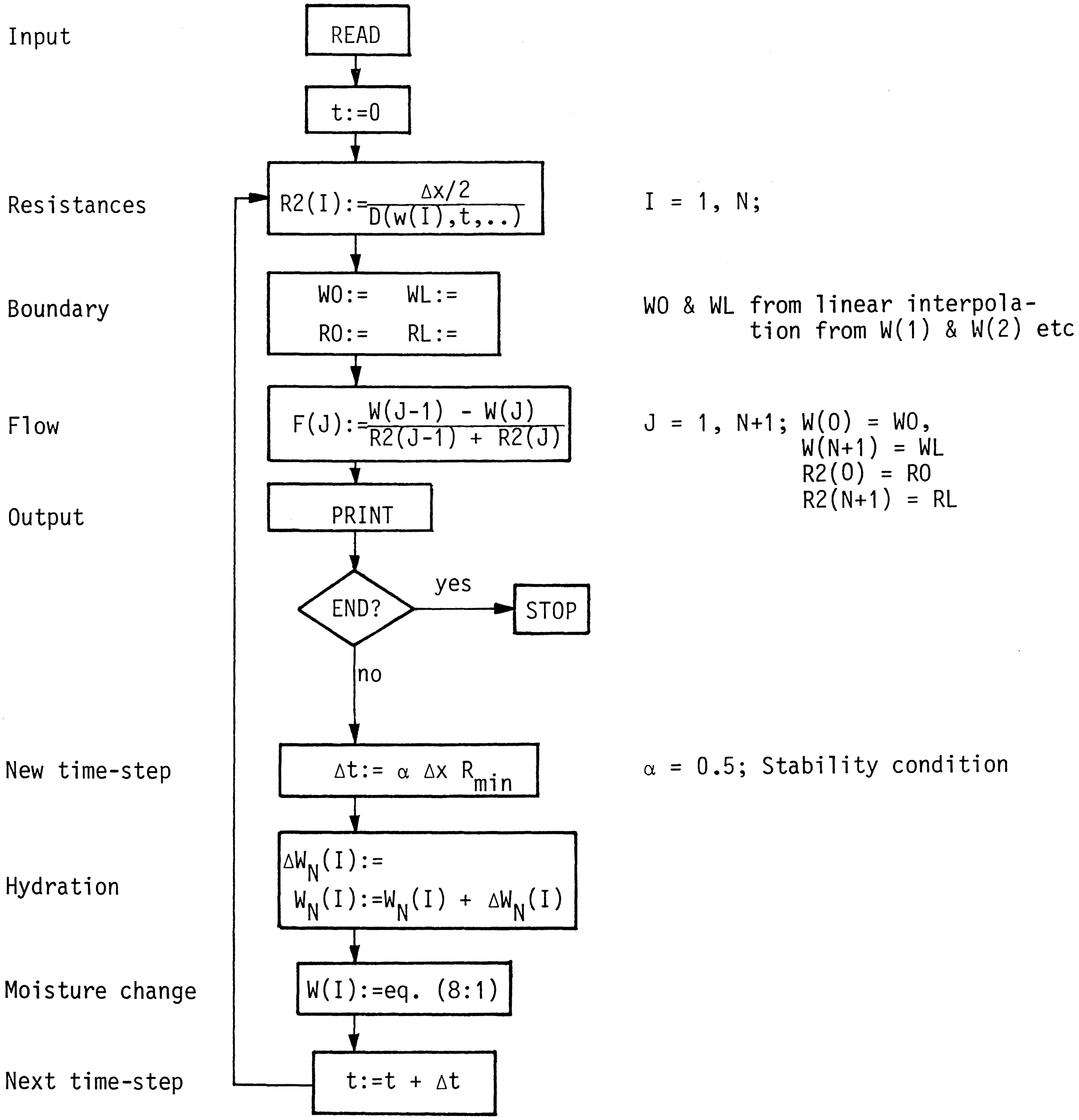


Fig. 8.2 Flow chart, in principle, for the solution of eq. (1:1).

8.3 Description of material properties

Material properties regarding moisture for concrete of varying compositions and age are needed in order to obtain correct solutions and they should be expressed in terms of the moisture content to suit the used computer program. Available material properties, as presented in previous chapters, are rather extensive but far from complete and some simplifications and approximations are necessary. The descriptions used are presented below.

The rate of hydration is described by eq. (3:9) and Fig. 3.9 together with moisture dependence according to Fig. 3.4 approximated to a straight line between zero at 80% RH and the full rate of hydration at 100% RH. In terms of moisture content this is expressed by a quadratic approximation of the upper part of the desorption isotherm.

The diffusivities at different compositions and at different ages have been described in three steps. The moisture dependence and diffusivities of cement mortars determined by the flow measurements described in 5.3.1, cf. Fig. 5.12, have been used as the starting point called $D^o(w_e)$. The moisture dependence at different ages is unknown, in principle, and an assumption has to be made. In this case the moisture dependence expressed as a function of pore humidity has been assumed to be independent of age. Expressed as a function of moisture content the moisture dependence consequently varies with age according to the sorption isotherm. In Fig. 8.3 an example is shown where $w_o/C = 0.6$.

The diffusivity at higher humidities has not been determined and is therefore estimated from the results of Bazant & Najjar (1972), who found a diffusivity of approximately $30 \cdot 10^{-11}$ m^2/s more or less independant of the composition. This diffusivity is however dealt with as a parameter later on. Where concrete is concerned the diffusivity is then obtained by multiplying D^o with another parameter, a factor estimated with the result of the drying experiments in 5.3.2 as a guide, showing a factor of around 2 for $w_o/C = 0.6$. At lower ages the diffusivity thus obtained on the one hand is changed in moisture dependence using the desorption isotherm as a function of age and on the other hand increased by a factor as in Fig. 5.18 describing the effect of age on the magnitude of the diffusivity.

The resistance to the moisture flow of a surface layer or combined material expressed in terms of moisture content of the concrete has been obtained according to Appendix II. The slope of the sorption isotherm has then been approximated to be constant ~0.1 kg/Nm, cf. Fig. 4.11, an over-estimation at very high humidities.

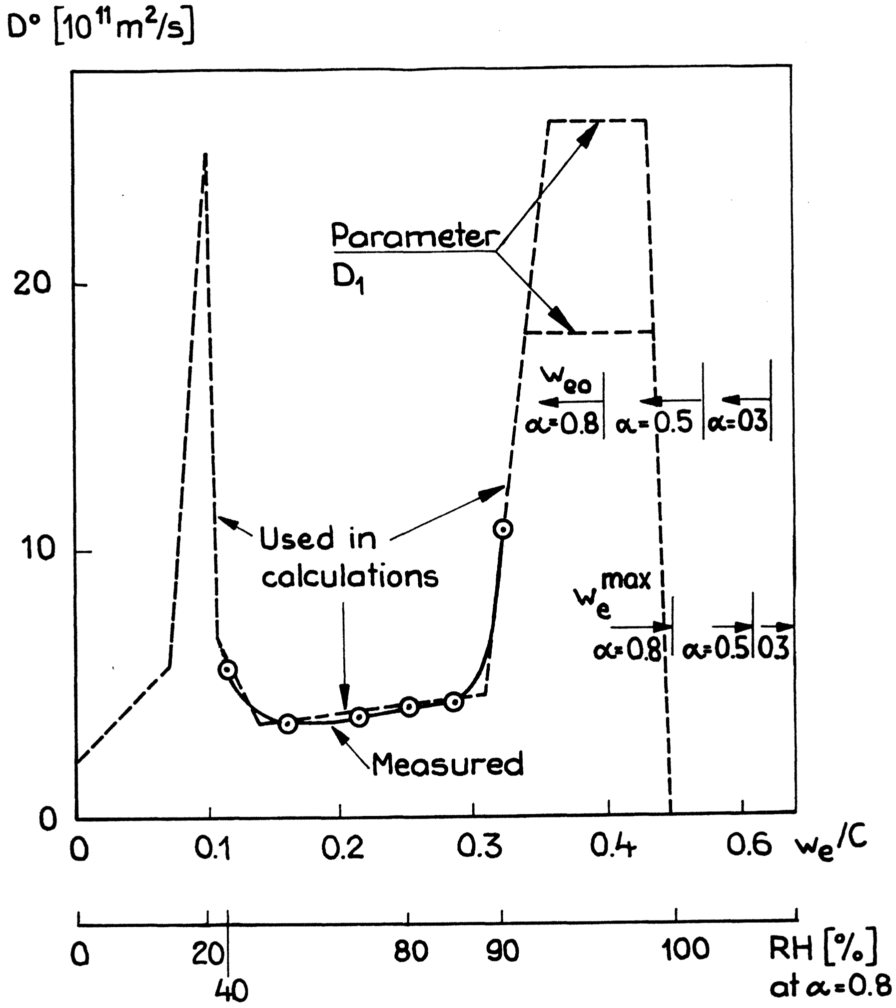


Fig. 8.3 Diffusivity D^0 of a cement mortar, with $w_0/C = 0.6$, as a function of moisture content at $\alpha = 0.8$.

The desorption isotherm as a function of age or degree of hydration is used to obtain the effect of age on the diffusivity as mentioned above. The description of the boundary conditions requires this information as well and so does the translation of the calculation result in terms of moisture content into a description in terms of relative humidity. The desorption isotherms have been obtained as described in 4.2.3 and an example used for $w_0/C = 0.6$ is shown in Fig. 8.4.

Equilibrium moisture content are obtained by simple linear interpolation in Figures such as Fig. 8.4 expressed mathematically in the computer program. Conversion between moisture contents at different ages, when describing the moisture dependence of the diffusivity at low ages, is for example carried out by approximating the distance between the desorption isotherms in Fig. 8.4 as constant, independent of the humidity.

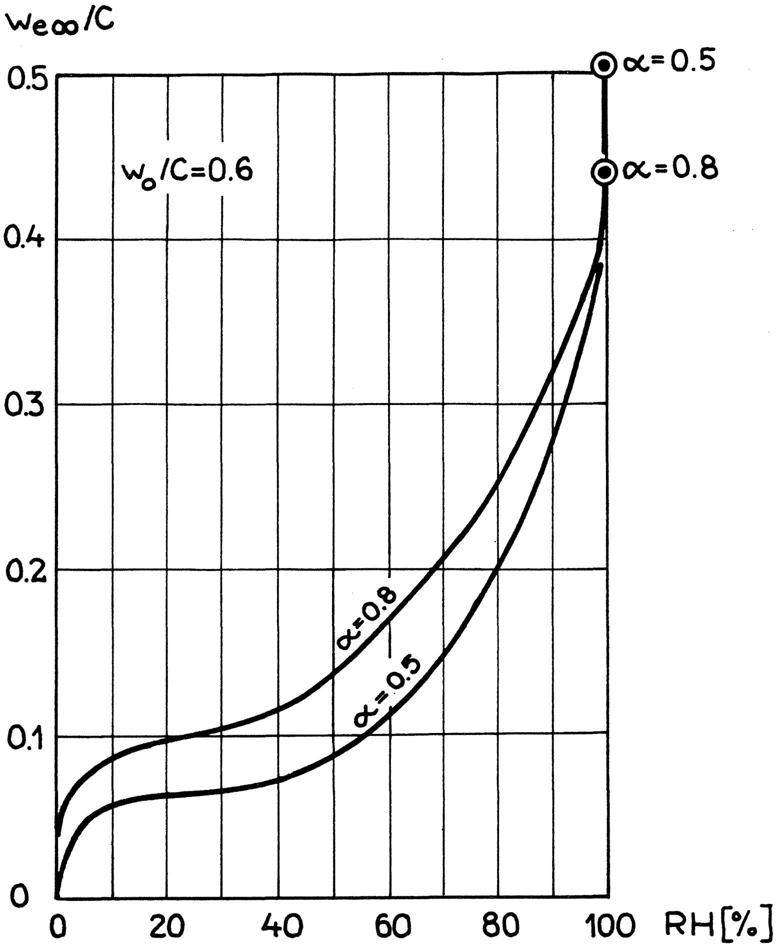


Fig. 8.4 Used desorption isotherms for concrete with $w_0/C = 0.6$ as a function of the degree of hydration.

The material properties used could easily be described mathematically in a more precise way when using a computerized model to obtain a solution of a non-steady moisture change. The accuracy of the material properties available at present however does not justify such a precise description. With the used simplifications and approximations the obtained solutions will still be much better than the solutions obtained previously with more uncertain diffusivities and the hydration not taken into consideration.

8.4 Comparison with linear solutions

If the moisture flow is described by a constant diffusivity, eq. (1:1) becomes very simple and analytical solutions are possible to obtain. The solutions can be expressed with the Fourier number F_0 as a parameter, cf. 5.2.2, and in Figs. 8.5 and 8.6 an example is shown for drying.

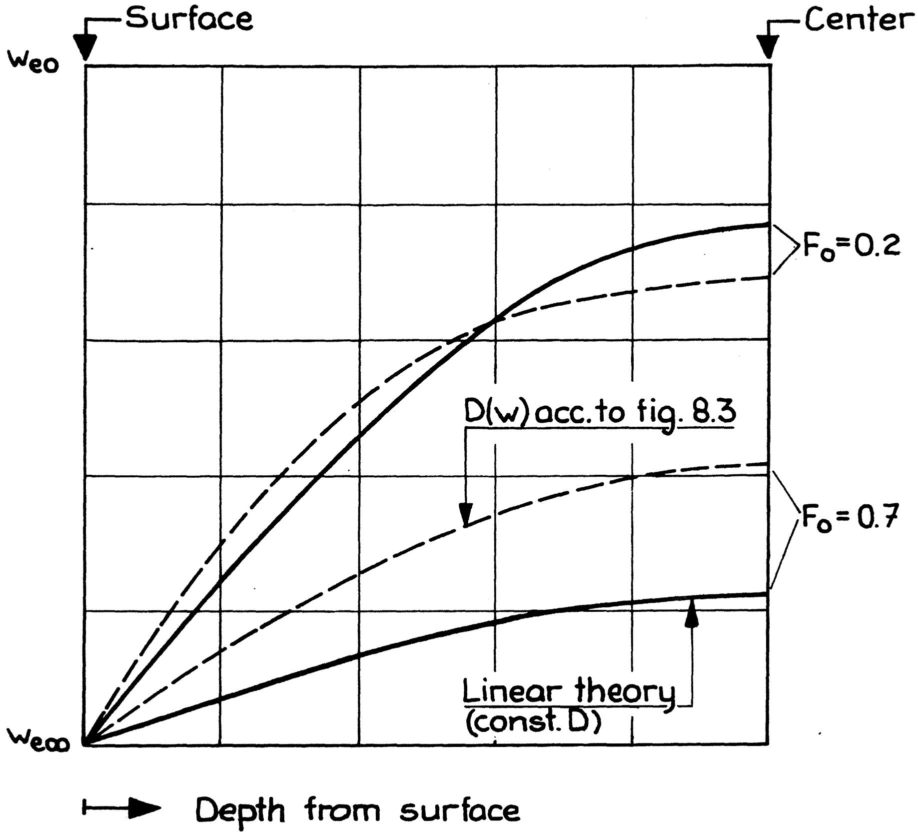


Fig. 8.5 Moisture distribution during drying of a slab with linear theory, Pihlajavaara (1963), compared to computerized model.

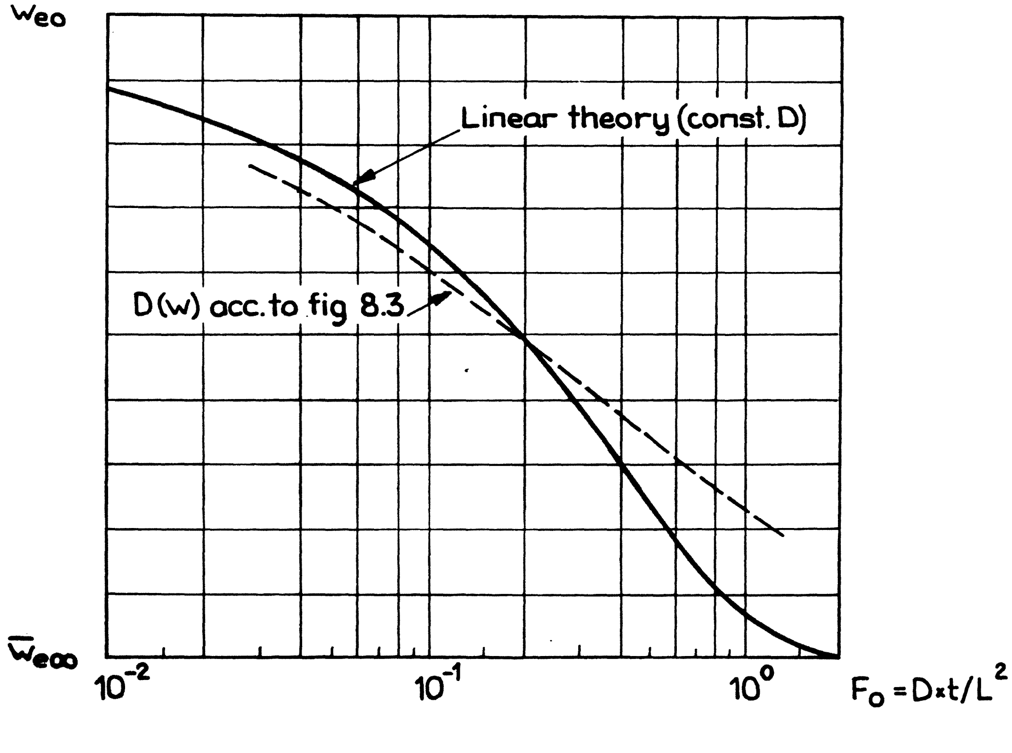


Fig. 8.6 Average moisture contents during drying of a slab, cf. Fig. 8.5.

As a comparison an example of a typical solution, with the model described above, is also shown in Figs. 8.5 and 8.6. The moisture dependence of the diffusivity is the one shown in Fig. 8.3 and the two solutions are adopted to each other so that they have the same average moisture content half-way through the drying, in linear theory when $F_o = 0.2$. With an equal average moisture content at this time, the moisture is distributed in different ways, the linear theory having a larger amount of moisture in the center of the slab. On other occasions, e.g. when $F_o = 0.7$ in linear theory, the average moisture contents differ very much, about factor 2, and a 3-4 times as long drying time is required to reach the same degree of drying. The linear theory is obviously only applicable during a short interval close to where the solution has been adapted and using the linear theory to extrapolate the drying of concrete for example causes considerable errors.

8.5 Summary

The method of solving the equation expressing the "law of mass conservation", taking hydration into consideration, is described. By expressing all material properties in terms of moisture content a very simple and rapid computerized model is obtained. The way of doing this description is shown and exampled and the assumptions made are pointed out. Finally the obtained solutions are compared in principle with the linear solutions. The linear theory is found to cause very great errors if an obtained linear solution is used for extrapolation.

9 DRYING OF CONCRETE

9.1 Introduction

To be able to carry out an estimation of the drying process of concrete of a certain composition under different conditions, is of very great interest in order to avoid moisture damages, but also when describing and evaluating many other moisture dependent phenomena in concrete. This significance was previously discussed to some extent in Chapter 7.

Since the drying of concrete proceeds very slowly, excess moisture is present in a concrete structure for a very long period of time, usually several years. Consequently a sufficient part of the excess moisture must be dried out before materials sensitive to moisture are combined with the concrete. The remaining amount of excess moisture must be able to remain in the structure for perhaps a couple of years without causing any damage. The problem that arises is therefore that of being able to state the drying-times required under different conditions to dry out a sufficient part of the excess moisture. In accomplishing this profound knowledge is required regarding those moisture properties of concrete and combined materials described in the previous chapter.

The drying of the concrete is firstly described qualitatively and then the calculation model is quantitatively compared with some drying experiments. The model is finally used to describe the effect of some essential factors.

9.2 Qualitative description

After mixing and casting the concrete contains large amounts of mixing-water, a part of which gradually becomes chemically bound to the cement. During this hydration a contraction is obtained due to the fact that the reaction products have a smaller volume than the original constituents. Consequently water in the largest pores is gradually replaced by air sucked in from the surface.

Usually the hydration is supposed to decrease the amount of evaporable water in such a way that the remaining part is evenly distributed in the structure. Whether this assumption is true or not is not known at present, but it is reasonable to presume that the amount of air sucked in is greater close to the surface and consequently the moisture content is less. The state of the moisture, i.e. the pore water pressure, should however be approximately equal throughout the entire structure as less pressure in the center of the concrete very soon causes the water to be imbibed and thereby the pressure is equalized.

The drying starts when the climate around the concrete allows evaporation to take place, i.e. at equal temperatures when the relative humidity is less than 100%. The drying proceeds as a combination of a moisture flow inside the material up to the surface and an evaporation at the surface. According to Krisher (1963) the rate of drying of most porous materials is a function of the moisture content as shown in Fig. 9.1.

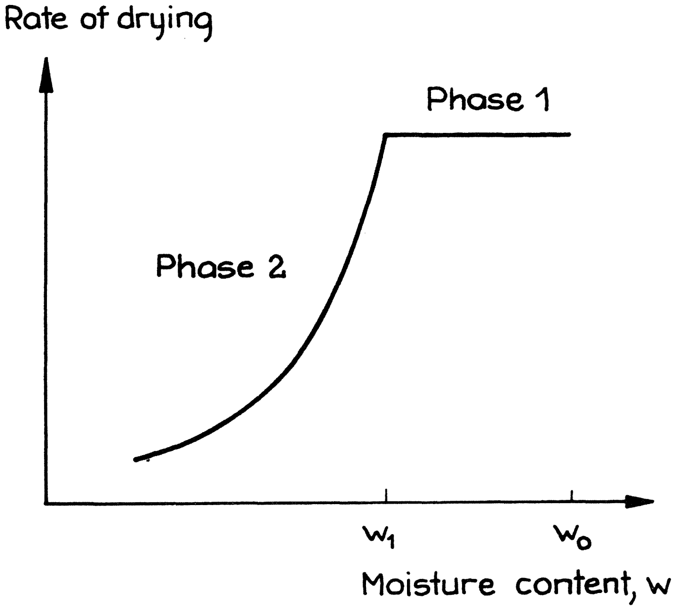


Fig. 9.1 Drying rate, in principle, of a porous material according to Krischer (1963).

At the beginning, phase 1, the drying is limited by the evaporation from the surface and the rate of drying is almost constant. This continues as long as the capacity of the moisture flow is sufficient to keep the surface wet so as to continue the constant evaporation.

When the moisture content has decreased to w_1 according to Fig. 9.1, the capacity of the moisture flow becomes too small and the rate of drying decreases, phase 2. In the future the moisture flow up to the surface will have a deciding effect on the rate of drying. At the surface equilibrium with the surrounding climate is soon obtained and the moisture content at the surface will shortly be close to the equilibrium moisture content corresponding to the ambient air. As was seen in Chapter 6 the phase 1 is usually not present for concrete due to the very slow moisture flow and very soon there will be an equilibrium at the surface.

The drying proceeds as long as there is a gradient in the material driving the moisture flow. After a very long period of time the equilibrium moisture content is reached inside the material and a moisture flow no longer takes place; the drying is finished. In practice drying is in many cases interrupted much earlier, e.g. by the application of a tight surface layer through which the evaporation from the surface is drastically decreased. This means that the moisture content close to the surface increases as the moisture flow still continues towards the surface. This proceeds until a new equilibrium is reached between the very slow evaporation through the surface layer and the moisture flow up to the surface. With a very tight surface layer this means that the moisture load on the surface layer is approximately given by the relative humidity corresponding to the average of the remaining moisture content, please see below.

9.3 Experiments - comparison with model

Some full scale drying experiments have been carried out in order to check the calculation model and determined material properties. The comparisons have been made in terms of relative humidity instead of moisture contents mainly for two reasons. The measurement of the distribution of the moisture content in concrete is very inaccurate, cf. Chapter 10, and a reliable non-destructive method for concrete does not exist. The possibility of using weight changes of small specimens has proved to produce misleading results, due to simultaneous hydration and carbonation, which affect the weight changes considerably.

In an experimental series investigating the influence of specimen thickness the effect of hydration and carbonation can clearly be seen. The experiments have been carried out with cylindrical specimens sealed with a moisture barrier and aluminium foil and allowed to dry from both ends. The type of concrete used and the results for different thickness and curing times are shown in Fig. 9.2.

According to linear theory the size has a quadratic influence, expressed by the Fourier number. This means that in terms of t/L^2, or $\sqrt{t}/L$, the drying is independent of size. As is clearly seen in Fig. 9.2 this is not valid for concrete. Similar results have been obtained by Campbell-Allen (1973).

Simultaneous hydration functions in two ways, partly by decreasing the available amount of excess moisture and partly by decreasing the rate of the moisture flow. Both of these factors should cause a quicker drying of smaller specimens as the drying takes place at lower degrees of hydration. This is not valid for the experiments presented in Fig. 9.2 either. On the contrary there is a tendency to an increasing rate of drying with an increase in the specimen thickness, the rate of drying is naturally expressed in terms of t/L^2. The effect is more clearly seen in Fig. 9.3 where the drying times required to reach a certain weight loss are seen as a function of size.

In principle the effect of hydration was estimated with the calculation model. The model was adapted to the result of the thickest specimens in the drying experiments, which was obtained with a diffusivity as in $w_0/C = 0.6$, cf. Fig. 8.3, with $D_1 = 10^{-10}$ m^2/s and $D/D_0 = 0.5$. The results of the calculations as a function of the specimen thickness are shown as a comparison in Fig. 9.3. The correct effect of hydration is obviously perceptible in the experiments but only for thicknesses L greater than 5 cm. For the smaller specimens carbonation ruins the possibility of comparing measurements of weight changes with the calculations. To do this moisture distributions and relative humidities are obviously more suitable.

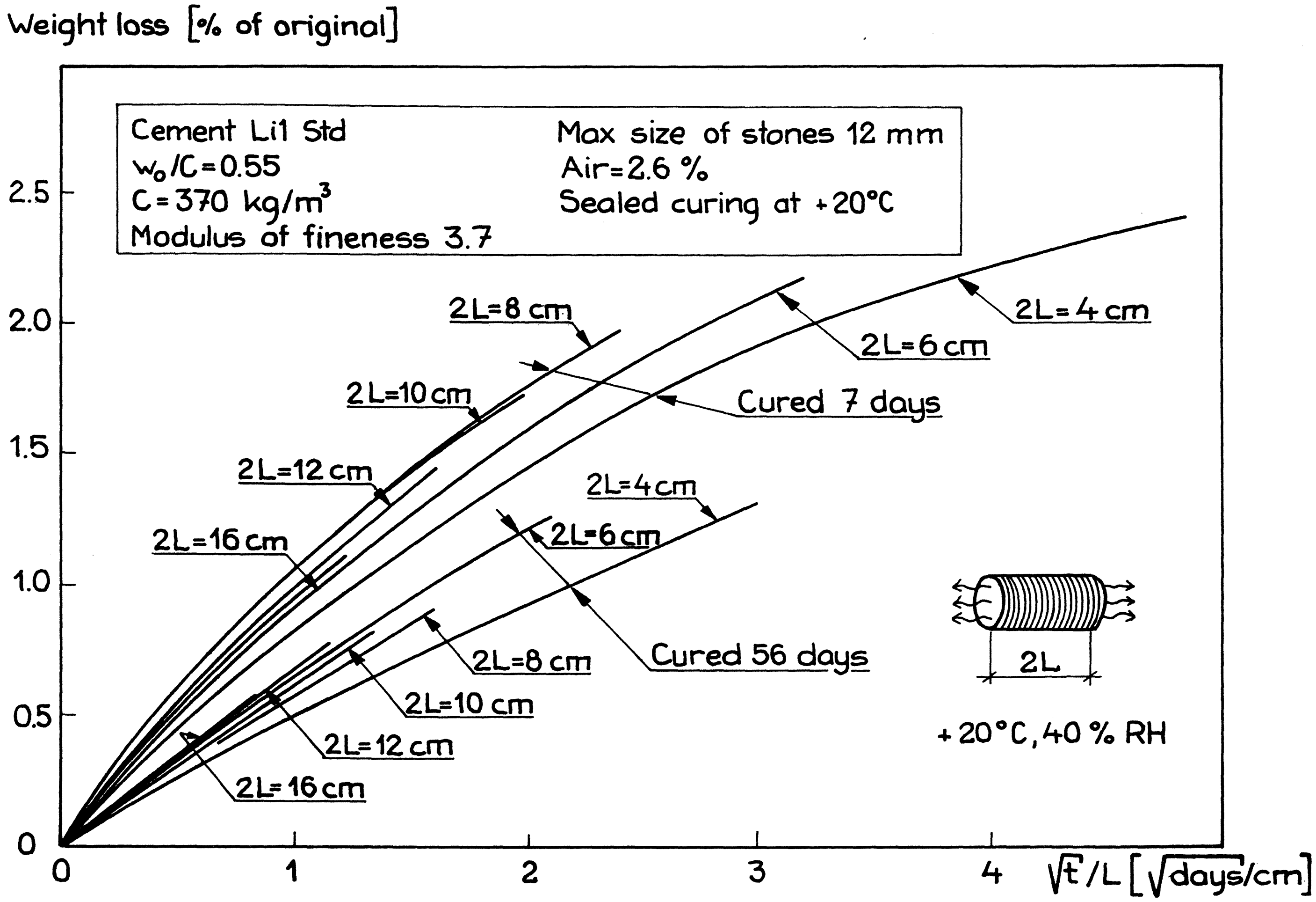


Fig. 9.2 Weight changes during drying of hydrating and carbonating concrete. Different specimen thicknesses and curing times. Each curve represents the mean value of three specimens.

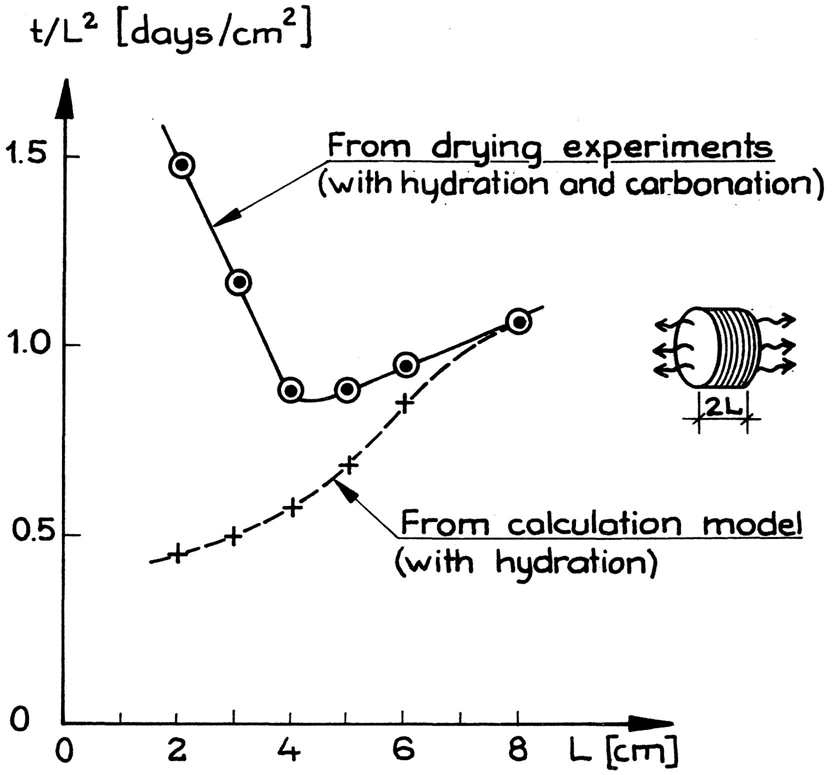


Fig. 9.3 Required drying times to obtain a weight loss of 1% of original. Concrete with $w_0/C = 0.55$ cured 7 days.

9.3.1 Moisture distribution

One experimental series has been carried out, where the distribution of the pore humidity was measured in specimens with a thickness of 160 mm. Three water-cement ratios were used, 0.4, 0.6 and 0.8, and the aggregate consisted of 50% of the aggregate used for the "standard cement mortar", cf. 5.2.2, and 50% of aggregate 7, i.e. macadam 4-8 mm. The specimens were sealed with a moisture barrier and aluminium foil on four sides in order to obtain one-dimensional moisture flow. For the measurement of RH, holes, perpendicular to the moisture flow, were used, as shown in Fig. 9.4.

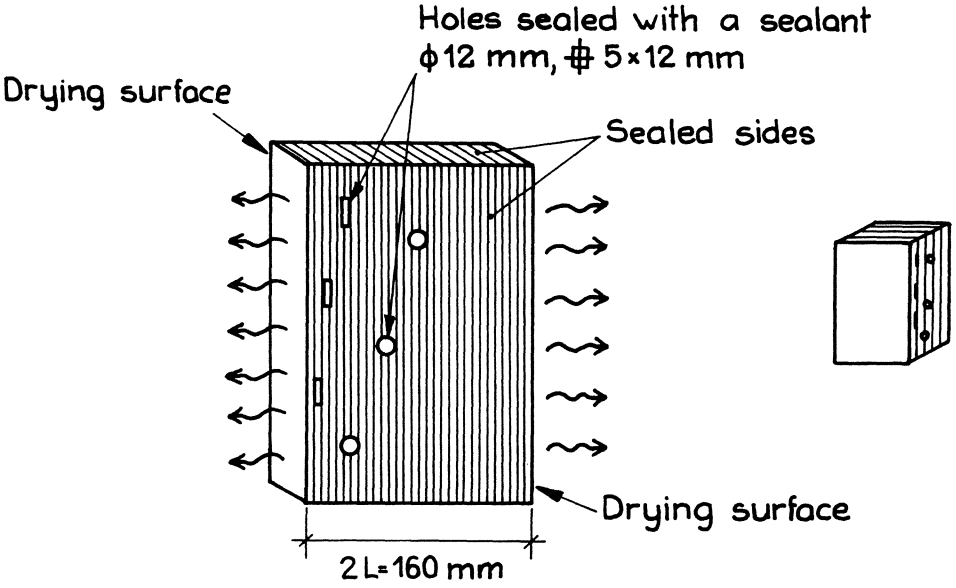


Fig. 9.4 A specimen for measuring the distribution of RH during drying.

The moisture distribution was determined from time to time by placing hygrosensors, cf. Chapter 10, in the holes for at least four hours to come close to the equilibrium inside the hole. The results are shown in Table XXIV and Fig. 9.5.

From the results for $w_0/C = 0.6$ it can be seen that a shorter curing time results in a somewhat drier concrete after a drying-time of 260 days. A water-cement ratio of 0.4 produces very rapid drying at the start, due to hydration, after which the drying becomes very slow. After 260 days of drying the concrete with $w_0/C = 0.4$ is however somewhat drier than the one with $w_0/C=0.6$. The drying of the concrete with $w_0/C = 0.8$ is very slow at first but during longer drying times this concrete becomes considerably drier than concrete with a lower w_0/C.

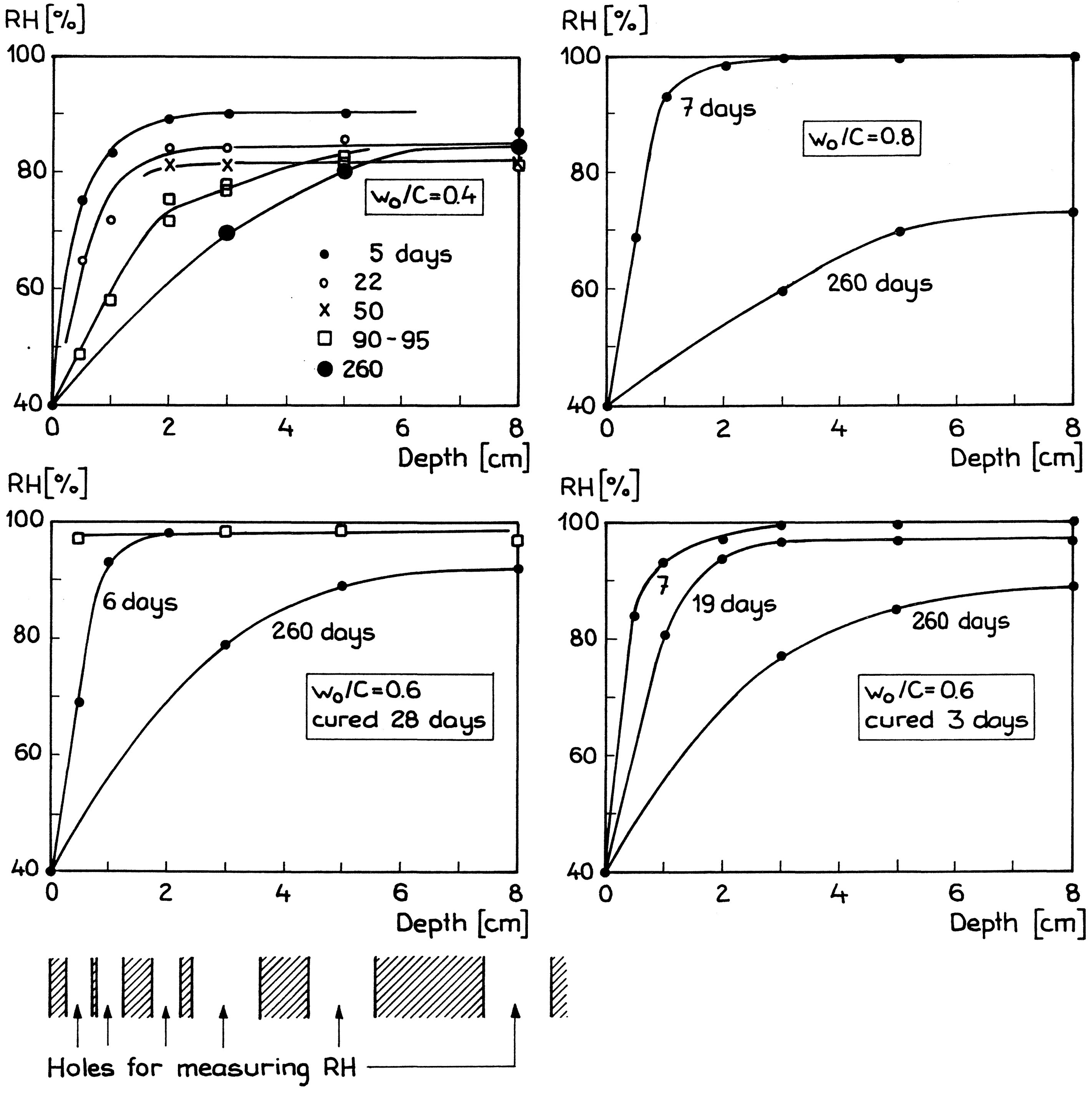


Fig. 9.5 Measured distributions of pore humidities in concrete specimens, with a thickness of 160 mm, drying from two sides in +20 ^{0}C and 40% RH. Different water-cement ratios and curing times under sealed conditions, cf. Table XXIV.

For $w_0/C = 0.6$ most of the required material properties are available, including the rate of hydration, and therefore a comparison between the measurements and calculations with the computerized model is possible. In the calculations the diffusivity $D^o(w)$ from Fig. 8.3 is used with the uncertain diffusivity D_1 at high moisture contents as one parameter. These diffusivities are valid for the cement mortar used in the flow measurements, cf. 5.3.1, and the "translation" to concrete is done with parameter number two, D/D^o.

The comparison is carried out by adopting the calculated moisture distribution on one occasion, to the measured distribution, by varying the two parameters. The distribution after 260 days of drying the concrete cured for 28 days before the start of drying has been chosen for the adoption. In Fig. 9.6 the results of different attempts are shown, and as can be seen there is good agreement with $D_1 = 10 \cdot 10^{-11}$ m^2/s and $D/D^o = 1.6$. The latter value agrees well with the results from the drying experiments analysed in 5.3.2.3, where an estimation would give $D/D^o = 1.4$-1.7.

With the two parameters, estimated in this way, further calculations have been made for this concrete with two curing times of 3 and 28 days, used in the experiments. The same material properties are used in both cases and the difference in the curing time will affect the results by the difference in the rate of hydration and the diffusivity at low ages. The results of the comparison between measured and calculated moisture distributions are shown in Fig. 9.6. and Fig. 9.7. The agreement at the longer drying time is almost perfect and also during the shorter drying times the agreement is fairly good. Some of the discrepances close to the surface may be an effect of the bad reliability of the hygrosensor used in these holes. The result of this comparison indicates however that the calculation model and the determined material properties are very useful.

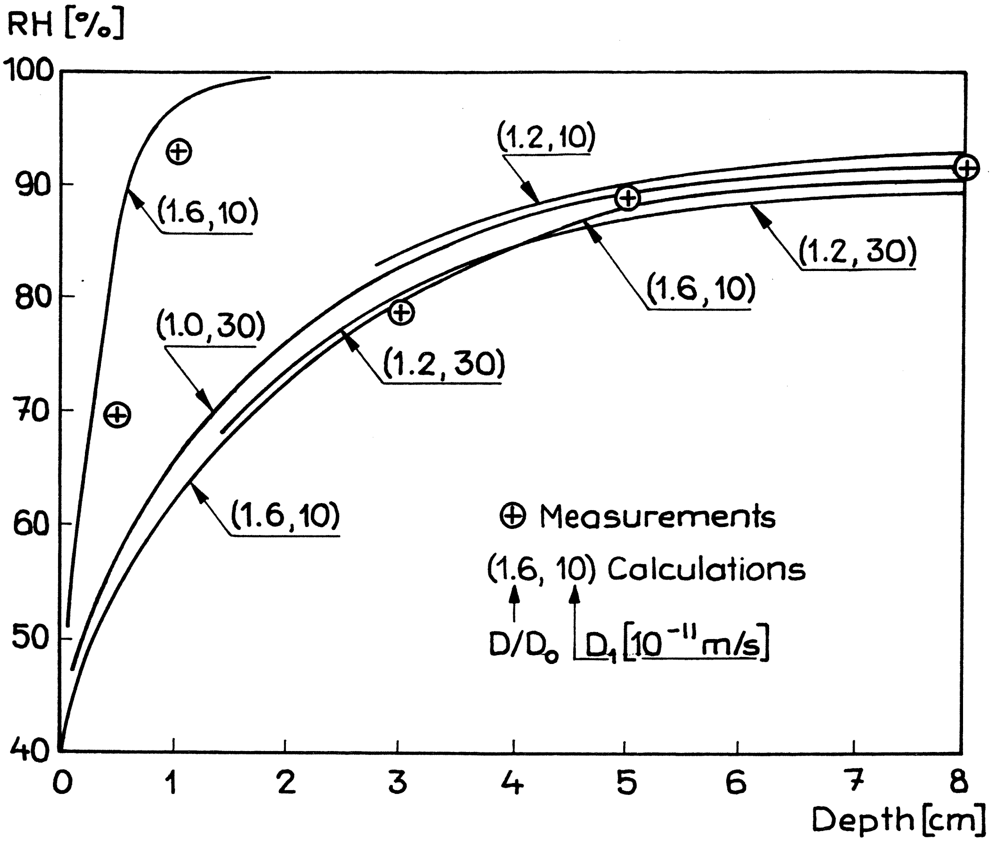


Fig. 9.6 Measured and calculated moisture distribution in a concrete slab with a thickness of 160 mm drying from two sides in +20 °C and 40% RH. Water-cement ratio 0.6, cured 28 days under sealed conditions.

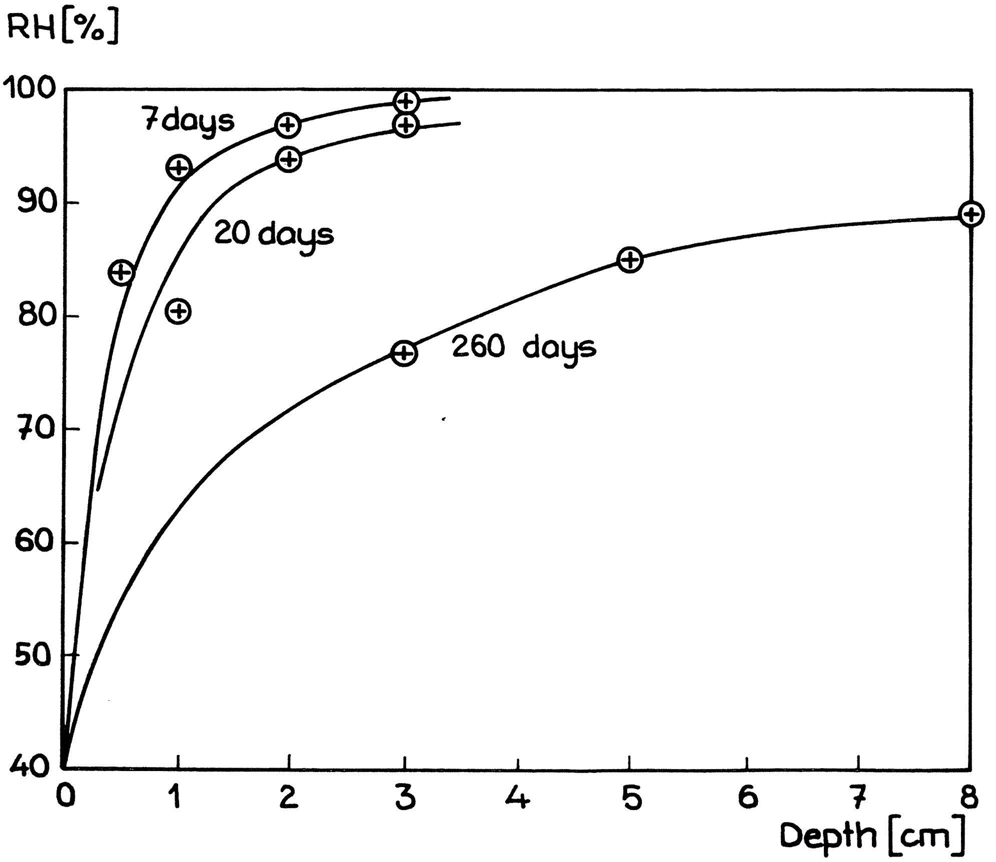


Fig. 9.7 Comparison between measured and calculated moisture distributions with material properties obtained from Fig. 9.6. $w_0/C=0.6$, sealed cured 3 days.

9.3.2 Moisture loads at surface layers

To be able to estimate required drying times before a surface layer is applied is of very great interest for applications in practice. An experimental series with a normal slab thicknesses has therefore been carried out to imitate what happens in practice. Concrete quality, curing condition and drying times have been varied and the moisture load, in terms of RH, has been measured after a tight surface layer has been applied and the remaining moisture has been redistributed. The appearence of the used specimens is shown in Fig. 9.8 together with the moisture distribution in principle during drying and after redistribution.

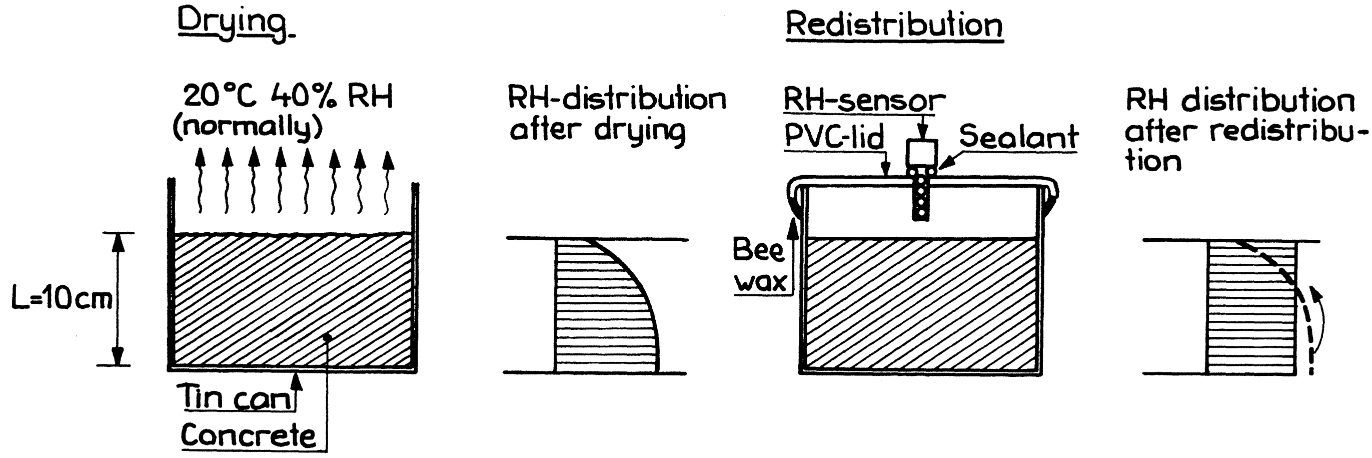


Fig. 9.8 Specimen during drying and redistribution. Moisture distributions in principle are shown.

After the intended drying time, the specimens were sealed with a PVC lid in order to imitate the application of a tight surface layer. After one to two months, when the redistribution was almost terminated, the relative humidity was measured in the air-volume between the concrete surface and the lid. This RH corresponds to the moisture load arising from a floor adhesive under a PVC-carpet for example. The result of this experimental series is presented in Table XXV, with the concrete qualities and drying times graded from the highest to the lowest moisture loads obtained.

The concrete quality K150, with the lowest cement content, dries very slowly. But after 8 weeks of drying the remaining moisture corresponds to a RH of 94%. To achieve a dryness corresponding to approximately 90% RH, the used critical moisture conditions for floor adhesives, K150 require a drying time twice as long as for K250, and this in turn needs almost twice the drying time required for K400, with the highest cement content. With a substantial air-entrainment the required drying time can be reduced to half that time, partly due to the simultaneous increased cement content.

For concrete quality K250 calculations with the computer model have been done for comparison with the experiments in order to estimate the parameters valid for this rather normal concrete quality. A reasonable agreement was obtained with $D_1 = 20 \cdot 10^{-11}$ m^2/s and $D/D^0 = 3$ for this concrete with $w_0/C = 0.65$ and maximum size of stones of 12 mm. In Fig. 9.9 the result of such a calculation is shown for a 10 cm thick concrete slab drying from one side only. The concrete is cured under sealed conditions for one month. The moisture load, in RH, has been obtained from the desorption isotherm and the calculated _average moisture content_, as this settles the moisture load after the redistribution. This is not quite true because the sorption hysteresis influences this translation to some extent.

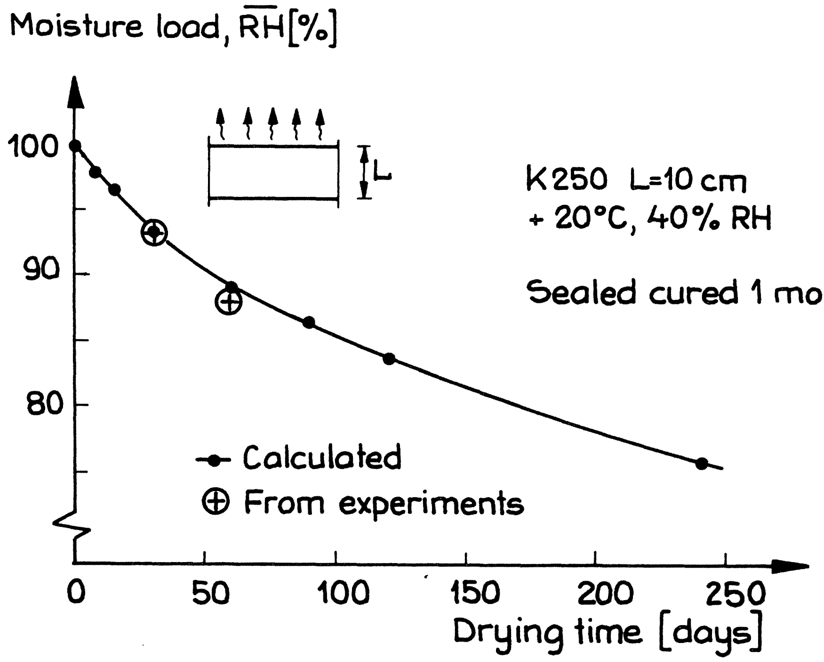


Fig. 9.9 Average moisture content expressed as RH of a 10 cm thick concrete slab; concrete quality K250. Calculated and measured values.

In Fig. 9.9 the measured values from the experiments with this concrete quality are shown. The agreement between calculated and measured moiature loads is rather good. This way of comparing calculations and experiments is however very inaccurate as several uncertain factors affect the results. Hysteresis effects influence the translation from average moisture content to relative humidity and this translation is also difficult because the degree of hydration is not constant at different depths from the surface. The redistribution takes time and may not be completely finished when the measurements are carried out. Finally the uncertainty of the RH-measurement, having an accuracy of ± 2-3% RH, means that the comparison carried out is not precise. The obtained parameters for this normal concrete quality are consequently uncertain to some extent but in spite of this they are useful when estimating the effect of different factors using calculations with the model.

9.4 Calculations with the model

The effect of various factors can easily be estimated by calculations with the computerized model and taking hydration into consideration. This is carcied out in order to study the effect of slab thickness, drying climate and a combined heat insulation.

The calculations are made for the normal concrete quality K250, with $w_0/C =$ $= 0.65$, also dealt with in 9.3.2. The diffusivity parameters above were found to be approximately $D_1 = 20 \cdot 10^{-11}$ m^2/s and $D/D^0 = 3$. The moisture distributions in a 10 cm thick slab, drying from one side in +20 °C and 40% RH, are shown in Fig. 9.10 as obtained from a calculation with these parameters. In the following calculations only the average moisture contents, or the corresponding relative humidities, are shown. The distributions are however similar in principle to those in Fig. 9.10, and they can serve as a guide.

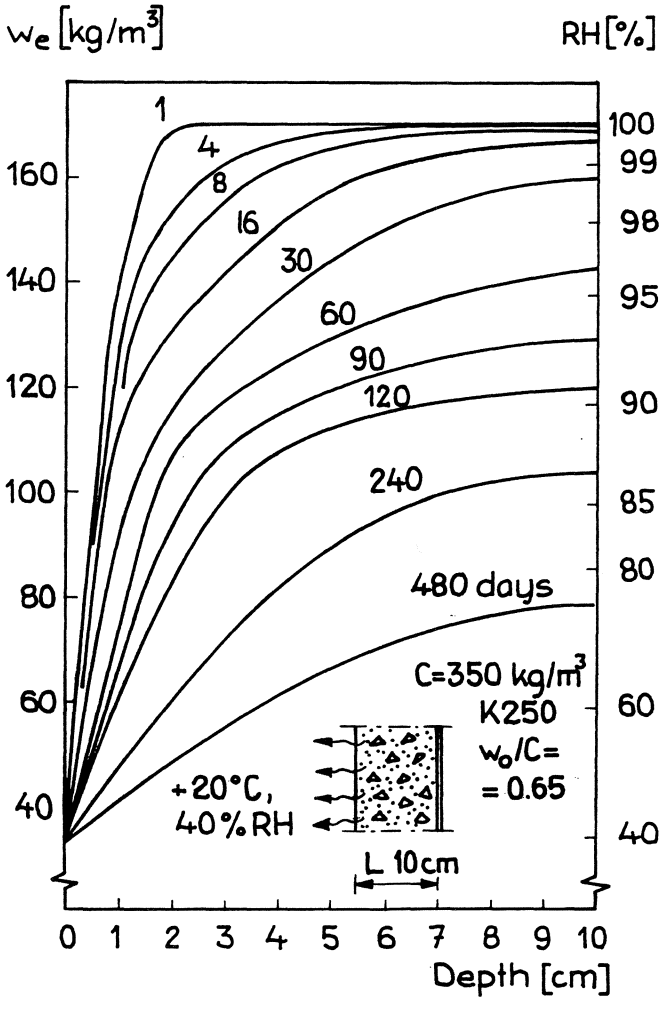


Fig. 9.10 Calculated moisture distributions, in terms of moisture content and relative humidity, in a "normal" concrete quality. Cured one month under sealed conditions before drying begins.

9.4.1 Effect of slab thickness

From the preceding sections it is clear that the drying courses of different slab thicknesses deviate from the usual diffusion theory, not taking hydration and the age dependent diffusivity into consideration. The frequently used rule, that a doubling of the slab-thickness means four times the drying time, is therefore not valid for hardening concrete. According to this rule the drying time required to obtain a certain dryness, divided by the slabthickness squared, t/L^2, is constant. This is consequently not quite true where concrete is concerned.

In the case of the calculation model the drying of concrete slabs of different thicknesses has been calculated. The results for concrete cured one month before drying are shown in Fig. 9.11. If the simple diffusion theory had been valid, the drying curves would have coincided with each other as the drying times were divided by the square of the slab thicknesses.

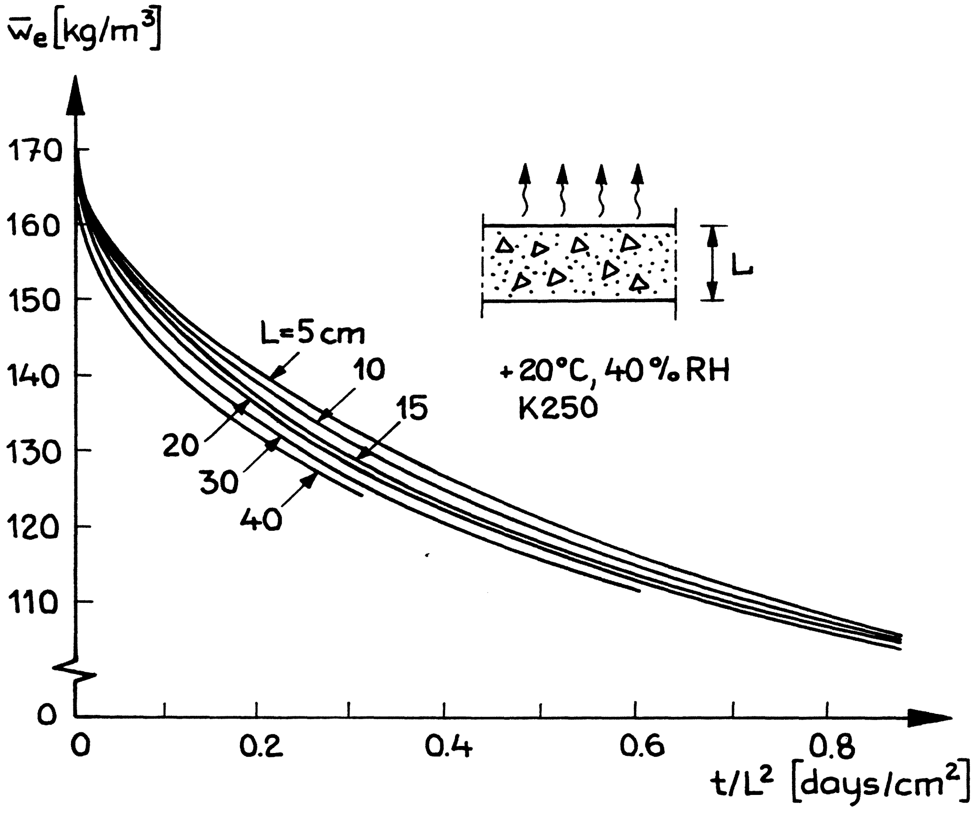


Fig. 9.11 Effect of the slab thickness on the drying of concrete, sealed cured for one month.

Similar calculations have also been carried out for concrete cured only for one week before drying starts. The results of both calculations are shown in Fig. 9.12 in terms of required drying times to obtain an average moisture content corresponding to 90% RH.

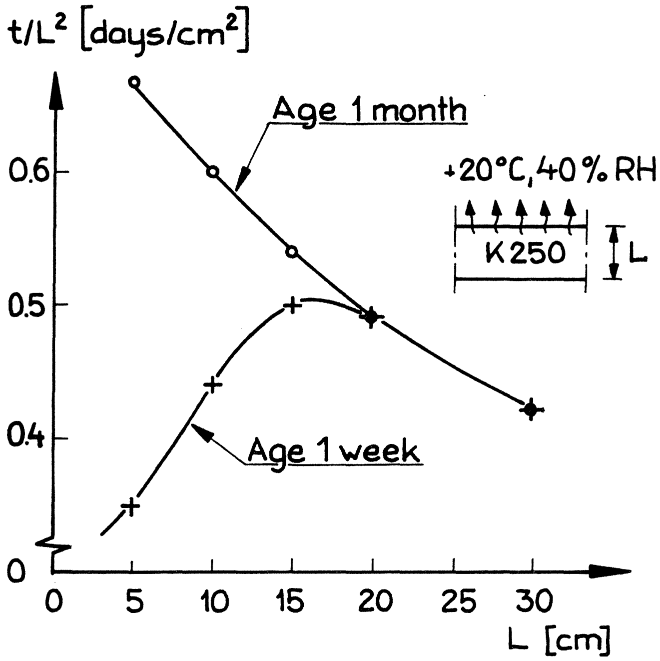


Fig. 9.12 Effect of the slab thickness on the required drying time to reach an average moisture content corresponding to 90% RH. Different ages at start of drying.

From the Figure it can be seen that a concrete, older than one month at the start of drying, dries more rapidly with large slab thicknesses, proportionately, due to the self-dissiccation that proceeded to a greater extent in the thicker slab. For a younger concrete, with slab thicknesses less than 15 cm, the greater moisture flow capacity at the beginning of the drying has a major effect and the drying is very rapid. With slab thicknesses greater than 15 cm the age at the start of drying is of less significance.

When slab thickness L is stated above, this refers to the thickness of a slab drying from only one side, the other side being sealed. In the case of two-sided drying of e.g. a wall, L corresponds to one half of the slab thickness. With other concrete structures than slabs, an estimation of the drying can be made by using a "thickness" of

$$L = \frac{V}{A} = \frac{\text{volume of the drying structure}}{\text{area of the surface of evaporation}}$$

For a cylinder, e.g. a column, one obtains L = r/2, with r = the radius of the cylinder. For a more accurate calculation the one-dimensional solution of the "law of mass conservation" cannot be used for other structures than slabs. Eq. (1:1) must be rewritten in other coordinates and new solutions must be obtained.

9.4.2 Effect of drying climate

The drying dealt with in the preceding sections usually took place in a climate of +20 °C and 40% RH. A climate with another temperature and another relative humidity naturally affects the drying. The temperature affect the diffusivity and thereby the drying time. The relative humidity affects the equilibrium moisture content at the surface and consequently the moisture gradient close to the surface resulting in a somewhat altered moisture flow up to the surface.

With the computer model calculations have been carried out on a "normal" concrete quality, K250, for a 10 cm thick concrete slab drying from one side at a temperature of +20 °C and varying relative humidities. The results of these calculations for humidities between 20 and 90% RH are shown in Fig. 9.13. Among other things it can be seen that drying time required to reach an average moisture content corresponding to 90% RH, about 115 kg/m^3, is about 60 days for drying in 20-50% RH while at 80% RH almost 90 days is required; an increase of about 50%.

The desorption isotherm shown in Fig. 9.13 is valid for an age greater than one month, with the upper part of the shaded area valid for an age of about three months, i.e. for a normal case of drying-out of excess moisture.

In Fig. 9.13 an example is also shown of how to use the calculation results for reading the required drying time in order not to exceed a certain moisture load. In the example the maximum moisture load allowed is assumed to be 90% RH and the drying climate is +20 °C and 60% RH. The desorption isotherm at 90% RH gives an average moisture content of about 115 kg/m^3. To reach this average moisture content at drying in 60% RH a drying time of about 70 days is required, as obtained by interpolation between the curves representing drying times of 60 and 90 days, respectively.

If the drying takes place at another temperature some quantities are changed. A different temperature usually causes a change in relative humidity as the water vapour pressure at saturation will change. A change in relative humidity in the ambient air results in a new equilibrium moisture content at the

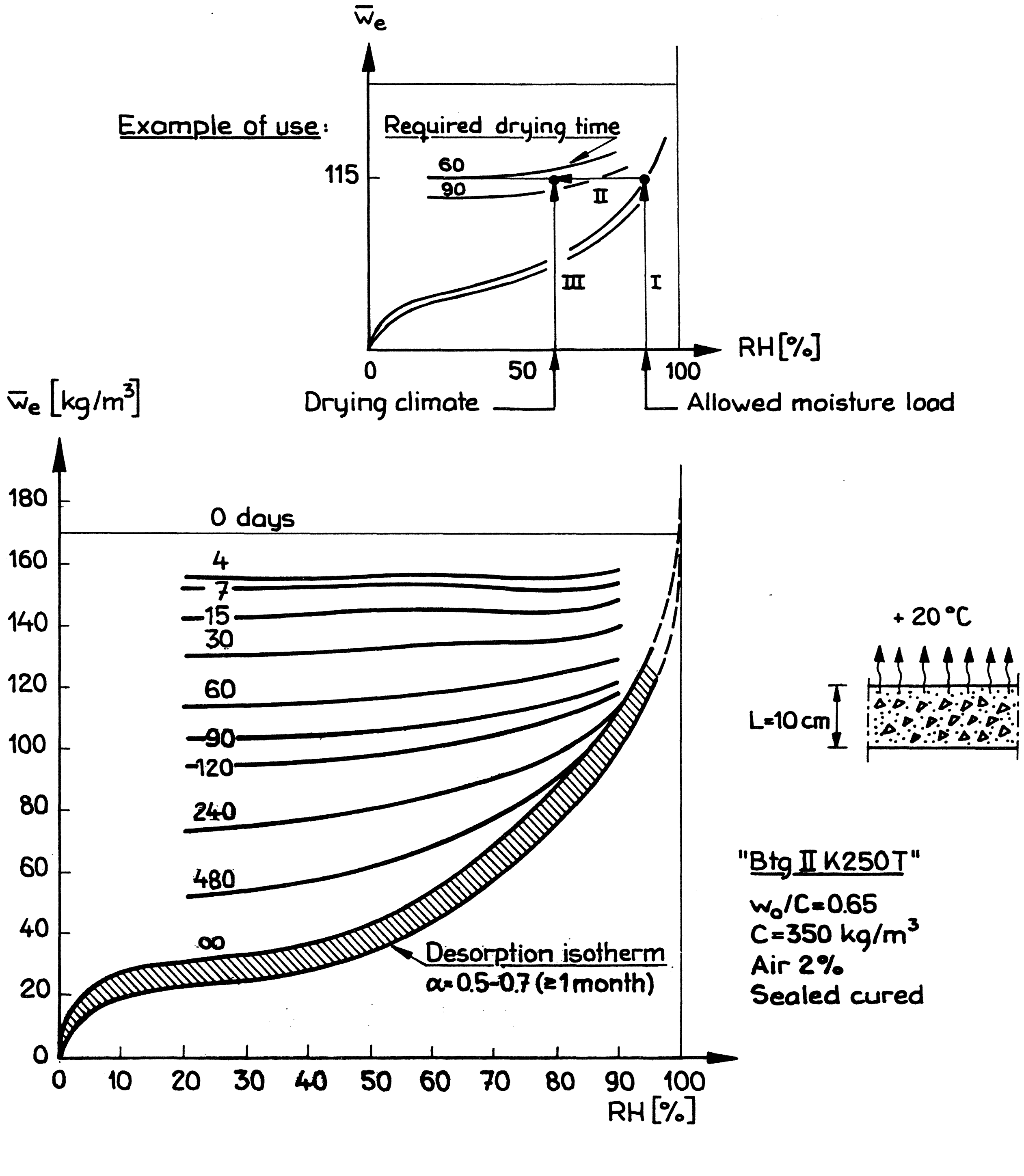


Fig. 9.13 The drying of a normal concrete at different humidities in surrounding air according to calculations.

surface of the structure.

Apart from the change in the moisture content equilibrium, the diffusivity and rate of hydration are increased with an increasing temperature. However for rough estimations Fig. 9.13 is useful at a temperature deviating slightly from +20 °C. In that case the change in rate of hydration is neglected, and causes a drying time on the safe side at an increase in temperature. If, for instance, the temperature in the example above is raised to +30 °C the relative humidity decreases to 33%. The increase in diffusivity can be estimated from Fig. 5.2 at $D_{30}/D_{20} \approx 1.5$, i.e. a 50% faster drying. From Fig. 9.13 a drying time of about 60 days is obtained for +20 °C and 33% RH. At +30 °C the required drying time can be estimated by $60/1.5 \approx 40$ days.

The calculations above are valid for curing under sealed conditions. If the curing takes place with access to water the initial conditions will of course be different, cf. 4.3. A calculation for the concrete composition dealt with above but cured for 28 days in water indicates an increase of only approximately 20% in the drying time required to reach 90% RH for this concrete quality. With higher cement contents the effect of water storage must be assumed to be much greater, cf. 4.3.

9.4.3 Effect of a combined heat insulation

The cases of drying dealt with previously correspond to a concrete slab drying from only one side, i.e. where drying from the other side is prevented, e.g. by using polyethen foil if a concrete slab directly on the ground has an underlying vapour barrier. However concrete slabs are often combined with a heat insulation in structures such as external walls and floors on the ground. A very common structure in Sweden in the latter case is a concrete slab on an underlying heat insulation placed directly on the ground. The heat insulation causes a temperature difference, and consequently a difference in water vapour pressure, between the under-side of the slab and the moist but cold ground. The result of this is the possibility of such a slab drying downwards through the heat insulation, the proportion depending on the permeability of the insulation. In Fig. 9.14 this structure and the way it functions are shown.

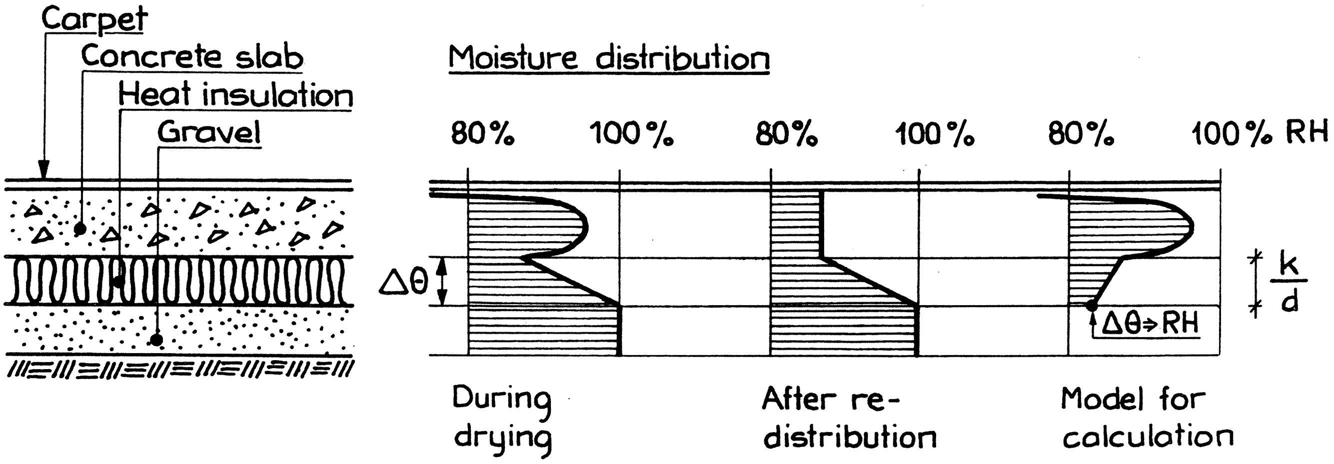


Fig. 9.14 The floor structure and moisture distribution of a concrete slab with an underlying heat insulation directly on the ground.

A illustrative example is the best way to show the effect. Suppose there is a temperature of +20 ^{0}C in the concrete slab and +17 ^{0}C and 100% RH in the ground. At the start of the drying the pore humidity in the concrete slab is close to 100% RH. This means a water vapour pressure of about 2340 Pa, $p_s(+20\ ^{0}C)$. As the vapour pressure in the ground is only about 1940 Pa, $p_s(+17\ ^{0}C)$, a vapour flow towards the ground takes place, i.e. the slab is drying downwards. This will continue until the slab is so dry that its vapour pressure is the same as that in the ground. This will occur when the pore humidity is 1940/2340 ≈ 83% RH. When the excess moisture has been dried out the pore humidity will consequently never exceed 83% RH as long as the temperature difference is greater than 3 ^{0}C. This is the case during most of the year in Sweden with floor structures in small houses due to the rather low average yearly temperature, <+8 ^{0}C, causing a low temperature in the ground all the year round. There will of course be a rise in temperature directly under a floor structure on the ground but rarely higher than that a temperature difference of at least 2 ^{0}C can be maintained over the heat insulation, cf. Adamson (1970).

The drying of a 10 cm thick concrete slab on an underlying heat insulation has been calculated with the model for different water vapour permeabilities of the insulating material, cf. 6.2. The used boundary conditions for the under-side of the concrete slab are shown in principle in Fig. 9.14. The equilibrium moisture content is chosen to correspond to the relative humidity given by the temperature difference as shown in the example above. The effect of the heat insulation on the evaporation from the lower surface, is described by its resistance to the moisture flow, cf. 8.3. The results of such calculations are shown in Fig. 9.15.

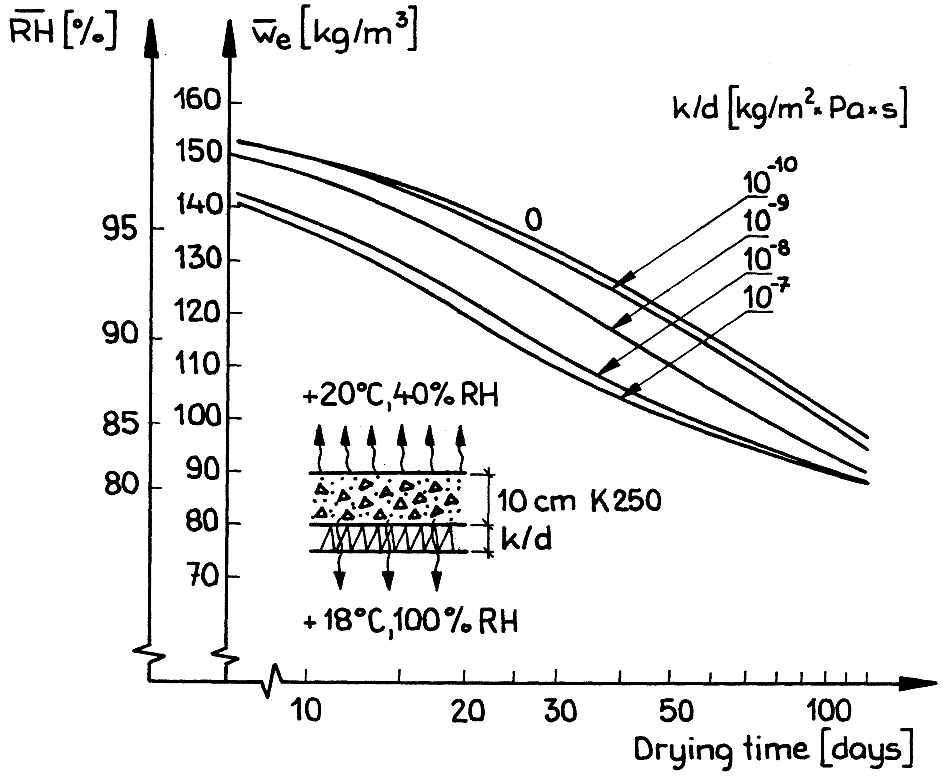


Fig. 9.15 Drying of a concrete slab on an underlying heat insulation with different water vapour permeabilities.

Similar calculations have been made for another temperature condition. From these calculations the effect of an underlying heat insulation on the drying of a concrete slab can be estimated. The drying times required to reach an average moisture content corresponding to 90% RH have been estimated from these calculations. The results for two temperature conditions as functions of the water vapour permeability of the heat insulation are shown in Fig. 9.16.

The heat insulation of expanded polystyrene has such a small vapour permeability that the effect is almost negligible. However the mineral wool reduces the drying time by about 30-40%. The effect of the expanded clay insulation is somewhat smaller. These figures are only approximate and depend among other things on the thickness of the heat insulation, temperature conditions and slab thickness.

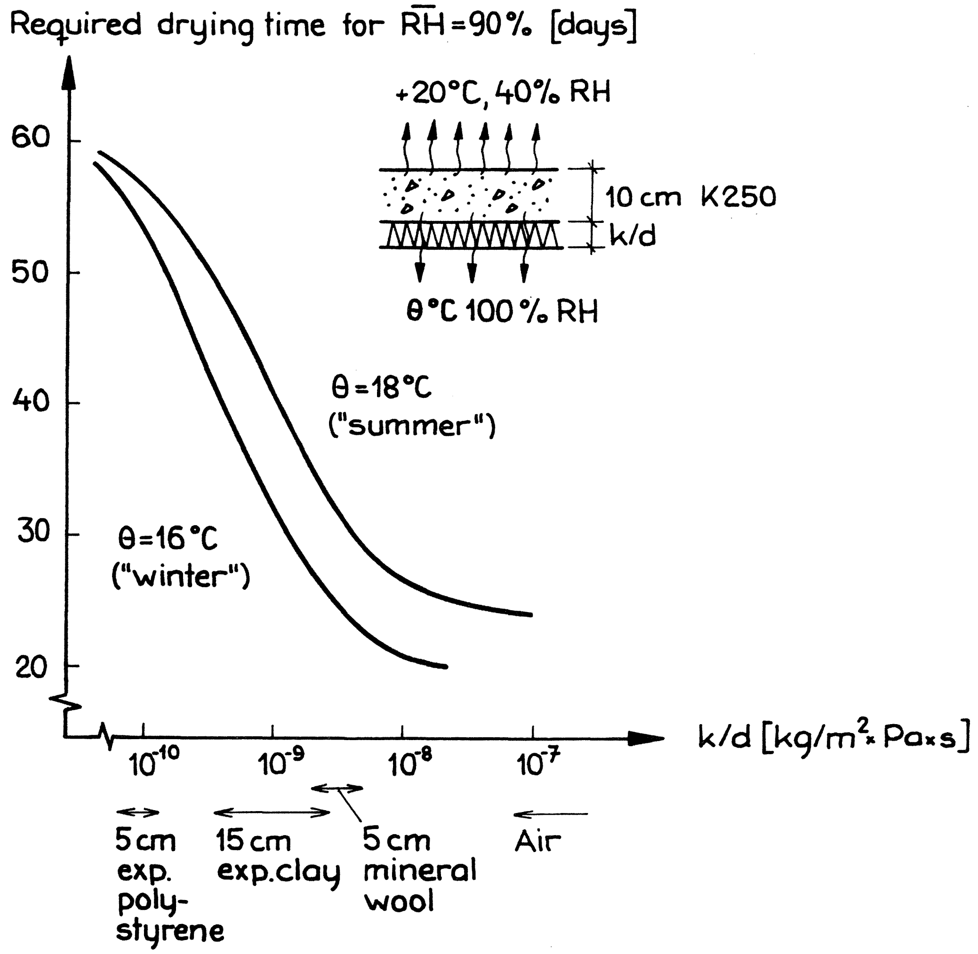


Fig. 9.16 The effect of an underlying heat insulation on the drying time required to reach an average moisture content corresponding to 90% RH.

The drying times mentioned above are required to reach a certain average moisture content corresponding to a maximum allowed moisture load at a surface layer. Before the redistribution is completed the slab will however continue to dry downwards. The average moisture content, when the maximum moisture load at the surface layer occurs, will consequently be somewhat lower than when the surface layer was applied.

9.5 Summary

In the preceding sections the drying of concrete is dealt with in different ways. A qualitative description is given of the conditions during different steps in the drying procedure. Some experiments are then compared to calculations with the computerized model. It is clearly shown that measurements of weight changes during the drying of small specimens are not useful for estimating the drying of concrete structures by extrapolation. If effected by carbonation the results will be completely misleading.

The computerized model and the determined material properties have been shown to give a very good description of the drying of concrete taking hydration into consideration. There is however some uncertainty regarding the description of drying concrete with a composition deviating from those dealt with in Chapter 5, and some experiments should be carried out for the composition in question if great accuracy is requested.

With the calculation model the effect of some essential factors has been estimated. The usual quadratic role for the influence of size is shown to be inaccurate and the actual effect is calculated and shown to be dependent on the curing time before the start of drying. The effect of the drying climate is also calculated and a diagram for rough estimations is given. Finally the effect of a combined heat insulation is calculated and the effect of an insulating material with a rather high water vapour permeability, e.g. mineral wool, is found to be considerable; a reduction in the required drying time can easily reach 40%.

10 MOISTURE MEASUREMENT USING THE HYGROMETRIC METHOD

10.1 Introduction

In some of the experiments in the preceding chapters measurements of the relative humidity in concrete have been carried out. In addition equipment and methods for use in practice have been developed to replace the moisture content measurements which are used at present, cf. Nilsson (1979). Usually it is not the moisture content that is of interest but the state of the moisture. By measuring the moisture content and using the sorption isotherm for just the material in question, the relative humidity could be estimated. A far more accurate way is however to measure the RH directly. The methods are presented below and the precision and accuracy of RH-measurements are analysed.

10.2 Equipment and calibration

Originally RH-sensors manufactured by "Hygrodynamics" were used in laboratory and field measurements. These sensors react to changes in relative humidity by means of a hygroscopic salt changing moisture content. The electric resistance of the salt is measured and by a calibration translated to relative humidity. In Fig. 10.1 one of the gauges containing such a RH-sensor is shown as used in the drying experiments presented in 9.3.1.

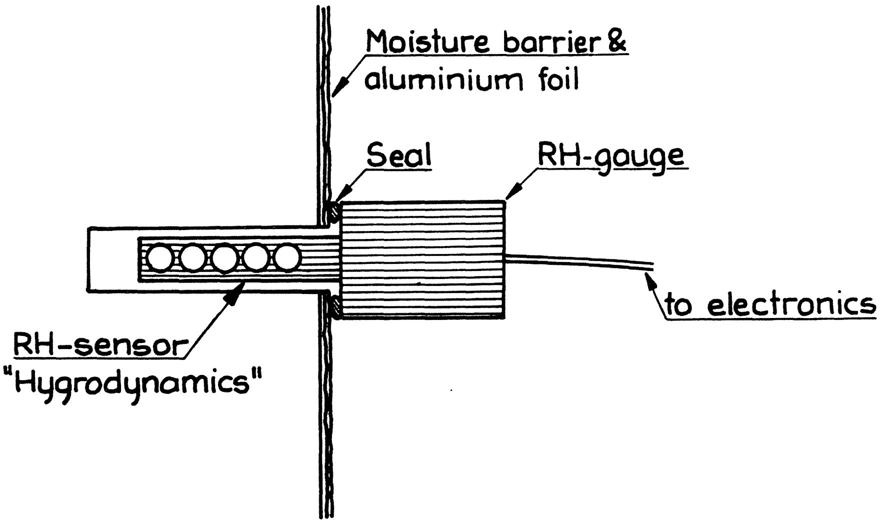


Fig. 10.1 RH-gauge applied in a cast hole in a concrete specimen. The diameter of the probe is 10 mm.

Another RH-gauge has been developed primarily for use in practice. It has proved to be very accurate and reliable and is also used regularly in laboratory measurements. The gauge is shown in Fig. 10.2.

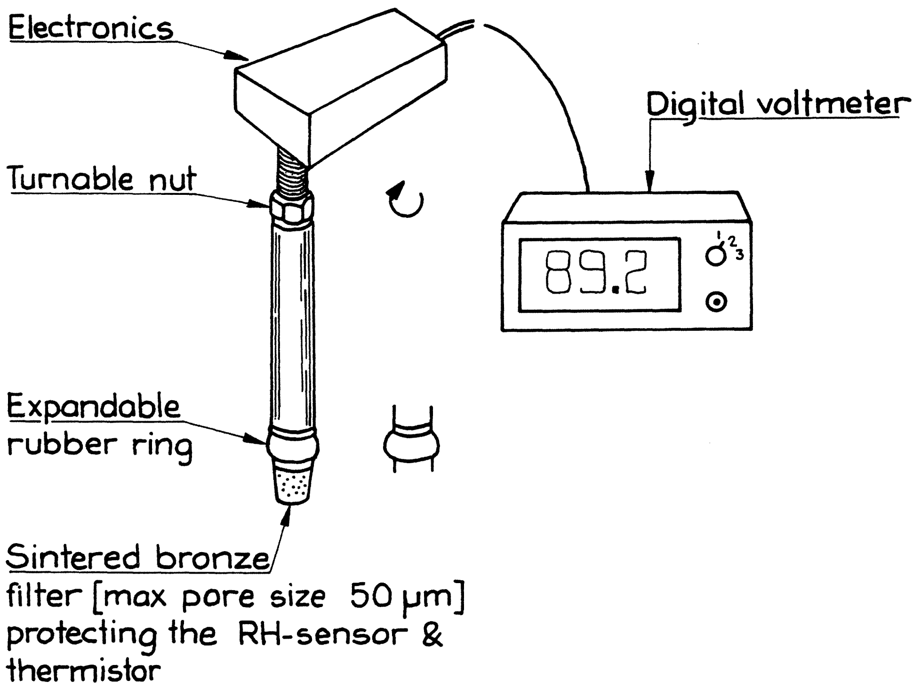


Fig. 10.2 RH-gauge used in laboratory and field measurements. The diameter of the probe is 18 mm.

The RH-sensor, made by "Vaisala OY" in Finland, consists of a capacitive transducer made from a thin PVC-film whose electric capacitance changes with the relative humidity in the ambient air. The sensor and a thermistor for temperature measurement are protected by a sintered bronze filter with a small pore size. The RH-sensor and thermistor are connected via the electronics at the top of the gauge to a voltmeter.

The RH-gauge has an expandable rubber ring close to the sensor. This is expanded to seal against, for instance, a test tube containing a sample by turning a nut at the top of the probe. The air volume thereby enclosed is very small.

The readings have to be converted into RH by a calibration curve; one for each gauge. Originally saturated salt solutions were used to obtain the calibration curves but later the calibrations are made in the precision moisture chamber described in 4.2.2. The effect of the temperature is determined in the same way. The accuracy of the calibration is in the order of ± 2-3% RH.

10.3 Principal method of measurement

The method of measuring RH of a sample is shown in principle in Fig. 10.3. A RH-gauge is placed into a sealed test tube together with the sample, and the relative humidity can be read when equilibrium conditions have been established.

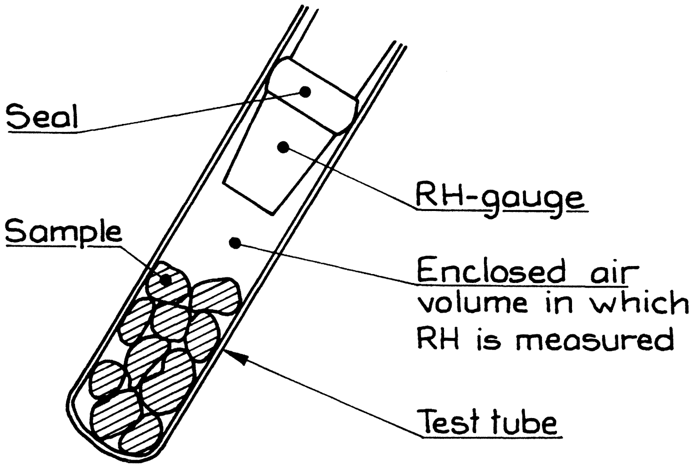


Fig. 10.3 Method of measuring the relative humidity of a sample.

To obtain equilibrium conditions a small amount of moisture leaves the sample to humidify the enclosed air and the RH-sensor. This creates an error in the measured relative humidity depending mainly on the ratio of the volume of enclosed air to the volume of the sample and the moisture capacity of the RH-sensor.

The amount of water leaving a concrete sample with a volume V_c and relative humidity ϕ_c, when a RH of ϕ is measured, can be expressed as

$$(\phi_c - \phi) \frac{\partial w_{e\infty}}{\partial \phi} V_c \tag{10:1}$$

where $\partial w_{e\infty}/\partial\phi$ is the moisture capacity of the concrete. The amount of water required to humidify the sensor and the air volume V_a, from RH = ϕ_o (~indoor RH) to RH = ϕ (measured) is

$$(\phi - \phi_o)\ v_s\ V_a + W_g\ (\phi, \phi_o) \tag{10:2}$$

where v_s is the vapour content of air at saturation for the temperature in question and W_g is the moisture capacity of the RH-sensor, which should be taken into account or be so small that it is negligible.

At equilibrium expression (10:1) equals (10:2) and the created error can be calculated from this equality. The most simple way to do this is to deal with the effect of the air and the sensor individually.

The effect of the air volume is obtained if W_g equals zero. The <u>error</u>, due to moisture leaving the sample to humidify the enclosed air volume, is consequently

$$\Delta\phi = \phi_c - \phi = \frac{\phi_c - \phi_o}{1 - \alpha\frac{V_c}{V_a}} \tag{10:3}$$

with $\alpha = \frac{1}{v_s} \frac{\partial w_{e\infty}}{\partial \phi}$

For a normal concrete $\partial w_{e\infty}/\partial\phi$ ~200 kg/m^3 if $0.6 < \phi < 0.9$. At +20 ^oC v_s = $17 \cdot 10^{-3}$ kg/m^3 which means that α is greater than 10^4. With the volume of the test tube as large as 100 times the volume of the sample, the error will be less then 0.5% RH. With the RH-gauge shown above, the volume of the enclosed air is not much greater than the volume of the sample, and the error due to the air absorbing some moisture is quite negligible.

The effect of the moisture capacity of the RH-gauge is obtained in the same way. The error becomes

$$\Delta\phi = \phi_c - \phi = \frac{W_g\ (\phi,\ \phi_o)}{\frac{\partial w_{e\infty}}{\partial \phi}\ V_c} \tag{10:4}$$

The moisture capacity of the RH-gauge used has to be known in order to be able to estimate the error. The maximum moisture capacities of the two RH-gauges have been determined by measuring the weight change when conditioned for one day in 97% RH (saturated K_2SO_4-solution) after having been in equilibrium with the laboratory air. The results were:

RH-gauge	Moisture capacity W_g (0.97, 0.40) (g)
Vaisala RH-sensor	< 0.0005
Bronze filter	~0.0040
Hygrodynamics H3 RH-sensor	~0.0150

The moisture capacity of the sensor of a PVC-film is not measurable with available balance. For the RH-gauge containing this sensor it is the moisture capacity of the sintered bronze filter instead that is of significance. Its moisture capacity is approximately 4 mg at very high humidities but naturally decreases considerably for measurements under 90% RH.

With the same assumptions as above and a concrete sample of 10 g, i.e. $\sim 5 \cdot 10^{-6}$ m^3, the error, due to the RH-gauge absorbing moisture from the sample, can be estimates as

$$\Delta\phi < \frac{0.0004 \cdot 10^{-3}}{200 \cdot 5 \cdot 10^{-6}} = 0.004 = 0.4\% \text{ RH}$$

This is clearly much greater than the error due to the enclosed air volume, but is still so small that it is practically negligible. With the Hygrodynamics RH-sensor the error may however exceed 1% RH.

10.4 Precision - compared with moisture content measurements

A series of experiments has been carried out in order to determine the precision of the method and compare it to measurements of moisture content.

Concrete cylinders with a diameter of 100 mm have been cast in plastic bags to prevent drying. To get a high degree of self dessication a low water-cement-ratio has been chosen, $w_o/C \sim 0.3$. Specimens A and C have a maximum size of stones of 12 mm and specimens B 25 mm. Fifteen specimens of each kind were cast.

The specimens have been sealed and cured for four months in a 95% RH climate room.

From each specimen samples of different size have been taken to measure relative humidity as described above and moisture content in per cent by weight in three different ways. The moisture ratio has been determined on both small and large samples by weighing before and after drying at 105 °C as well as by using the calcium carbide method on crushed samples of 20 grams. The results are given in the table below.

Method of measurement		Moisture ratio u (% by dry wt) Drying in 105 °C		CaC_2	RH (%)
Weight of samples (g)		100-250	30-40	20	<10
Specimens A (max size of stones 12 mm	$\bar{u}$	6.12	6.13	5.0	87.4
	±2s	±0.48	±0.60	±0.8	±2.8
Specimens B (max size of stones 25 mm)	$\bar{u}$	6.21	7.01	5.5	90.3
	±2s	±1.30	±1.34	±0.8	±2.1
$\bar{u}$ = mean value, s = standard diviation, n = 15 samples					

With as large samples as 100 to 250 grams the accuracy is no better than ±0.5 - 1.3 per cent by weight expressed as twice the standard deviation. The higher value is for the higher maximum size of stones.

For normal concrete the slope of the sorption isotherm is in the order of 0.1 (% by wt/% RH) for 0.6 < RH < 0.9. Therefore an accuracy of ± 2-3% RH means that the accuracy of the RH-measurements is about ± 0.2-0.3% expressed in terms of moisture ratio. The accuracy is clearly much better than for measurements of moisture content.

Specimens C have been dried to different residual moisture content and then samples have been taken from the center of the cylinders and put into test tubes. The relative humidity has been determined at different temperature levels without separating the test tube containing the sample from the RH-gauge. This has given the relative humidity as a function of temperature at a constant moisture content, i.e. temperature dependence of the sorption isotherm. The results were shown previously in Table XI and Fig. 4.8.

If a sample is taken from a specimen or a concrete construction with one temperature and the measurement of its relative humidity is made at another temperature, the measured and actual RH differ. For the concrete used in the experiments, the influence is 0.3-0.4% RH per ^{0}C, i.e. 3 to 4% RH with a temperature difference of 10 ^{0}C. The effect is obviously not in any way negligible and has to be taken into account when measuring RH.

10.5 Further applications

Measurements of the relative humidity in concrete can be performed in many ways. In order to measure without the trouble-some sampling procedure, other methods of measuring the relative humidity at different depths have been devised, see Fig. 10.4.

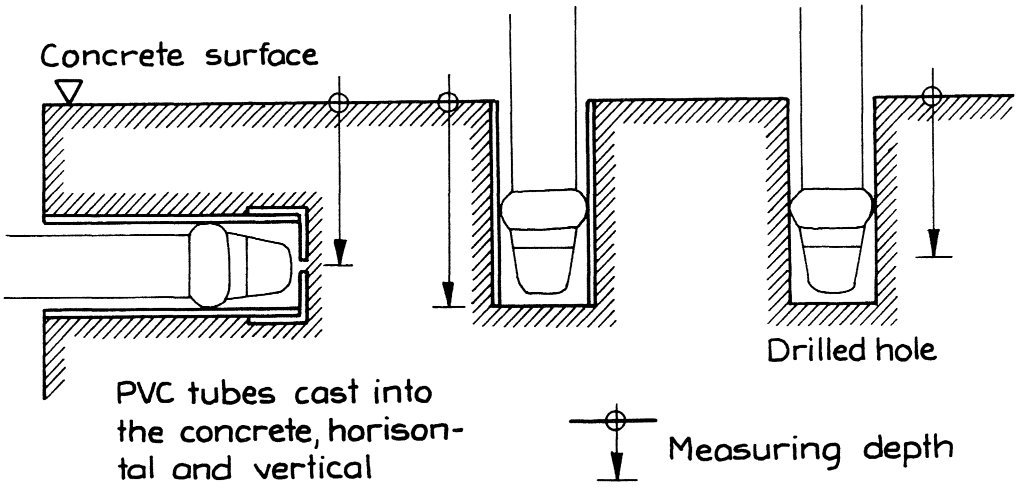


Fig. 10.4 Further applications in field and laboratory measurements using the same RH-gauge.

A PVC tube cast into the concrete with an opening at a certain depth gives the opportunity to measure the relative humidity at this depth several times in a non-destructive way. The method has been used for laboratory and field measurements with satisfactory results. The measurements should, however, be complemented with a measurement of the temperature in the concrete close to the tube opening. Even a small temperature difference between the concrete and the sensor gives an error. A calculation based on the assumption of constant vapour pressure quantifies the effect.

Drilling a hole to a certain depth is an easy way to make an isolated measurement in a concrete structure using the same RH-gauge as described above. Due to the rubber seal near the end of the probe, the measured RH is an integrated value for just a few centimeters at the bottom of the hole.

A measurement in a drilled hole is at present very time-consuming. The observed value is at first too high and diminishes to an equilibrium after one or two days in some cases. The effect has not yet been fully explained even though attempts have been made, cf. Pihlajavaara (1974). One probable explanation is a moisture transport from the concrete to the hole due to the heat evolved. This moisture is absorbed in the concrete dust at the bottom of the hole. If the dust is carefully removed the effect diminishes.

10.6 Summary

Determining the moisture content of concrete requires rather large samples in order to be accurate. The accuracy depends mainly on the size of the sample and the size of the stones. A small sample of concrete with large stones is usually not representative for the concrete composition and a measured moisture content may be very erroneous.

There are several advantages in measuring the ralative humidity in concrete instead of the moisture content. The RH expresses the state of the moisture in a far better way, and it is certainly the state and not the content, that is of interest in most cases. In addition the relative humidity can be measured on small samples, not necessarily representative for the concrete, with an accuracy shown to be much better than when measuring the moisture content.

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TABLES

Content:

TABLE I. Contraction measurements on mortars of standard portland cement, Sl 1, and sand 11, cf. Table III.

Time from mixing (days)	Mortar I 1:0.6:1.8;318 g		Mortar II 1:0.8:2.4; 359 g	
	Contraction (kg/kg cement)	Rate of contr (kg/kg cement/s	Contraction (kg/kg cement)	Rate of contr (kg/kg cement/s)
0.02	0		0	
				$1.9 \cdot 10^{-6}$
0.04		$2.3 \cdot 10^{-6}$	0.0034	
0.052	0.0061			$6.0 \cdot 10^{-7}$
0.10		$3.5 \cdot 10^{-7}$	0.0065	
0.63	0.0234			3.8 ·
0.67		2.2	0.0251	
				2.7
1	0.0305		0.0329	
		1.3		1.5
1.7	0.0386		0.0417	
		$8.9 \cdot 10^{-8}$		$8.5 \cdot 10^{-8}$
2	0.0409		0.0439	
		4.3 ·		4.2
4	0.0484		0.0511	
		2.6 ·		3.5
6	0.0529		0.0572	
		$7.5 \cdot 10^{-9}$		1.2
8	0.0542		0.0592	
		6.6		$8.8 \cdot 10^{-9}$
15	0.0582		0.0645	
		3.0		3.8
22	0.0600		0.0668	
		2.0		2.5
30	0.0614		0.0685	
		1.3		1.8
41	0.0626		0.0702	
		$2.0 \cdot 10^{-10}$		$3.9 \cdot 10^{-10}$
104	0.0637		0.0723	
		3.3		1.7
111	0.0639		0.0724	
		$3.5 \cdot 10^{-11}$		$8.7 \cdot 10^{-11}$
244	0.0643		0.0734	
Weight loss at heating; 244 days	105°C-600°C:	0.203 (kg/kg C)	0.263 (kg/kg C)	Corrected for weight loss of cement + sand
	105°C-1000°C:	0.230 (kg/kg C)	0.299 (kg/kg C)	
Regression curve	rate=$2.78 \cdot 10^{-7} \cdot t^{-1.61}$,t>2 ($r^2$=0.95)		rate=$2.45 \cdot 10^{-7} \cdot t^{-1.50}$,t>0.7 ($r^2$=0.99)	

TABLE II. Weight losses at heating and some data for the cements used. ($a_\theta=1-C_\theta/C_{20}$).

Cement		a_{105}	a_{600}	a_{800}	a_{1000}	
Li 1	"Limhamn Std"	0.010	0.019	0.019	0.022	Type I, low-alkali
Li 2		0.003	0.012	-	0.014	
LiLH	"Limhamn LH"	0.004	0.010	-	0.012	Type II, slow, low alkali
Sk SH	"Skövde SH "	0.004	0.010	-	0.014	Type III
Sl 2	"Slite Std"	0.003	0.008	-	0.011	Type I

TABLE III. Weight losses at heating and some data for the aggregates used. ($b_\theta=1-A_\theta/A_{20}$). cf. Fig 5.7.

Aggregate	b_{105}	b_{600}	b_{1000}	Fineness modulus	
11	0.0010	0.0047	0.0058	0.47	<0.5 mm "Fyle 4"
21	-	-	-	0.85	<0.5 mm "Fyle 1"
10	0.0008	0.0018	0.0023	1.14	<0.5 mm "Fyle 3M"
22	0.0019	0.0021	0.0021	2.50	0.5-1 mm "Fyle 2 Norm"
23	0.0008	0.0019	0.0019	3.50	1-2 mm, "Fyle 3 Norm"
18	0.0020	0.0045	0.0058	4.41	2-4 mm, crushed "Hardeberga"
I	0.0014	0.0027	0.0032	2.87	3:2:2:3 of 10/22/23/18

TABLE IV. Weight losses at heating to different temperature levels; Series A.

Time from mixing (days)	Weight loss[1] (kg/kg cement) at heating from 105°C to			[1] Corrected for weight loss of original cement
	600°C	800°C	1000°C	
1	0.067	0.085	0.082	Cement paste with $w_0/C=0.5$, cement Li1, sealed cured at +22°C. Crushed samples. Mean values of two samples or more.
2	0.080	0.098	0.093	
4	0.115	0.130	0.143	
7	0.123	0.143	0.145	
14	0.128	0.140	0.139	
28	0.141	0.171	0.176	
a^*	0.180	0.168	0.168	Acc. to eq. (3:10) (r^2=correlation coefficient)
b^*	-0.158	-0.207	-0.224	
r^2	0.95	0.93	0.84	

TABLE V. Weight losses at heating; series B: mortars with different cements and $w_0/C=0.6$. Cement/aggregate I in proportions 1:4.4. Cured in water, with an excess of $Ca(OH)_2$, at 20°C after 1 day.

Time from mixing (days)	Weight loss (kg/kg cement); means values of three samples							
	Cement Li 2		Cement Li LH		Cement Sk SH		Cement Sl 2	
	600°C	1000°C	600°C	1000°C	600°C	1000°C	600°C	1000°C
2	0.092	0.100	0.055	0.066	0.085	0.098	0.064	0.071
3	-	-	-	-	0.119	0.125	-	-
4	0.105	0.119	-	-	-	-	0.079	0.091
7	0.121	0.130	0.075	0.082	0.140	0.146	0.099	0.105
14	0.135	0.150	0.090	0.096	0.147	0.159	0.103	0.116
38	0.145	0.177	-	-	-	-	0.120	0.137
42	-	-	0.085	0.103	0.150	0.175	-	-
56	0.161	0.192	0.104	0.125	0.161	0.186	0.126	0.157
71	0.169	0.212	0.102	0.139	0.166	0.198	0.129	0.173
a*	0.183	0.215	0.202	0.209	0.163	0.182	0.199	0.216
b*	-0.176	-0.341	-0.073	-0.124	-0.153	-0.267	-0.117	-0.210
r^2	0.97	0.90	0.87	0.85	0.89	0.97	0.98	0.93

samples treated after this boundary probably contain carbonated calcium-hydroxide at the surface originating from the storage water.

TABLE VI. Weight losses at heating; series C: Mortars stored in water at $+20^{\circ}$C and crushed samples in different humidities after 2 days. Cement Sl 3, $w_0/C=0.6$, cement/aggregate 10/21 in proportions 1:1.25:1.25.

Time from mixing (days)	Weight loss at heating from 105°C to 1000°C (kg/kg cement)									
	Crushed and dried samples stored at (% RH): (mix)				Samples of pieces stored in water					
	58 (1)	75 (2)	82 (3)	91 (4)	Mix 1	Mix 2	Mix 3	Mix 4	Average	Std deviation
2	0.152	-	-	-	0.128	0.128	0.135	0.142	0.133	0.007
4	0.141	0.137	0.152	0.160	0.156	0.149	0.155	0.147	0.152	0.004
7	0.147	0.144	0.151	0.167	0.151	0.156	0.157	0.156	0.155	0.003
14	0.160	0.163	0.158	0.180	0.164	0.163	0.174	0.169	0.168	0.005
28	0.213	0.189	0.179	0.217	0.172	0.182	0.178	0.183	0.179	0.005
				a*	0.128	0.139	0.127	0.129	0.131	0.006
				b*	-0.152	-0.203	-0.178	-0.184	-0.179	0.021
				r^2	0.87	0.96	0.96	0.95	0.98	-

TABLE VII. Weight loss during curing and heating procedure series D. Mortar samples, mixed in the crucibles, of cement Sl 4 and aggregates 10/22/23 in proportions 1:1.65:1.1:1.1; $w_o/C \approx 0.6$. Sealed cured for one week.

Sample	Amounts after mixing (g)			Weight loss (kg/kg cement), corrected for weight loss of cement and aggregate						
	Cement	Water	w_o/C	Curing 7 days	105°C	600°C	1050°C	Total	$\Delta m_{105 \to 1050} / \Delta m_{105 \to 600}$	
1	2.320	1.405	0.605	0.005	-	-	0.601	0.606	-	
2	2.332	1.413	0.606	0.007	-	-	0.599	0.606	-	
3	2.486	1.510	0.607	0.165*	-	-	0.441	0.606	-	*leakage
4	2.729	1.642	0.602	0.007	-	-	0.594	0.601	-	
5	2.744	1.646	0.600	0.004	0.448	0.136	0.012	0.600	1.09	
6	3.040	1.854	0.610	0.005	0.464	0.124	0.016	0.609	1.13 average =1.11	
7	3.042	1.839	0.605	0.005	0.453	0.132	0.015	0.605	1.11	
Weight loss of cement + aggregate (kg/kg)					0.0009	0.0026	0.0011	0.0046		

TABLE VIII. Progress of hydration of the different cements. Evaluated by eq (3:11) and (3:12) with f=1.1. Cement Li 1 with $w_0/C=0.5$ and sealed cured at +22°C; the others with $w_0/C=0.6$ and stored in water at +20°C.

Time from mixing (days)	Non-evaporable water (kg/kg cement)								
	Li 1	Li 2		Li LH		Sk SH		Sl 2	
	eq (3:12)	(3:11)	(3:12)	(3:11)	(3:12)	(3:11)	(3:12)	(3:11)	(3:12)
1	0.077	-	-	-	-	-	-	-	-
2	0.090	0.101	0.101	0.061	0.063	0.094	0.095	0.070	0.071
3	-	-	-	-	-	0.131	0.128	-	-
4	0.135	0.116	0.117	-	-	-	-	0.087	0.089
7	0.139	0.133	0.132	0.083	0.082	0.154	0.151	0.109	0.107
14	0.140	0.149	0.149	0.099	0.098	0.162	0.161	0.113	0.114
28	0.164	-	-	-	-	-	-	-	-
38	-	0.160	0.167	-	-	-	-	0.132	0.134
42	-	-	-	(0.094)1)	(0.098)1)	(0.165)1)	(0.169)1)	-	-
56	-	0.177	0.184	0.114	0.119	0.177	0.181	0.139	0.147
71	-	0.186	0.197	0.112	0.124	0.183	0.189	0.142	0.155
a*	0.171	0.180	0.192	0.199	0.205	0.138	0.151	0.195	0.203
b*	-0.202	-0.221	-0.266	-0.092	-0.112	-0.167	-0.205	-0.140	-0.167
r^2	0.91	0.96	0.94	0.97	0.99	0.98	0.99	0.98	0.98

-------- eq (3:10) starts from 3 days for cement Sk SH

1) obviously erroneous, see text

TABLE IX. Moisture fixation at low ages. Evaporable water and loss on ignition as a function of curing time and drying climate. Mortar samples with cement Sl 3 and aggregates 10/21 in proportions 1:1.25:1.25. Stored in water at +20^{o}C, then crushed and sieved to sizes less than 0.5 mm and dried in an precision moisture chamber for one day. Mean values of four samples; standard deviation usually $\leqslant$ 0.005.

Drying climate (% RH)	Evaporable water (loss on ignition) (kg/kg cement) after curing time (days):				
	2	4	7	14	28
20	0.099(0.160)	0.100(0.181)	0.099(0.190)	0.111(0.199)	0.116(0.218)
40	0.126(0.169)	0.141(0.191)	0.144(0.205)	0.144(0.205)	0.152(0.226)
60	0.149(0.176)	0.161(0.199)	0.177(0.201)	0.167(0.227)	0.180(0.240)
80	0.183(0.187)	0.199(0.207)	0.203(0.221)	0.210(0.220)	0.206(0.302)
90	0.245(0.233)	0.268(0.211)	0.286(0.225) 0.209(0.162)*	0.265(0.236)	0.283(0.300) 0.277(0.249)
98	0.346(0.189)	0.357(0.280) 0.422(0.153)*	0.359(0.202)	0.376(0.217)	0.379(0.244)

*First two measurements with well functioning CO_2-filter. Equilibrium obtained.

TABLE X. Equilibrium moisture contents at 40-65 % RH. From drying experiments in climate rooms. Mortar specimens of 20 mm thickness drying from both surfaces. Cement Sl 2 and aggregate I in proportions 1:4.4, $w_0/C=0.6$. Sealed cured and stored in water, respectively, at +20^{o}C for 28 days before drying ~1.5 year. Mean values of four specimens.

Series	Storage at curing	Climate (% RH)	Evaporable water (kg/kg cement)	Weight loss at heating (kg/kg cement)		
				600^{o}C	1000^{o}C	eq(3:12)
101:1	Sealed	40*	0.074	0.152	0.244	0.201
101:2	Water		0.081	0.157	0.229	0.197
016:1	Sealed	40	0.070	0.133	0.265	0.198
016:2	Water		0.087	0.140	0.249	0.195
123:1	Sealed	50	0.081	0.149	0.270	0.210
123:2	Water		0.095	0.143	0.249	0.197
124:1	Sealed	65	0.111	0.160	0.275	0.219
124:2	Water		0.121	0.144	0.261	0.203

* CO_2-free at the beginning of drying, see chapter 5.

TABLE XI. Some results on relative humidity as a function of temperature at constant moisture content. Concrete samples from specimens C in 10.4 with $w_0/C \approx 0.3$. The temperature dependence of the sensors has been corrected for.

Temperature (^{o}C)	Relative humidity (%)		
	Sample 1	Sample 2	Sample 3
19.3	76.1	83.6	88.6
14.5	75.8	84.0	89.2
10.8	74.2	82.8	88.0
5.2	71.4	80.8	85.3
11.2	73.0	82.4	87.8
19.1	75.3	85.2	91.1
25.3	77.8	87.8	93.9
19.3	76.4	86.0	92.8
$(\frac{\partial\phi}{\partial\theta})_w$ (%/^{o}C)	0.31	0.33	0.41

TABLE XII. Flow measurements with the cup-method. Cement mortar specimens, thickness 5 & 10 mm, diameter 170 mm, cured at +20^{o}C in water for 28 days. Cement Sl 2, aggregate 10/22 in proportions 1/0.93. Cups stored in a climate room with +20^{o}C and RH_2=40 % for half a year.

Specimens	Measured property	Salt & RH_1 (%)				
		NaBr 58.5	NaCl 75.5	KCl 85	KNO_3 93	None 100 %
Mix I. w_0/C=0.6	d_0 (mm)	4.8	5.4	4.8	4.9	5.2
	ρ_{wet} (kg/m^3)	2160	2140	2130	2130	2130
d=5 mm;C≡420 kg/m^3	F (g/m^2·h)	0.54	1.07	1.71	2.16	2.85
Mix II. w_0/C=0.6	d_0 (mm)	5.0	5.1	4.8	5.4	5.1
	ρ_{wet} (kg/m^3)	2160	2170	2170	2130	2150
d=5 mm;C≡420 kg/m^3	F (g/m^2·h)	0.40	0.76	1.08	1.63	1.96
Mix III. w_0/C=0.6	d_0 (mm)	10.0	10.0	10.0	10.2	10.2
	ρ_{wet} (kg/m^3)	2160	2170	2140	2160	2160
d=10 mm;C≡420 kg/m^3	F (g/m^2·h)	0.23	-$^{1)}$	0.62	1.15$^{*)}$	1.73
Mix IV. w_0/C=0.4	d_0 (mm)	5.2	5.0	5.1	5.3	5.3
	ρ_{wet} (kg/m^3)	2260	2260	2280	2260	2270
d=5 mm;C≡640 kg/m^3	F (g/m^2·h)	0.19	0.43	0.68	0.83	1.09
Mix V. w_0/C=0.8	d_0 (mm)	5.2	5.2	5.2	5.2	-
	ρ_{wet} (kg/m^3)	2110	2110	2090	2100	-
d=5 mm C≡320 kg/m^3	F (g/m^2·h)	0.81	1.50	2.35	3.50	

*) $BaCl_2$ 91 % RH 1) Solution not saturated

TABLE XIII. Corrected results of flow measurements in Table XII. Water vapour permeability k graphically evaluated, cf. eq. (5:5).

Mix w_o/C	Corr. quant.	Cup No						
		"0"	1	2	3	4	5	
I	p_1	7.0	10.0	12.6	14.1	15.2	16.0	(mmHg)=(*133.3 Pa)
	F	0	0.52	1.15	1.64	2.12	2.96	$(g/m^2 \cdot h) = (* \frac{10^{-6}}{3.6} kg/m^2 \cdot s)$
0.6	k	8	10·	15·	20·	30·	80·	$(10^{-4} g/mhmmHg = (* 2 \cdot 10^{-13}$ kg/mPas)
	ϕ_1	40	57	72	80	87	91	(%)
II	p_1	7.0	10.1	12.8	14.4	15.5	16.5	
	F	0	0.40	0.78	1.04	(1.76)*	2.00	
0.6	k	7	7·	8·	~30			
	ϕ_1	40	57	73	82	88	94	
III	p_1	7.0	10.1	-	14.6	15.3	16.6	
	F	0	0.23	-	(0.62)*	1.17	1.77	d=10 mm
0.6	k	7	8·	-	~50			
	ϕ_1	40	58	-	83	87	95	
IV	P_1	7.0	10.2	13.0	14.6	15.9	16.9	
	F	0	0.20	0.43	0.69	0.88	1.16	
0.4	k	2	3·	6·	8·	10·	15·	
	ϕ_1	40	58	74	83	90	97	
V	p_1	7.0	9.8	12.4	13.7	14.5	-	
	F	0	0.81	1.50	2.35	3.50	-	d=5.2 mm
0.8	k	15	15·	15·	70·	100·	-	
	ϕ_1	40	57	71	78	82	-	

*) deviating values probably due to the differences in compactness, cf. the wet density in Table XII.

TABLE XIV. Drying experiments series 01. Different w_0/C at constant aggregate content of 1600 kg/m^3, aggregate I. Mean values of four specimens, :1 & :2 cured 28 days (:3 & :4 3 days, :5 & :6 1 day, :7 & :8 91 days,) sealed and in water respectively. Drying climate +20°C 40 % RH.

Series	w_0/C	Air content of "paste" (%)*)	Time (days) to reach required degree y of drying					
			y=0.1		y=0.25		y=0.5	
			:1	:2	:1	:2	:1	:2
013	0.3	10.2	3.0	0.53	24	10	-	130
014	0.4	12.3	1.9	0.39	15	5.7	210	60
015	0.5	12.7	1.1	0.28	9.0	3.8	82	37
016	0.6	12.9	0.70	0.13	4.7	1.5	28	14
017	0.7	14.2	0.47	0.059	3.1	0.60	16	5.9
018	0.8	16.4	0.27	0.052	2.0	0.27	9.9	3.4
019	0.9	17.9	0.14	0.053	1.1	0.19	5.5	1.6
010	1.0	16.1	0.070	0.054	0.63	0.17	3.5	0.90
Curing 3 days			:3	:4	:3	:4	:3	:4
014	0.4	12.6	1.5	0.18	14	5.3	33	36
016	0.6	13.6	0.097	0.035	0.98	0.16	13	3.5
018	0.8	14.4	0.046	0.038	0.16	0.11	2.0	0.64
010	1.0	15.4	0.048	0.044	0.14	0.13	0.70	0.38
Curing 1 day			:5	:6	:5	:6	:5	:6
016	0.6	12.4	0.040	0.046	0.13	0.14	0.90	0.95
Curing 91 days			:7	:8	:7	:8	:7	:8
016	0.6	13.6	0.60	0.33	3.5	1.7	20	10

*) "Paste" = system cement + water + air.

TABLE XV. Drying experiments series 03; different aggregate contents at constant $w_0/C=0.6$. Aggregate I. Mean values of four specimens, cured 28 days sealed (:1) and in water (:2).

Series	Aggregate content (kg/m^3)	Air content of "paste" (%)	Time (days) to reach required degree y of drying					
			y=0.1		y=0.25		y=0.5	
			:1	:2	:1	:2	:1	:2
031	1400	8.3	0.78	0.080	5.9	1.1	37	13
032	1500	10.4	0.82	0.098	5.4	1.2	30	12
033*	1600	13.3	0.83	0.13	5.3	1.5	34	14
034	1700	13.4	0.81	0.17	4.9	1.4	24	11
035	1750**	14.7	0.64	0.077	3.2	0.76	17	6.3

*033: same composition as 016

**Maximum possible

TABLE XVI. Drying experiments series 04; different contents of filler (<025 mm) at constant $w_0/C=0.6$ and aggregate content 1600 kg/m^3.

Series	Filler % <0.25 mm	Air (%) of paste	Time (days) to reach required degree y of drying						Aggregate
			y=0.1		y=0.25		y=0.5		
			:1	:2	:1	:2	:1	:2	
041	4	14.2	0.65	0.069	3.7	0.80	20	6.4	X
(042)	10	cf. series 052							I
043	13	13.8	0.64	0.11	4.5	1.2	26	12	IX
044	25	11.4	0.54	0.076	4.0	0.89	25	9.4	VIII

TABLE XVII. Drying erperiments series 05; different modulus of fineness at constant w_o/C=0.6 and aggregate content 1600 kg/m^3 (050:∿1400 kg/m^3).

Series	Modulus of fineness	Air content of "paste" (%)	Time (days) to reach required degree y of drying						Aggregate
			y=0.1		y=0.25		y=0.5		
			:1	:2	:1	:2	:1	:2	
050[1)]	1.80	14.7	0.92	0.65	5.4	2.9	36	-	10/22 1:0.92
051	1.96	14.5	0.62	0.13	4.0	1.2	21	9.8	II
052*	2.87	11.7	0.61	0.13	4.5	1.3	26	12	I
053	3.90	8.7	0.52	0.085	3.9	0.95	30	11	III

*052 same somposition as 016

1) Same as at flow measurements; one year after 051-053

TABLE XVIII. Drying experiments series 06, different gradations of aggregate at constant modulus of fineness =2.87 and constant w_o/C=0.6 and aggregate content 1600 kg/m^3.

Series	Aggregate 0.5-2 mm (%)	Air Content of "paste" (%)	Time (days) to reach required degree y of drying						Aggregate
			y=0.1		y=0.25		y=0.5		
			:1	:2	:1	:2	:1	:2	
061	75	16.3	0.62	0.15	3.8	1.4	19	9.7	IV
062	65	14.7	0.67	0.13	4.3	1.2	22	9.9	V
(063)	45	cf. series	052						I
064	30	10.2	0.62	0.15	4.6	1.4	28	13	VI
065	10	12.6	0.47	0.11	3.5	0.93	21	9.8	VII

TABLE XIX. Drying experiments series 07; different amounts of entrained air at constant $w_o/C=0.6$ and aggregate content of 1600 kg/m^3. Air entrainment agent "Barra 55L".

Series	Entrained air (vol-% of total)	Air content of "paste" (%)	Time (days) to reach required degree y of drying					
			y=0.1		y=0.25		y=0.5	
			:1	:2	:1	:2	:1	:2
071	0	cf. 016, 033 & 052						
072	∿5	25.7	0.43	0.065	2.7	0.73	15	5.8
073	∿7	32.0	0.35	0.064	2.2	0.61	12.5	4.1

TABLE XX. Drying experiments series 08; different proportions of "stones" (4-8 mm) at constant $w_0/C=0.6$ and aggregate content of 1700 kg/m^3 including aggregate I and 7. Specimen thickness 2L=40 mm. Mean values of two specimens.

Series	Aggregate 4-8 mm (%)	Air content of "paste" (%)	Time (days) to reach required degree y of drying					
			y=0.1**		Y=0.25		y=0.5	
			:1	:2	:1	:2	:1	:2
081*	0	12.1	2.3	0.67	16	6.7	71	47
082	40	10.2	1.3	0.41	13	5.1	66	42
083	50	6.0	1.9	0.47	13	5.6	69	47
084	60	5.4	1.3	0.24	12	3.4	62	29

*cf. 034

**)weighing error at 2 days, uncertain results

TABLE XXI. Drying experiments series 09; different maximum sizes of stones at constant $w_o/C=0.6$, aggregate content 1700 kg/m^3 and proportions of stones 50 % >4 mm. Aggregate I (50 %), 7 (4-8 mm) and 8-16 & 16-32 mm, stones in equal proportions.
One specimen with thickness 2L=80 mm.

Series	Maximum sizes of stones	Air content of "paste" (%)	Time (days) to reach required degree y of drying				
			y=0.1		y=0.25		
			:1	:2	:1	:2	
091	4 mm	11.5	11	3.3	56	29	cf. 034 & 081
092	8	7.8	8.9	2.1	58	28	t(0.5)>230
093	16	6.2	8.3	1.9	64	31	
094	32	7.3	8.4	1.2	66	26	

TABLE XXII. Drying experiments series 12 (d 10); different drying climates. Cement mortars of "standard composition" dried in climate rooms at +20°C (121 & 101 in climate boxes).

Series	RH (%)	Air content of "paste" (%)	Time (days) to reach required degree y of drying					
			y=0.1		Y=0.25		y=0.5	
			:1	:2	:1	:2	:1	:2
121	10	11.7	0.19	0.17	2.0	0.85	9.5	6.7
(122)	40	cf. 016, 033 & 052						
123	50	14.7	0.54	0.14	3.8	0.95	22	8.7
124	65	14.7	0.68	0.18	4.4	1.1	27	9.7
101	40 less CO_2	13.1	0.60	0.38	2.9	1.4	11	7.0

TABLE XXIII. Drying experiments series 13; different directions of drying. Cement mortars of "standard composition", specimen thickness 8 cm, drying from one or two sides, vertical or horisontal.

Series	Direction of drying	L (cm)	Air content of paste (%)	Time (days) to reach required degree y of drying			
				y=0.1		y=0.25	
				:1	:2	:1	:2
131	Vertical,1-sided	8	14.7	61	28	-	-
132	Vertical,2-sided	4	14.7	24	5.6	-	49
133	Horizontal,1-sided	8	14.7	58	23	-	-
134	Horizontal,2-sided	4	14.7	23	4.8	110	39

TABLE XXIV. Measurements of RH-distribution.
Concrete specimens, thickness 160 mm, drying from two sides in +20°C and 40 % RH.
Cement S12; aggregate 10/22/23/18/7 in proportions 3/2/2/3/10.
Cured under sealed conditions.

Specimen:	Drying time (days)	Relative humidity (%) at depth (mm) from surface: 5	10	20	30	50	80
$w_o/C=0.6$ $C=325$ kg/m^3 Cured 28 days	0	97	-	-	98	98	97
	6	69	93	98	98	98	97
	260	-	-	-	79	89	92
$w_o/C=0.6$ $C=325$ kg/m^3 Cured 3 days	0	-	-	-	99	99	99
	7	84	93	97	99	99	99
	8	-	91	97	99	99	99
	11	-	93	-	-	-	-
	19	-	81	94	97	97	96
	260	-	-	-	77	85	89
$w_o/C=0.4$ $C=490$ kg/m^3 Cured 3 days	5	75	83	89	90	90	87
	22	65	72	84	84	86	84
	50	-	-	82	81	85	82
	90	-	58	76	78	83	-
	95	48	-	72	77	84	81
	260	-	-	-	70	81	85
$w_o/C=0.8$ $C=240$ kg/m^3 Cured 3 days	7	69	93	98	>98	>98	>98
	260	-	-	-	60	70	73

TABLE XXV. Measurements of moisture loads, as RH, on a surface layer. Different concrete compositions and drying times. Most specimens sealed cured 1 month and dried in +20°C and 40 % RH.

Concrete quality and treatment (K 150 corresponds to a compr. strength of 15 MPa)	Drying time (weeks)	Moisture load RH (%)
K 150	4	96
K 250 cured in water 1 month	4	95
K 150	8	94
K 250	4	93
K 250, air entrained air	2	92
K 250, dry climate ∿10 % RH	4	91
K 400	4	89
K 250, air entrained air	4	88
K 250	8	88
K 400, air entrained air	2	85
K 400, air entrained air	4	82

Concrete compositions:

(Aggregate: maximum sizes of stones 12 mm, modulus of fineness 3.7)

	w_0/C	$C(kg/m^3)$	air(%)	slump (cm)
K 150	0.88	270	3.3	10.5
K 250	0.65	350	3.5	6.5
K 250,air	0.52	390	8.5	7.0
K 400	0.52	420	3.1	8.5
K 400,air	0.45	490	7.4	5.5

APPENDIXES

Content:

APPENDIX I Deduction of eq. (3:12)

Assumptions: 1) The amount of non-evaporable water released by carbonation, $\Delta w_n = 18 \Delta m_{CO_2}/44$, originates from the calcium-hydroxide, whose water all is liberated at heating to 600 ^oC.

2) The originally non-evaporable water, w_n^o, is liberated at heating to 600 ^oC respectively 1000 ^oC in proportions 1:f, cf. eq. (3:11), if no carbonation has occured.

3) All of the carbon-dioxide is liberated over 600 ^oC.

With these assumptions the remaining weights at the heating temperatures can be expressed in the following way:

$$105\ ^oC:\quad m_{105} = C + A + w_n^o - \Delta w_n + \Delta m_{CO_2} \qquad (1)$$

$$600\ ^oC:\quad m_{600} = C + A + w_n^o \frac{f-1}{f} + \Delta m_{CO_2} \qquad (2)$$

$$1000\ ^oC:\quad m_{1000} = C + A \qquad (3)$$

where the weights are corrected for weight loss of cement and aggregate.

Eq. (2) & (3) gives: $\Delta m_{CO_2} = m_{600} - m_{1000} - w_n^o \frac{f-1}{f}$ (4)

Eq. (1) & (3) gives: $m_{105} = m_{1000} + w_n^o + \frac{26}{44} \Delta m_{CO_2}$ (5)

and if this is combined with eq. (4) one obtains

$$m_{105} = m_{1000} + w_n^o + \frac{26}{44} m_{600} - \frac{26}{44} m_{1000} - \frac{26}{44} w_n^o \frac{f-1}{f}$$

and

$$w_n^o = \frac{m_{105} - m_{1000} - \frac{26}{44} m_{600} + \frac{26}{44} m_{1000}}{1 - \frac{26(f-1)}{44\,f}} \qquad (6)$$

$$w_n^o = \frac{m_{105} - m_{600} + \frac{18}{44} m_{600} - \frac{18}{44} m_{1000}}{\frac{44\ f\ -\ 26\ f\ +\ 26}{44\ f}}$$

This can be transformed to

$$w_n^o = \frac{44f}{26+18f} \left[m_{105} - m_{600} + \frac{18}{44} (m_{600} - m_{1000}) \right] \qquad (3{:}12)$$

APPENDIX II Translation of moisture transport coefficients.

Assumptions: 1) Isothermal conditions

2) The moisture flow in one dimension is described by

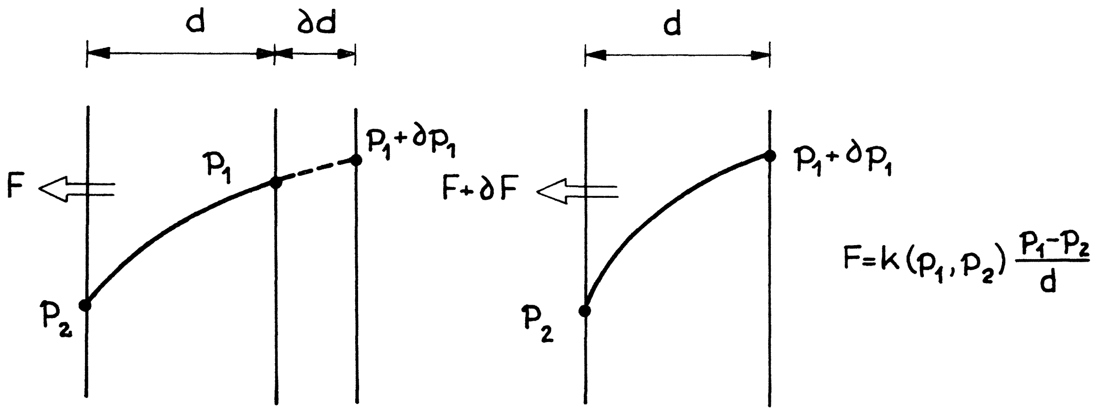
$$F = - k_\psi \cdot \frac{\partial \psi}{\partial x} \ (\mathrm{kg/m^2 \cdot s})$$

where ψ stands for various descriptions of the moisture condition.

Translation to a description in					from
Vapour content v	Vapour pressure p	Moisture content w	Moisture ratio u	Relative humidity ϕ	
$k_v =$	$k_p =$	$k_w =$	$k_u =$	$k_\phi =$	
$\frac{RT}{M} *$	-	$\frac{1}{\frac{\partial w}{\partial p}} *$	$\frac{\rho}{\frac{\partial w}{\partial p}} *$	$p_s *$	$*k_p$
$\frac{RT}{M} \cdot \frac{\partial w}{\partial p} *$	$\frac{\partial w}{\partial p} *$	-	$\rho *$	$p_s \cdot \frac{\partial w}{\partial p} *$	$*k_w$
$\frac{RT}{M\rho} \cdot \frac{\partial w}{\partial p} *$	$\frac{1}{\rho} \frac{\partial w}{\partial p} *$	$\frac{1}{\rho} *$	-	$\frac{p_s}{\rho} \cdot \frac{\partial w}{\partial p} *$	$*k_u$
$\frac{1}{v_s} *$	$\frac{1}{p_s} *$	$\frac{1}{p_s \frac{\partial w}{\partial p}} *$	$\frac{\rho}{p_s \frac{\partial w}{\partial p}} *$	-	$*k_\phi$
$\partial w/\partial p$ is the moisture capacity, $\partial w_{e\infty}/\partial p$, in $(\mathrm{kg/m^3\ Pa})$ ρ is the density in $(\mathrm{kg/m^3})$					

APPENDIX III Deduction of eq. (5:5)

The equation (5:5) can be deducted by studying two plates; one plate with a thickness d, with a vapour pressure of $p_2 + \partial p_1$ on one side and a constant pressure p_2 on the other; one plate with the same vapour pressure as the other plate, but a thickness of $d + \partial d$ in such a way that the vapour pressure is p_1 at a depth of d, cf. the figures below.



The flow through the thicker plate becomes

$$F = k(p_1 + \partial p_1,\ p_2)\ \frac{p_1+\partial p_1-p_2}{d+\partial d} \tag{1}$$

Through the thinner plate one obtains a flow of

$$F + \partial F = k(p_1 + \partial p_1,\ p_2)\ \frac{p_1+\partial p_1-p_2}{d} \tag{2}$$

(1) & (2) give

$$F + \partial F = F\ \frac{d+\partial d}{d} = F + F\ \frac{\partial d}{d}$$

i.e.

$$\partial F = F\ \frac{\partial d}{d} \tag{3}$$

The flow through the thicker plate is also obtained from

$$F = k(p_1 + \partial p_1,\ p_1)\cdot\frac{\partial p_1}{\partial d} \tag{4}$$

(3) & (4) give

$$\partial F = k(p_1 + \partial p_1, p_1) \cdot \frac{\partial p_1}{\partial d}$$

or

$$d\frac{\partial F}{\partial p_1} = k(p_1 + \partial p_1, p_1) \qquad (5)$$

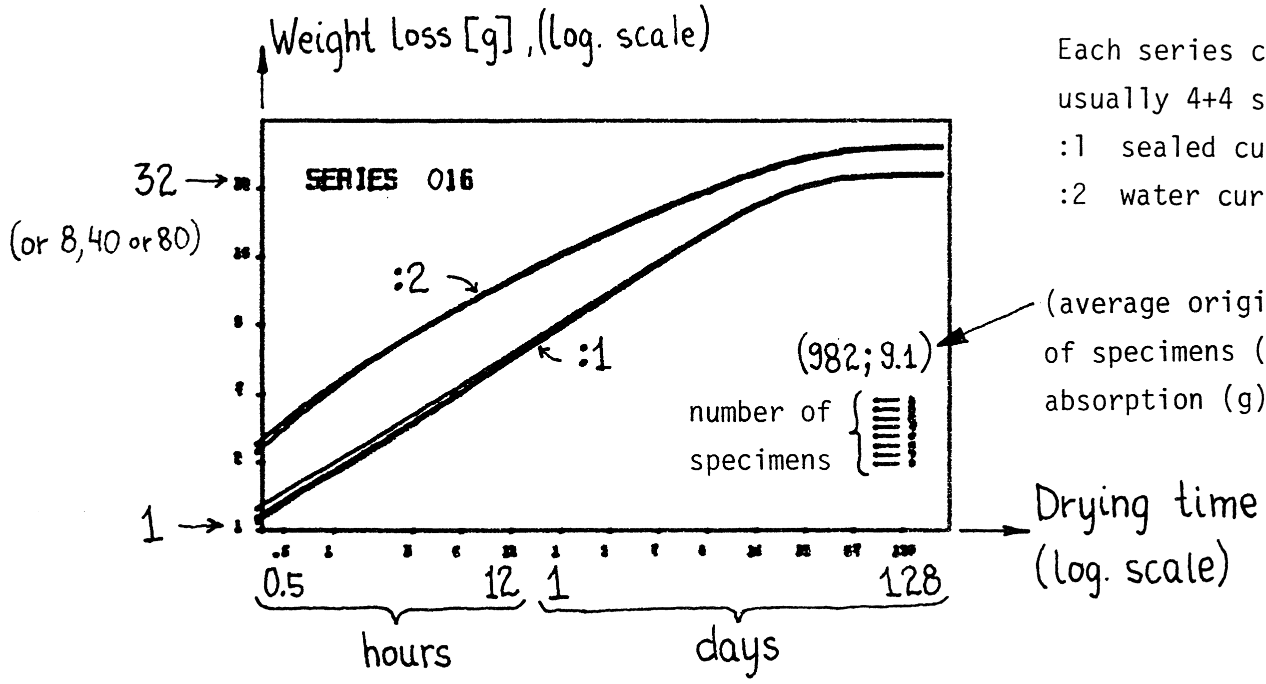
When ∂p_1 (and ∂d) approaches 0 one obtains

$$d\frac{\partial F}{\partial p_1} = k(p_1) \qquad \text{eq. } (5{:}5)$$

APPENDIX IV Results from drying experiments

The complete results of the drying experiments described in 5.2.2 and Tables XIV-XXIII are shown in diagrams on the following pages as weight losses as function of time.

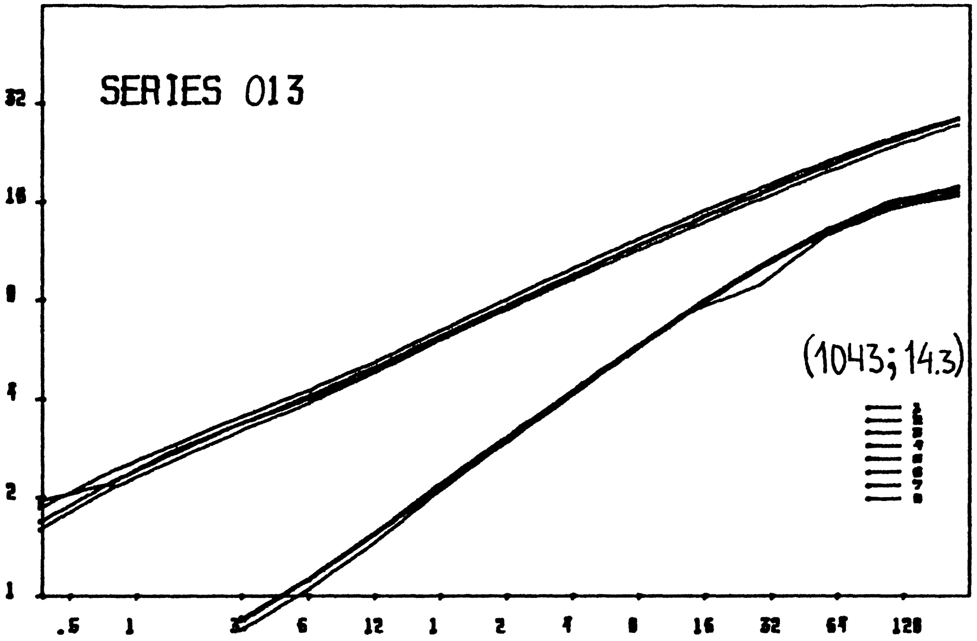
The figures are diminished but in principle they are as follows:



Each series contains usually 4+4 specimens
:1 sealed cured
:2 water cured

(average original weight of specimens (g); water absorption (g) at curing)

Appendix IV contains: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.5
1
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6
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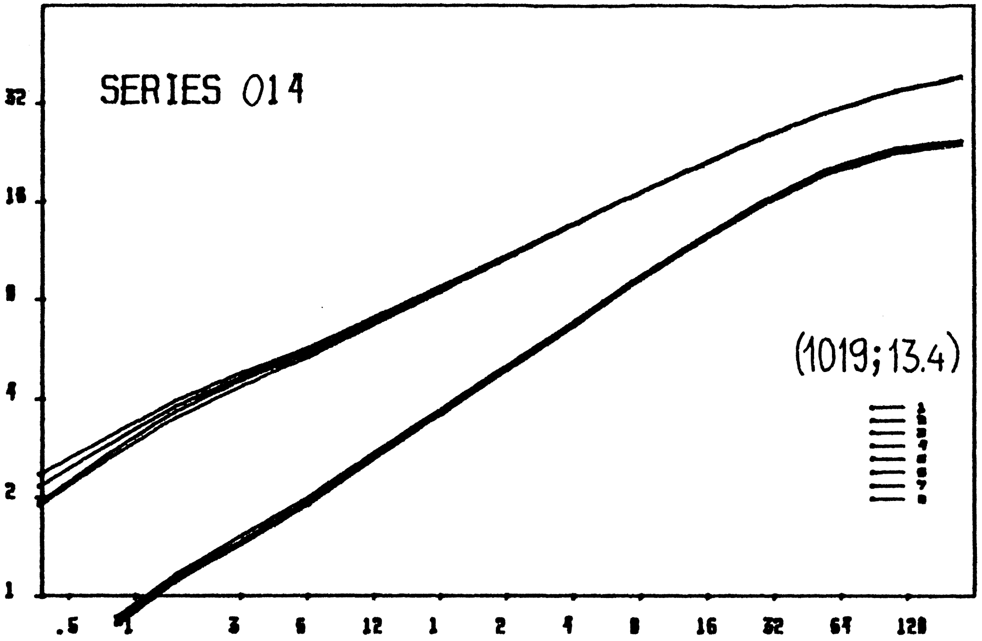
32
64
128
(1043; 14.3)
1
2
3
4
5
6
7
8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128
(1019; 13.4)
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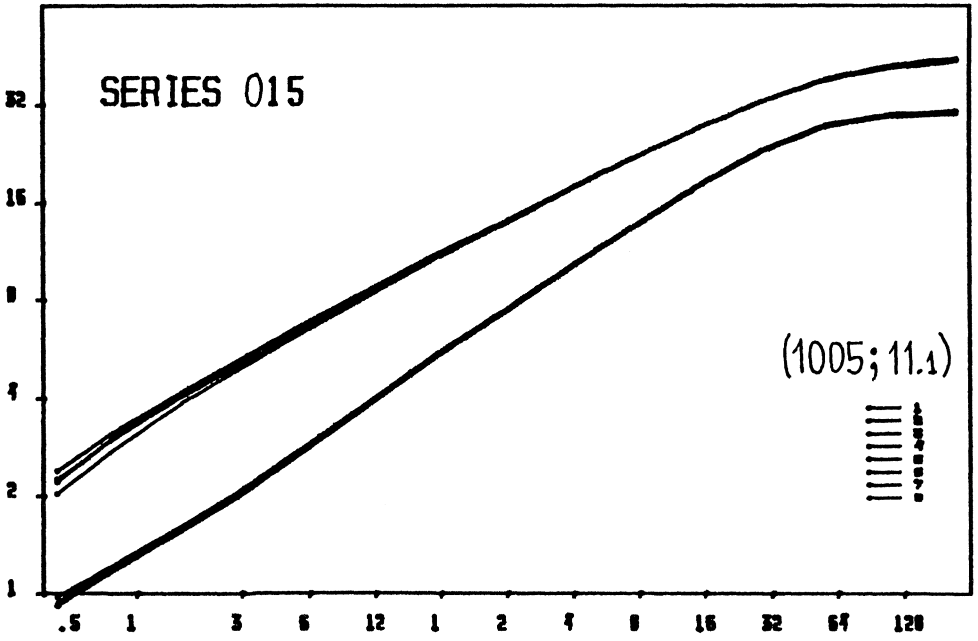
7
8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(1005; 11.1)
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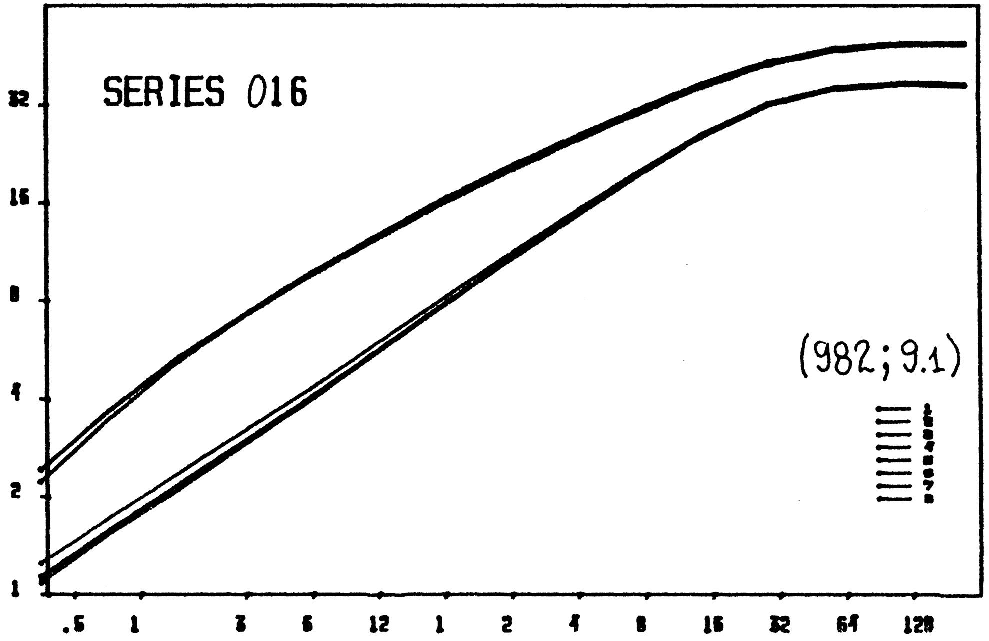
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7
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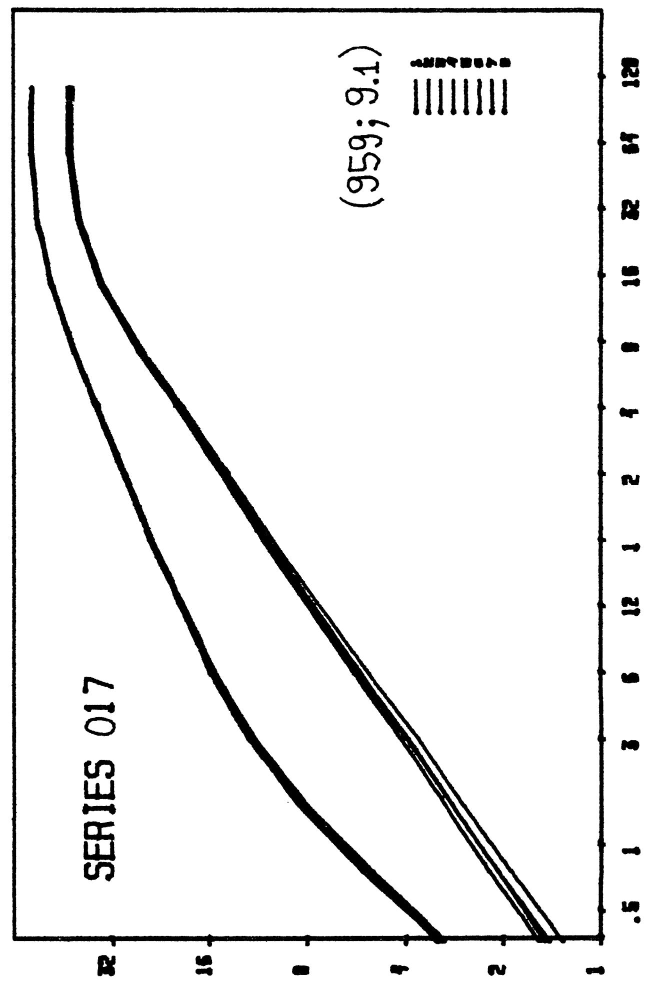
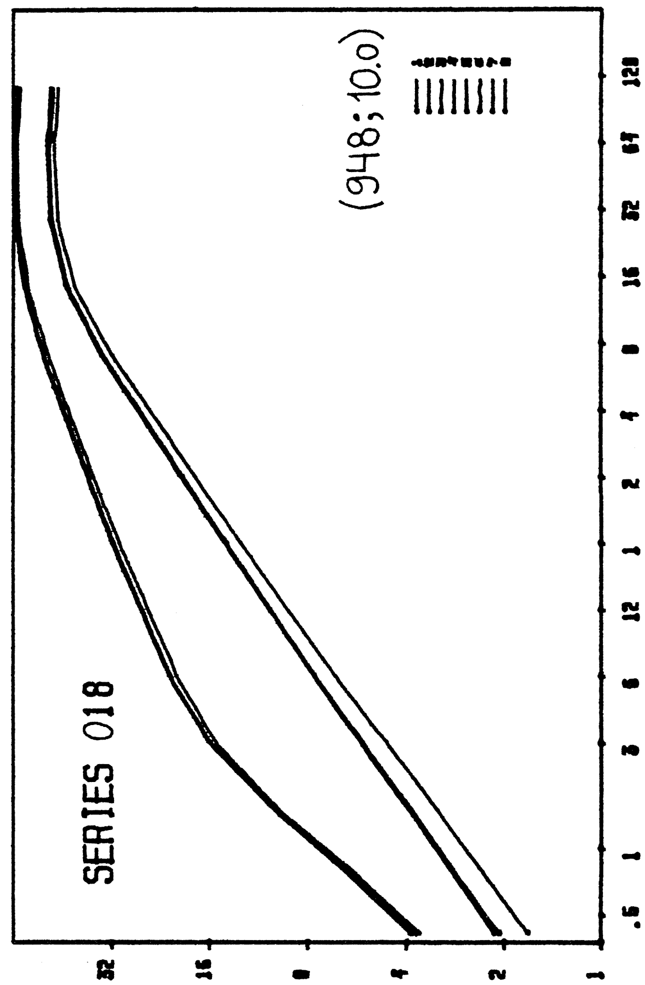


SERIES 017

(959; 9.1)



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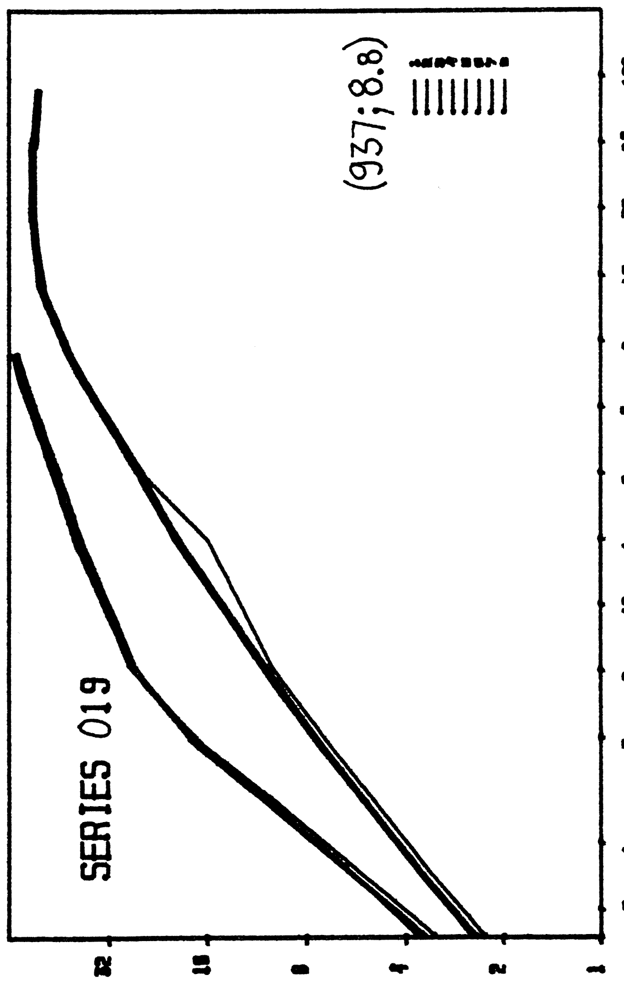

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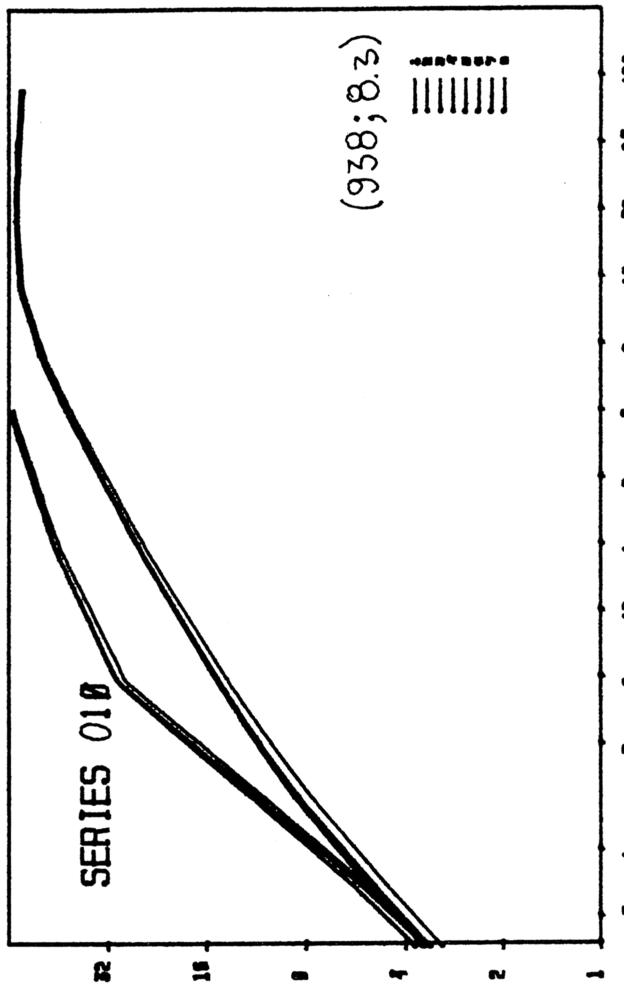

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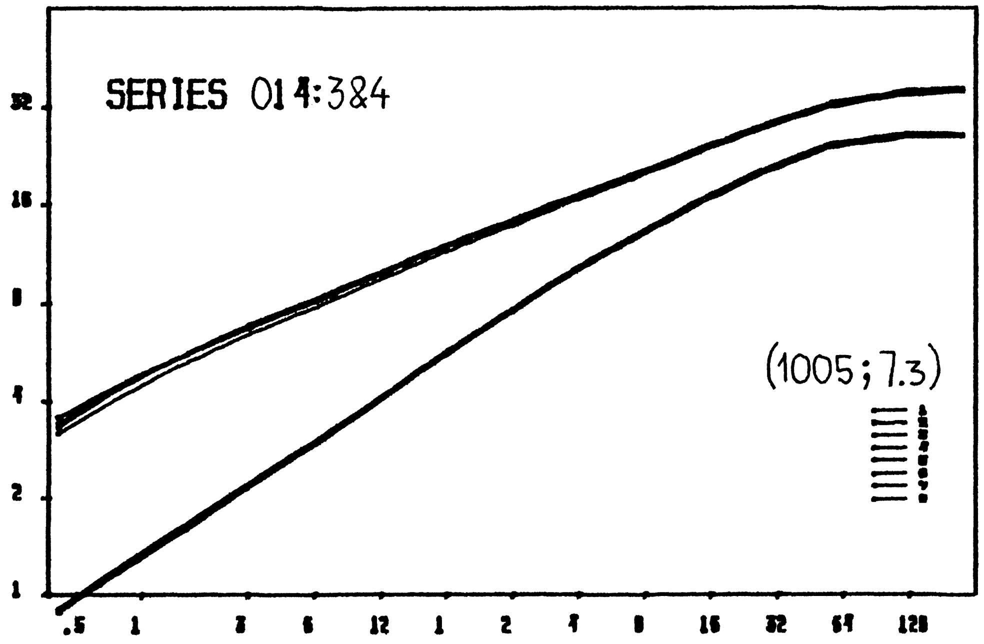
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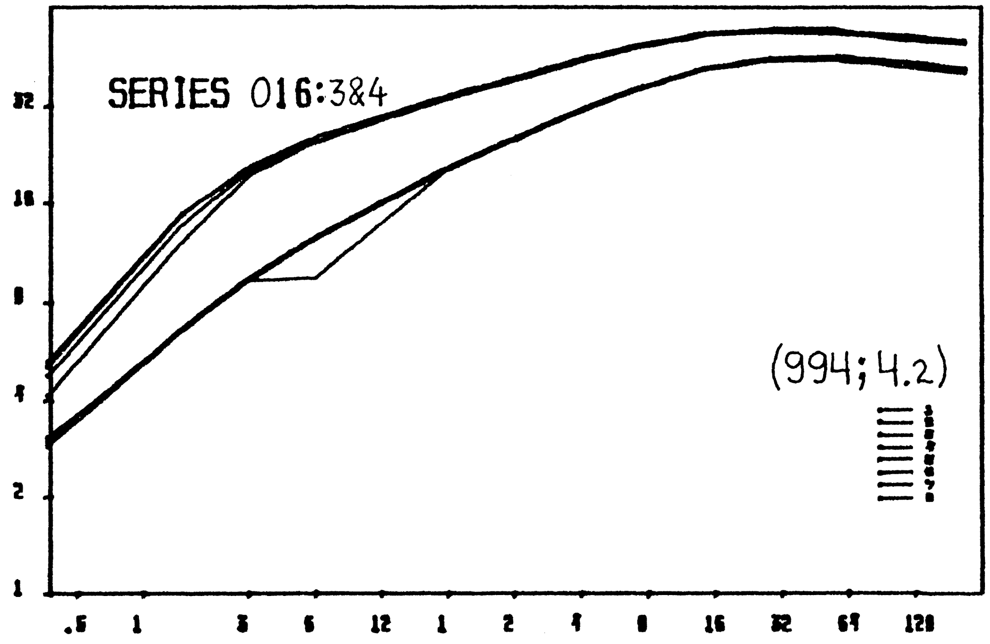
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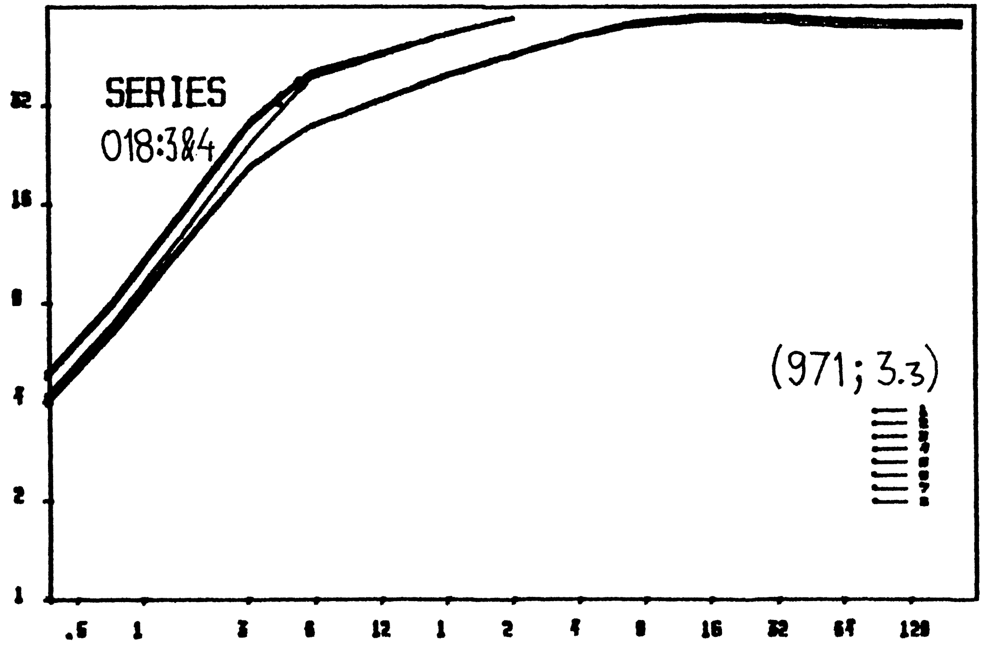
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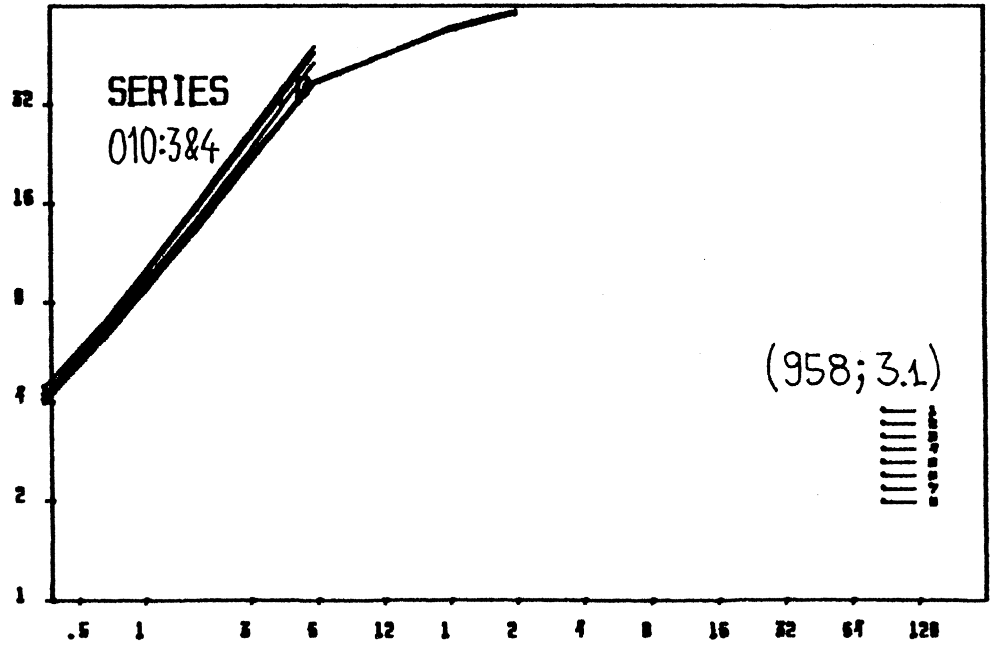
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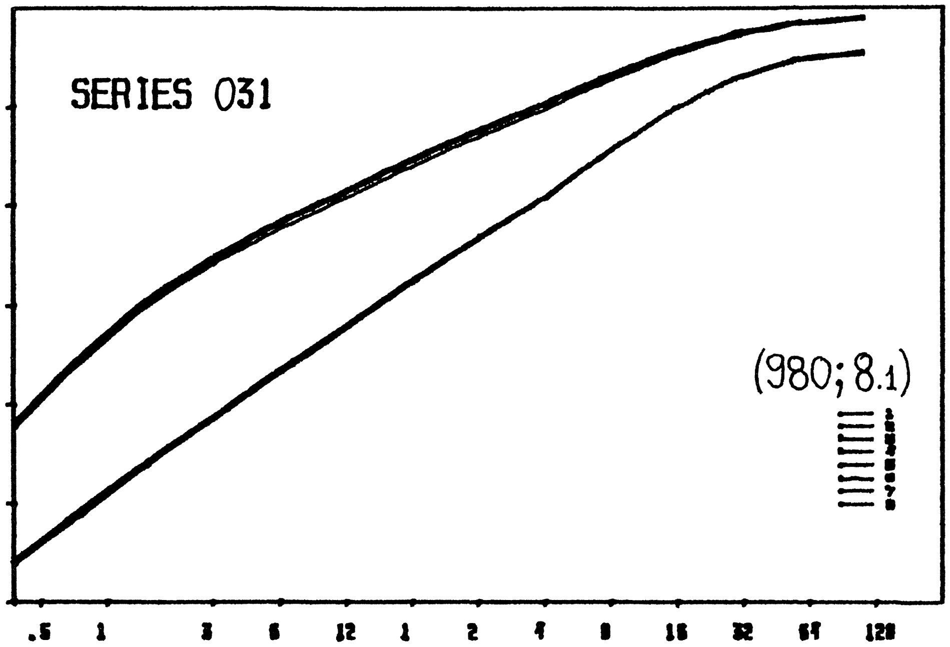
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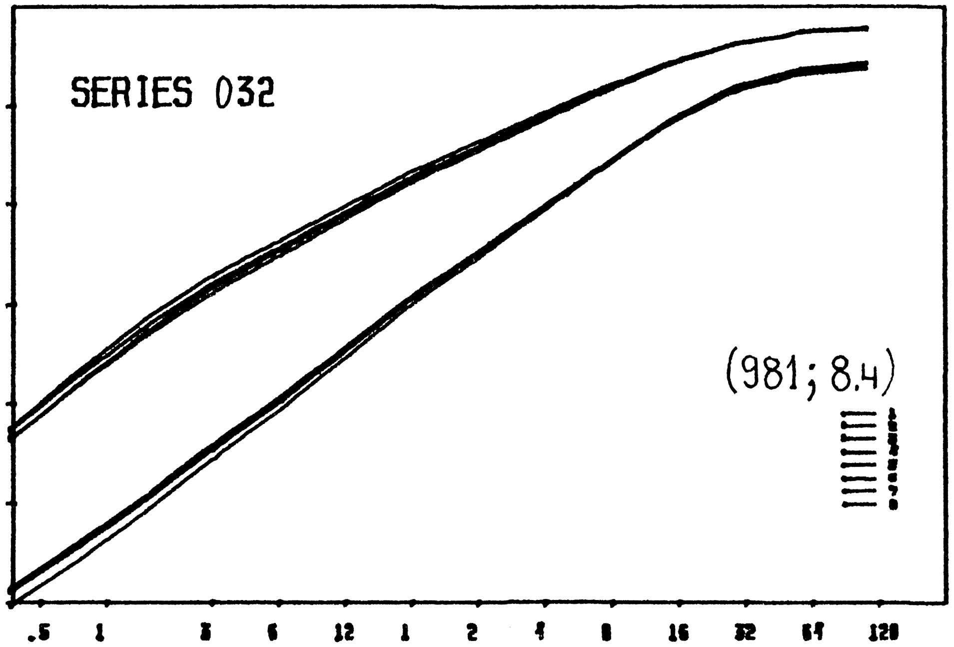
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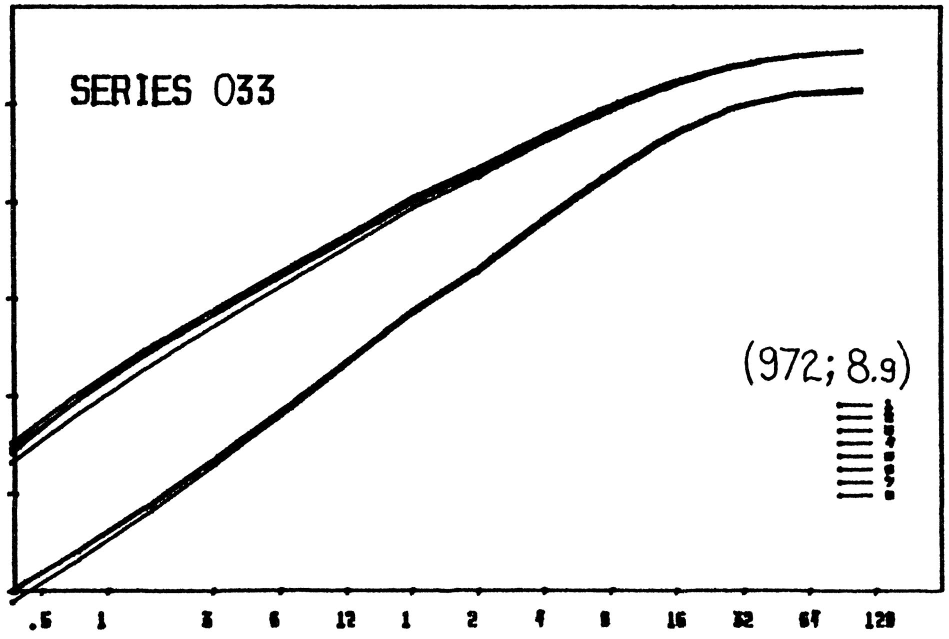
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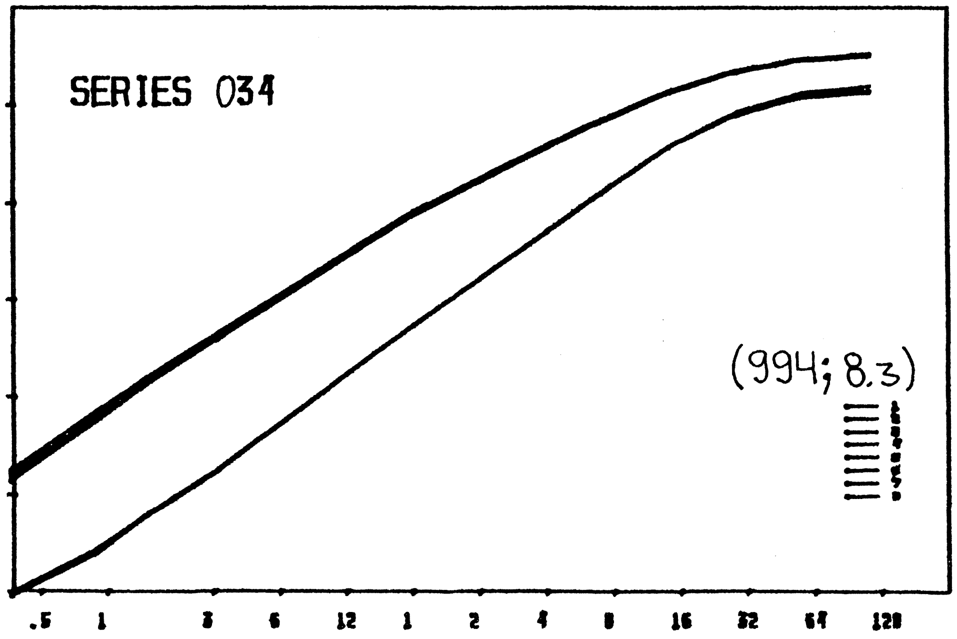
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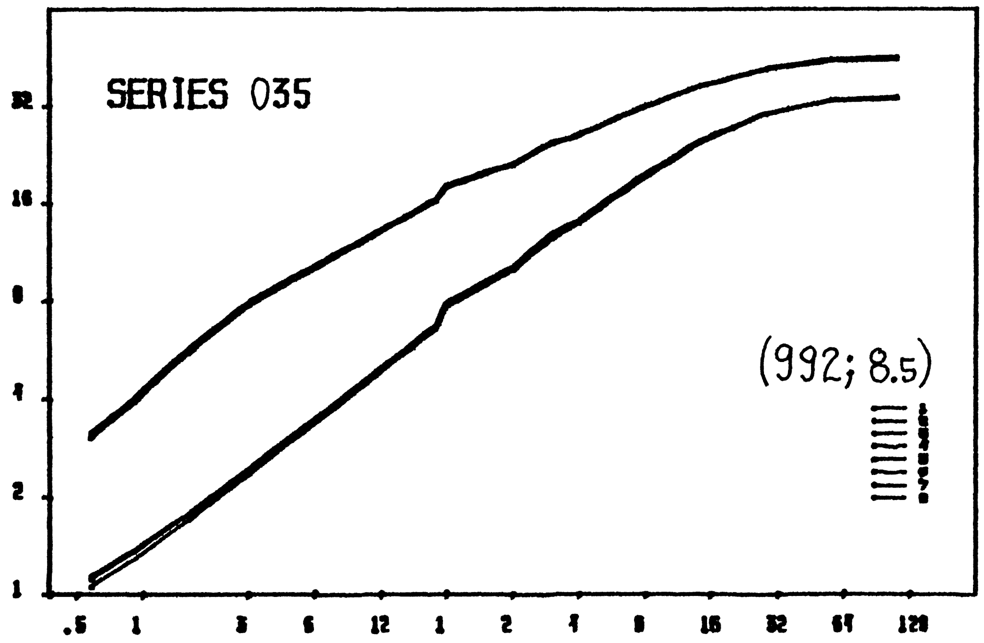
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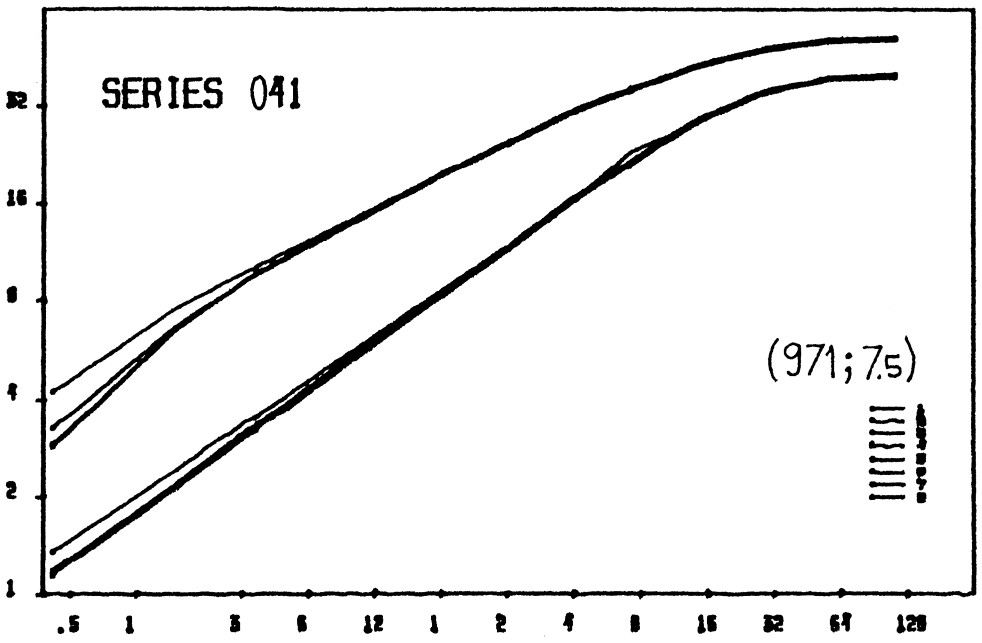
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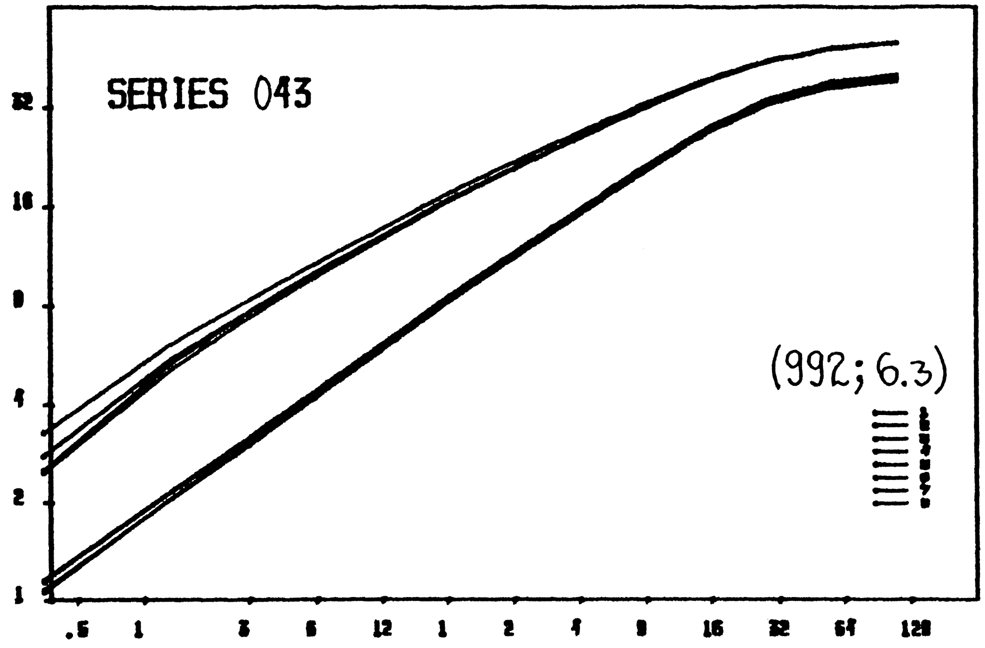
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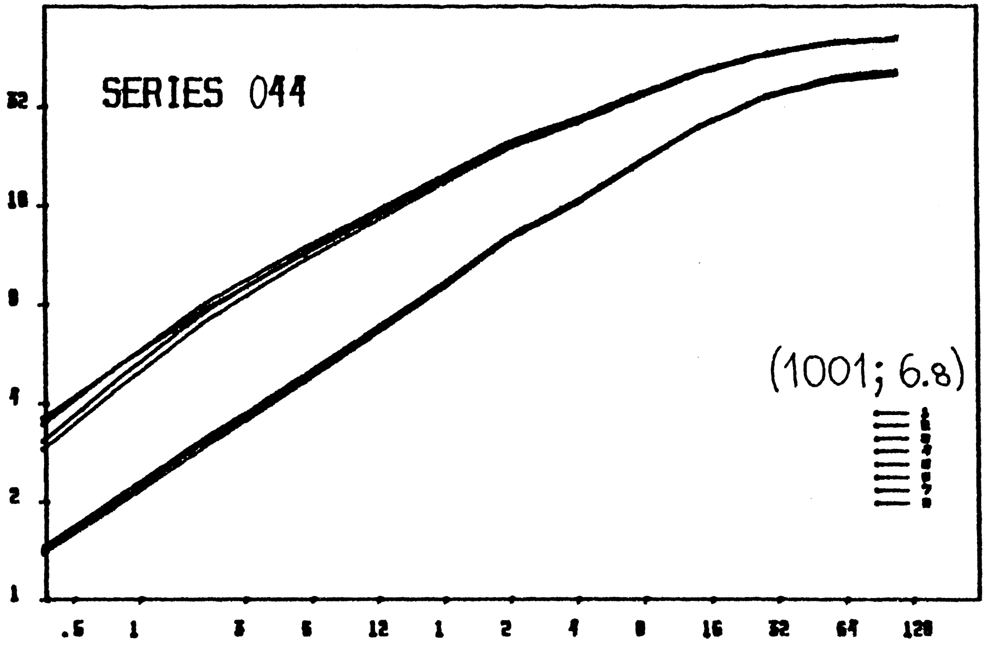
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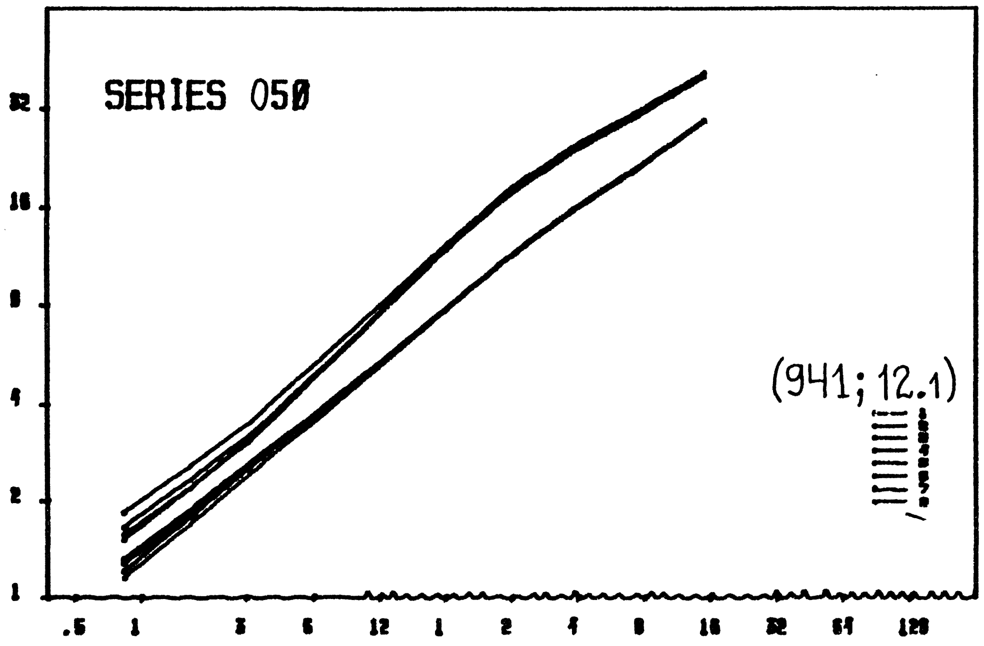
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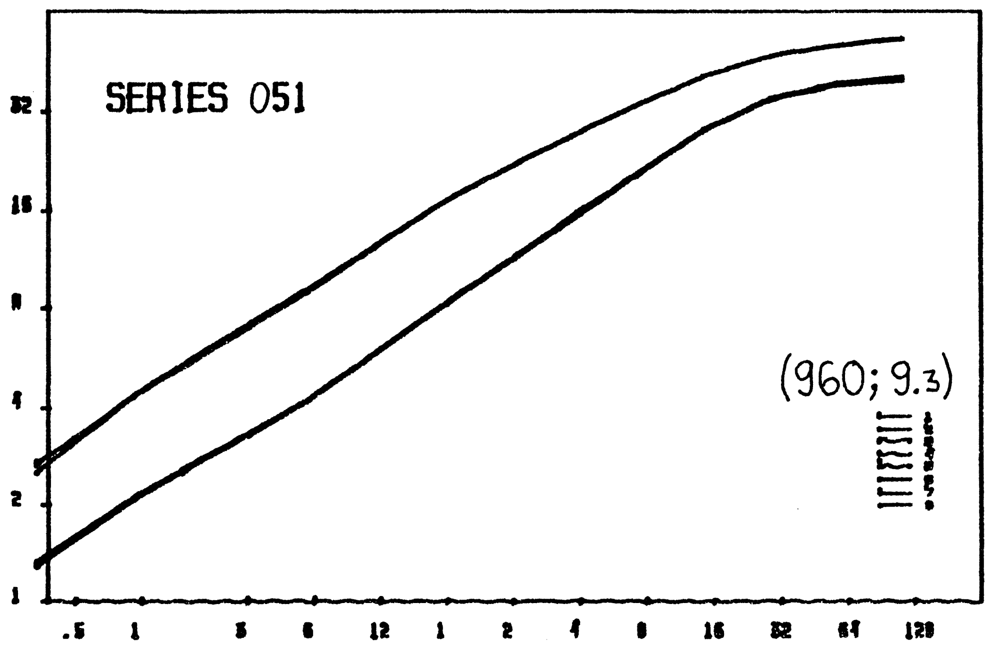
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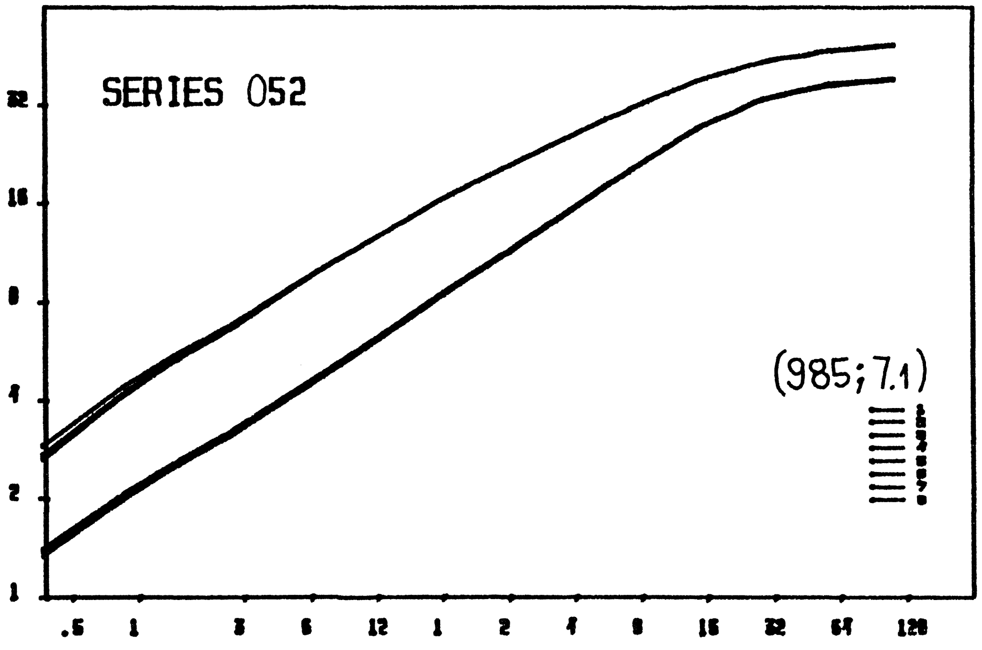
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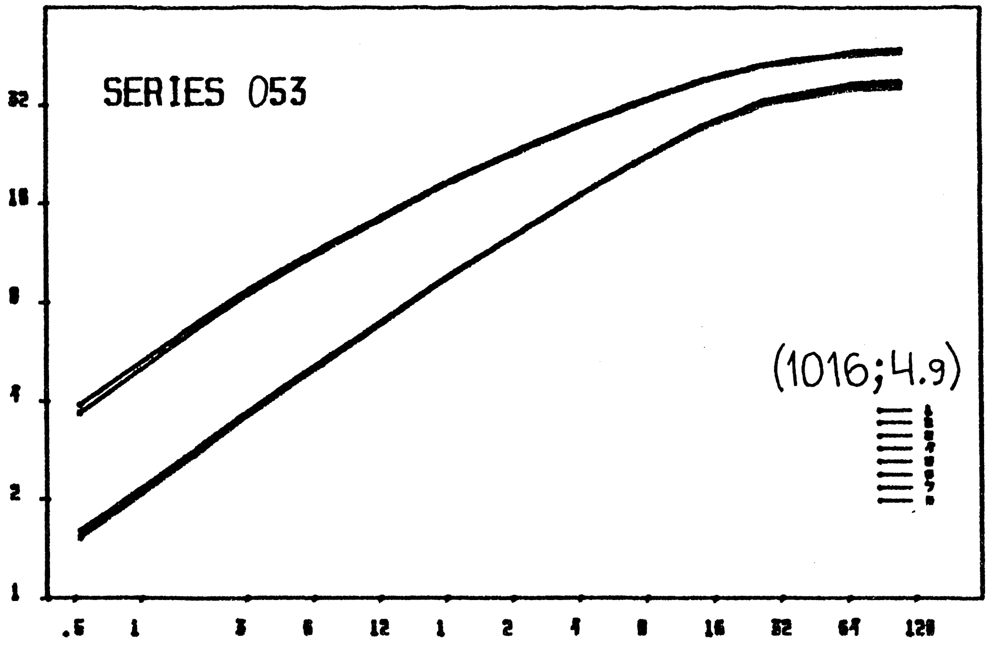
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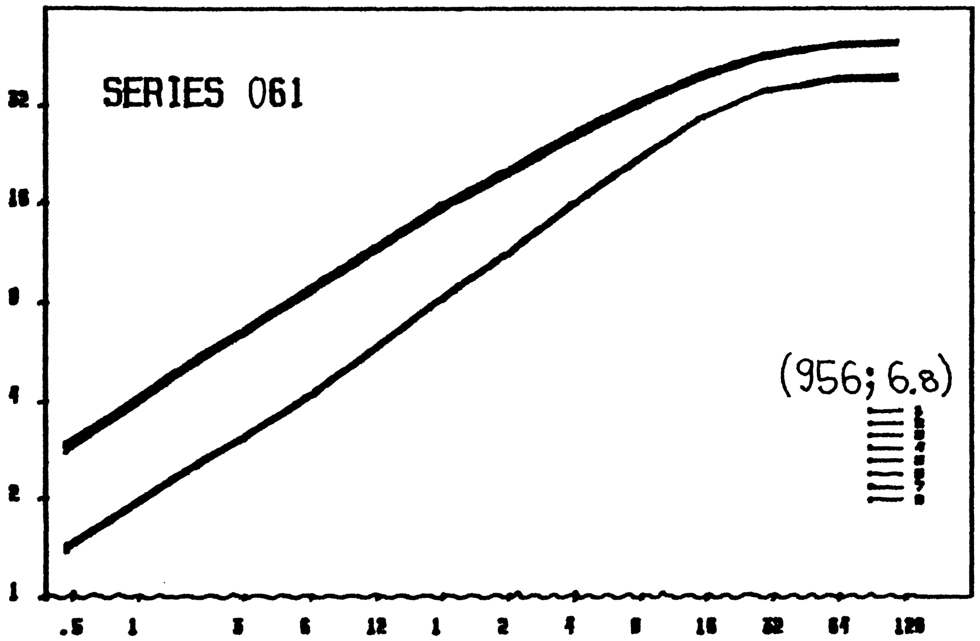
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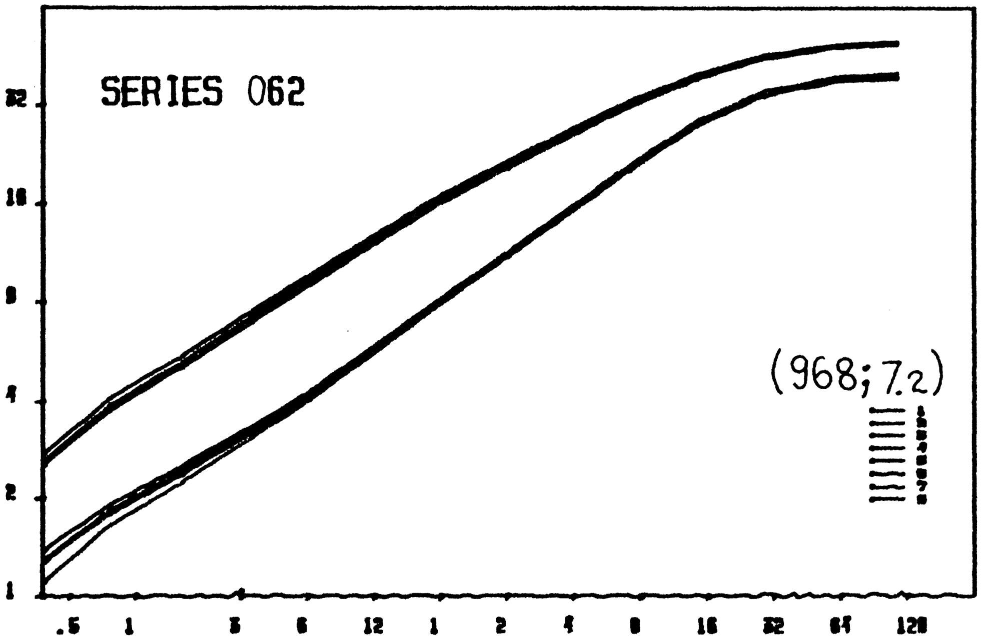
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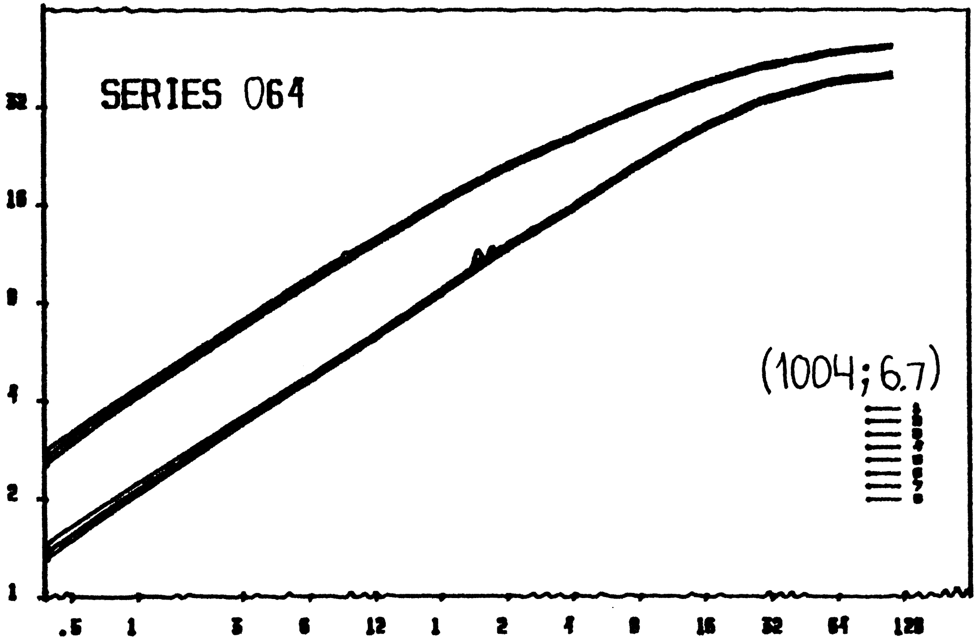
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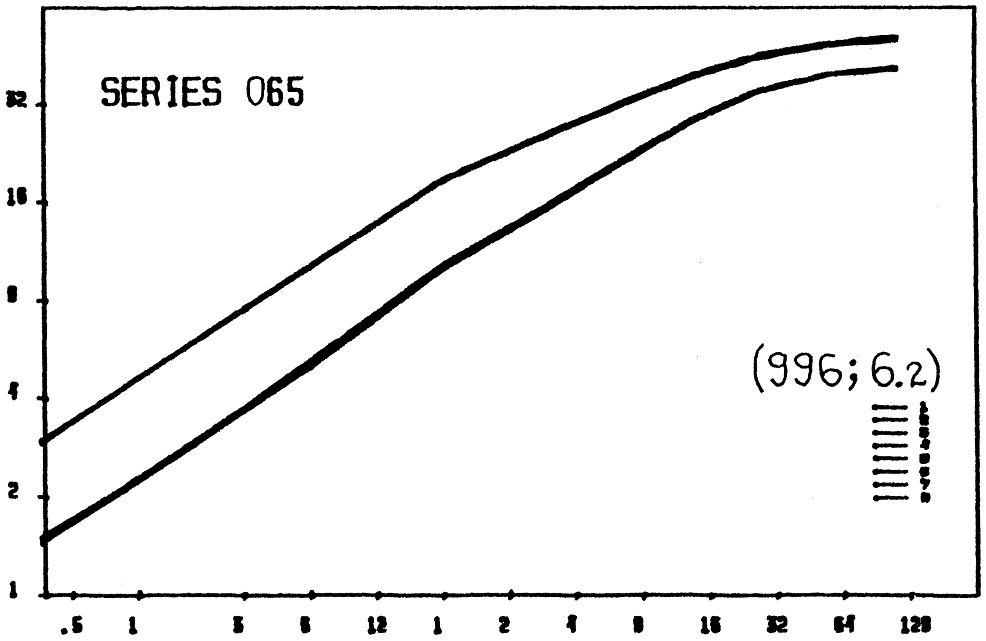
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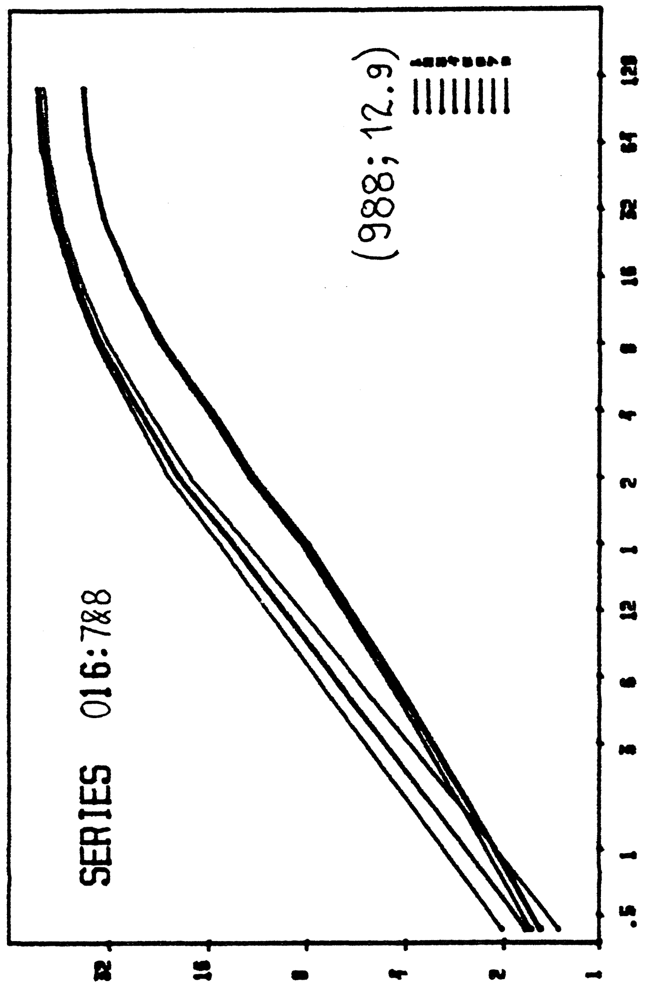
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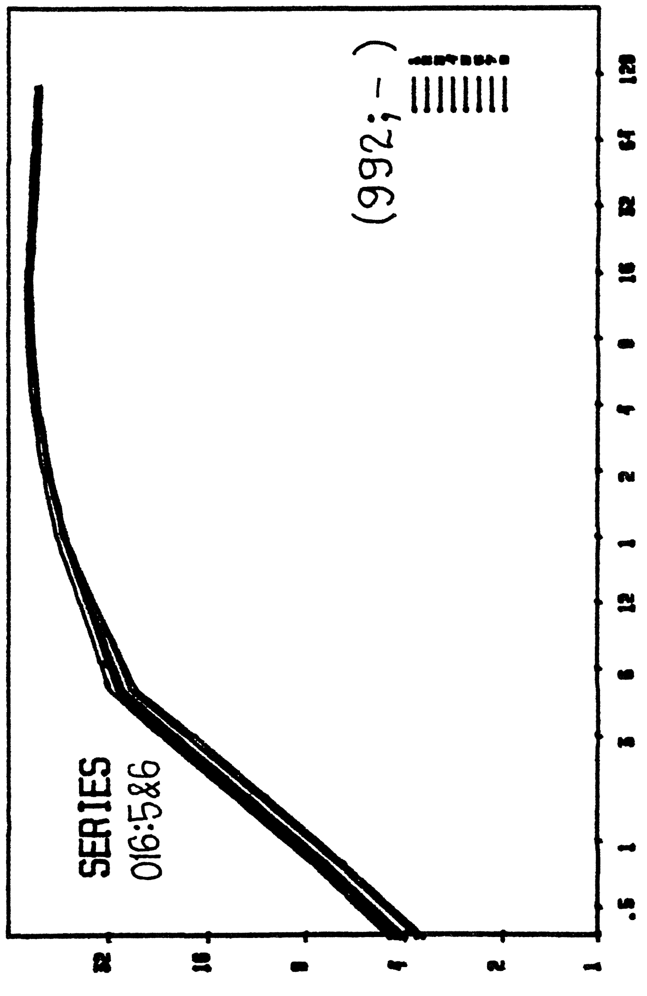
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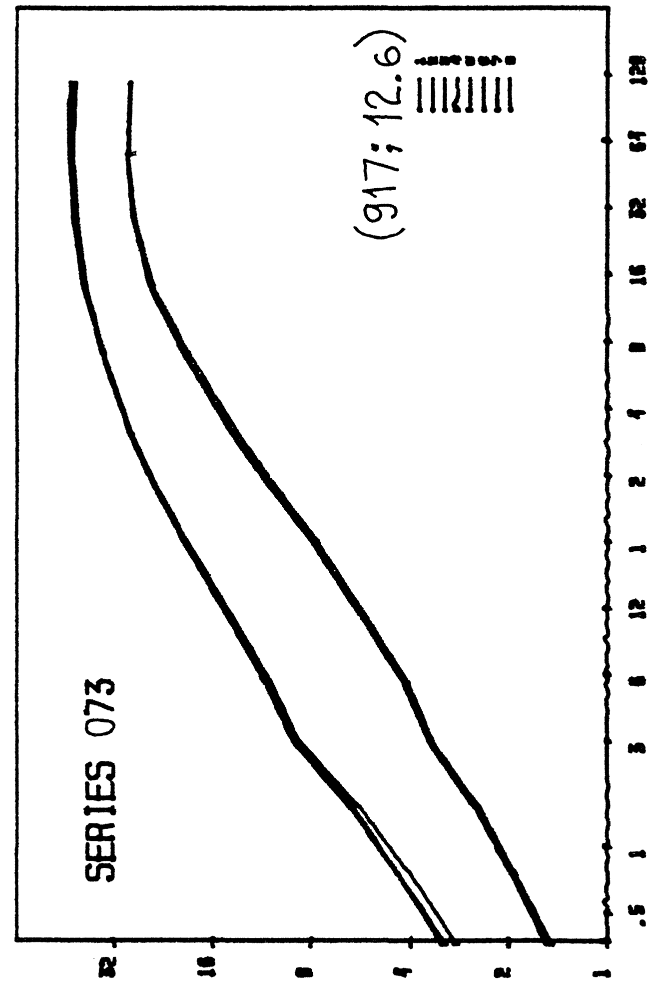
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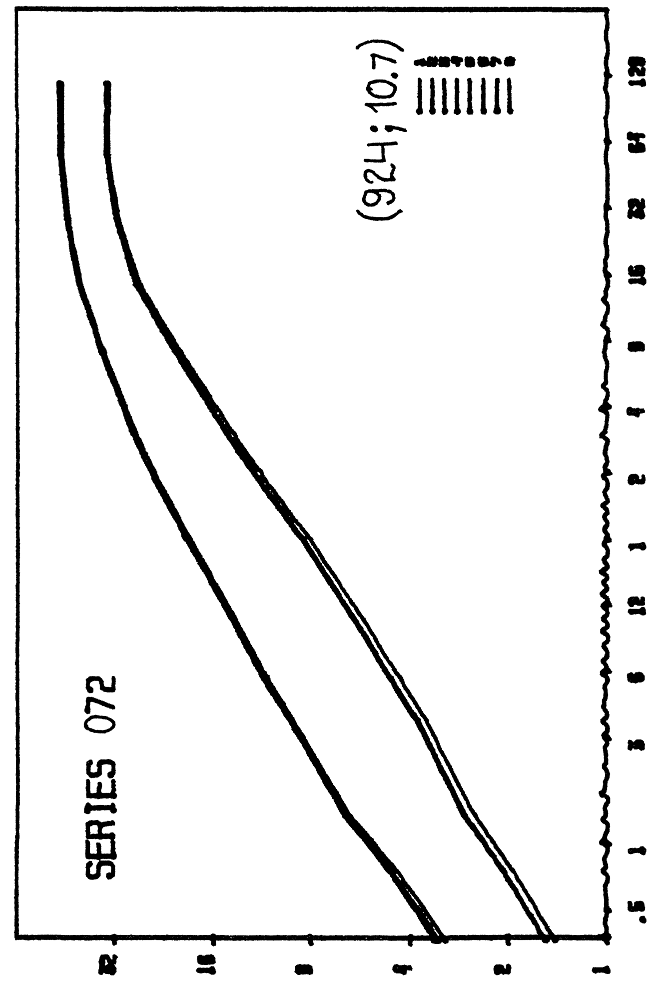
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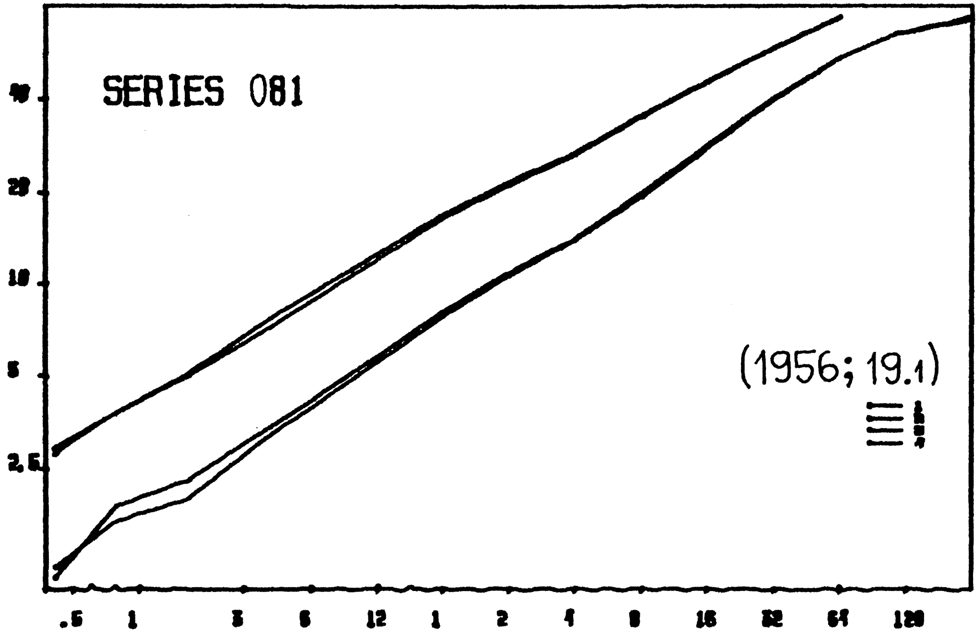
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(1956; 19.1)
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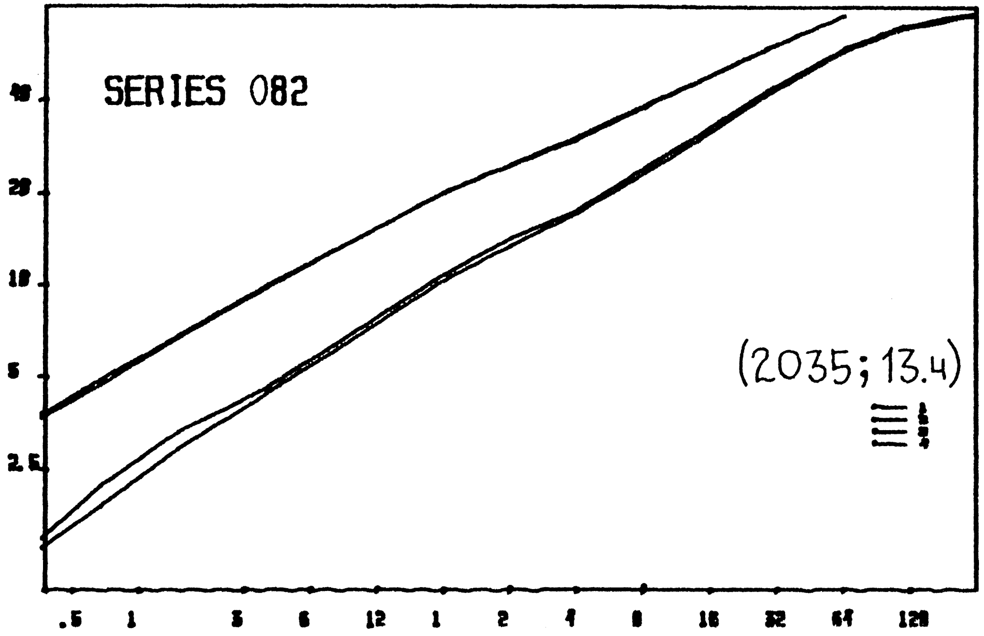
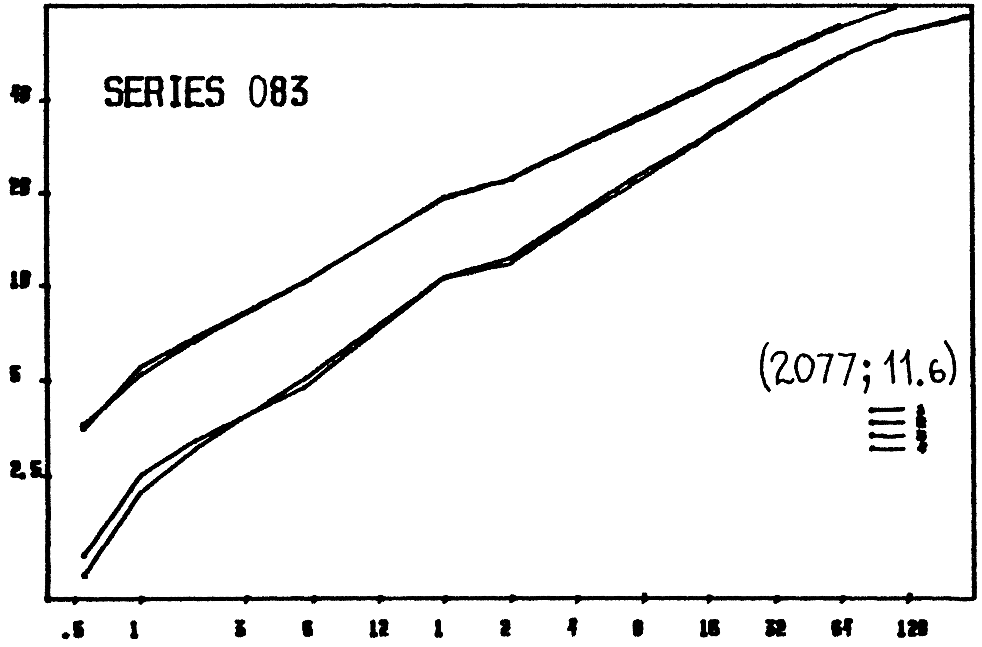
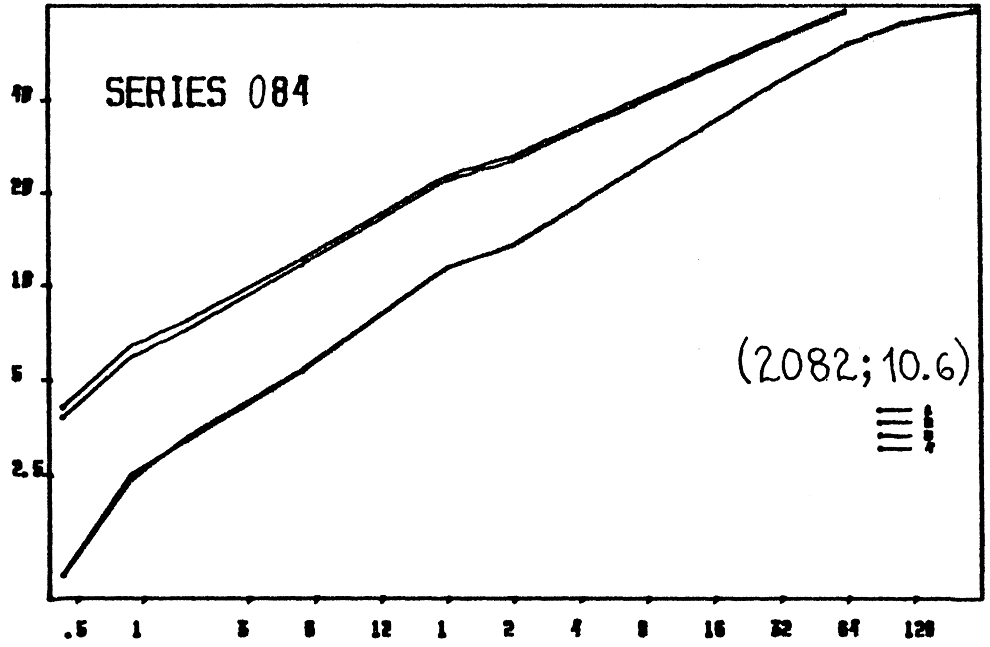
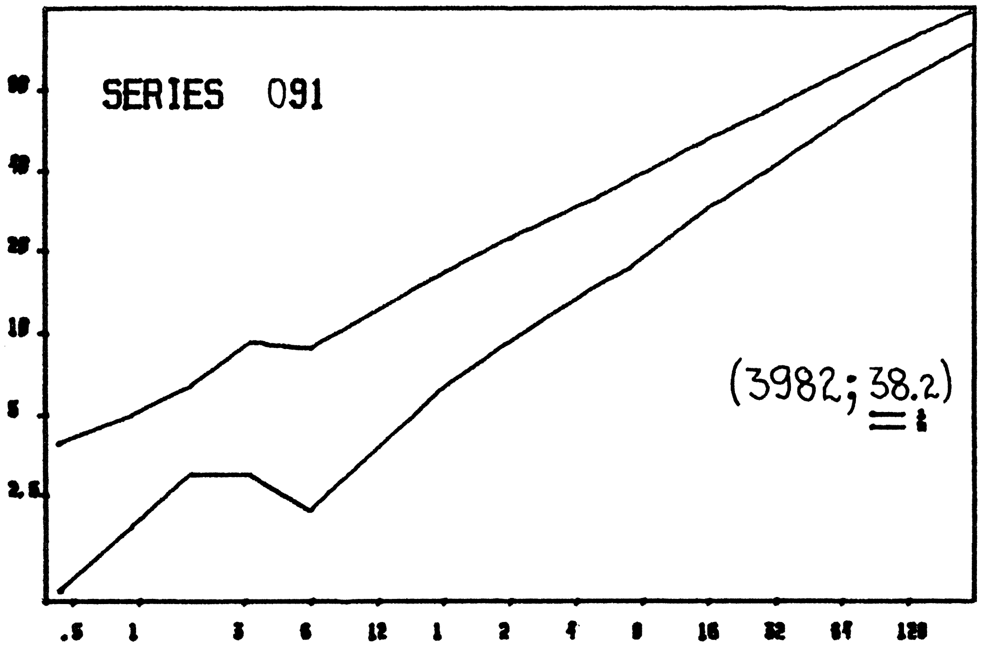
8
16
32
64
128

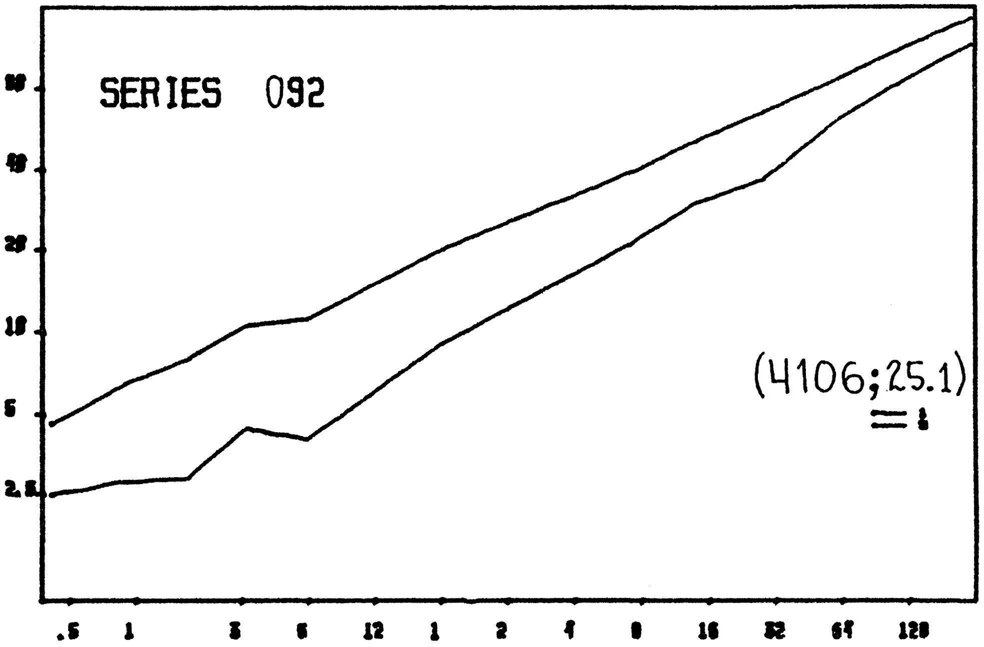

SERIES 082
40
20
10
5
2.5
(2035; 13.4)
.5
1
3
6
12
1
2
4
8
16
32
64
128

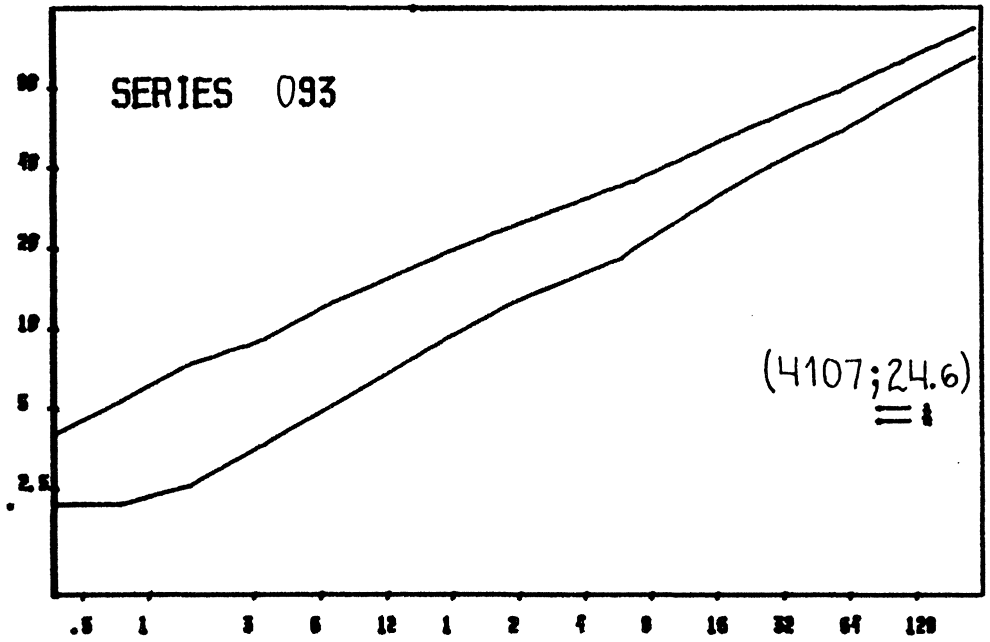

SERIES 083
40
20
10
5
2.5
(2077; 11.6)
.5
1
3
6
12
1
2
4
8
16
32
64
128

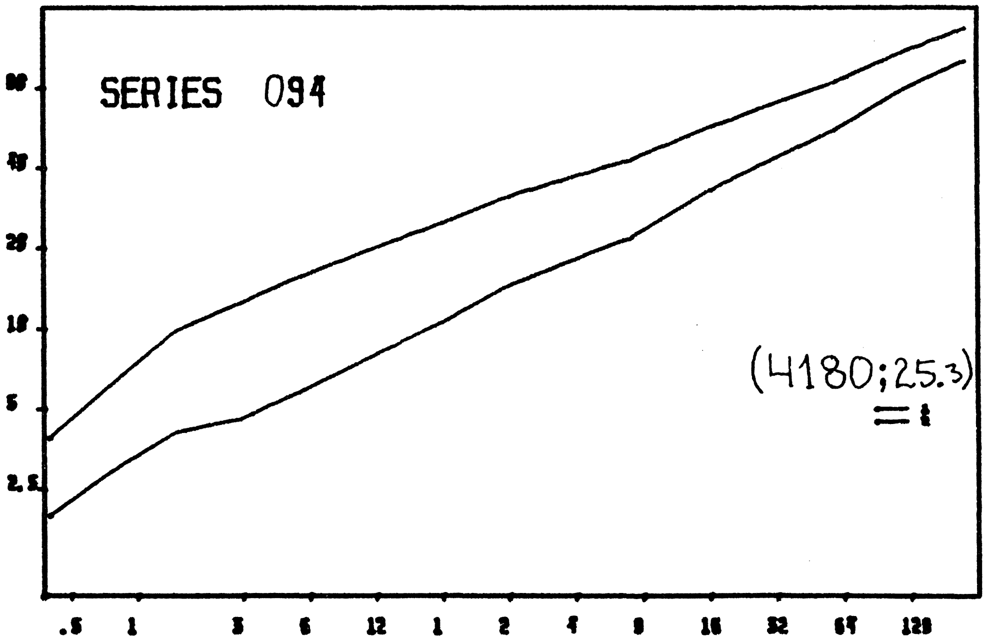

SERIES 084
40
20
10
5
2.5
(2082; 10.6)
.5
1
3
6
12
1
2
4
8
16
32
64
128

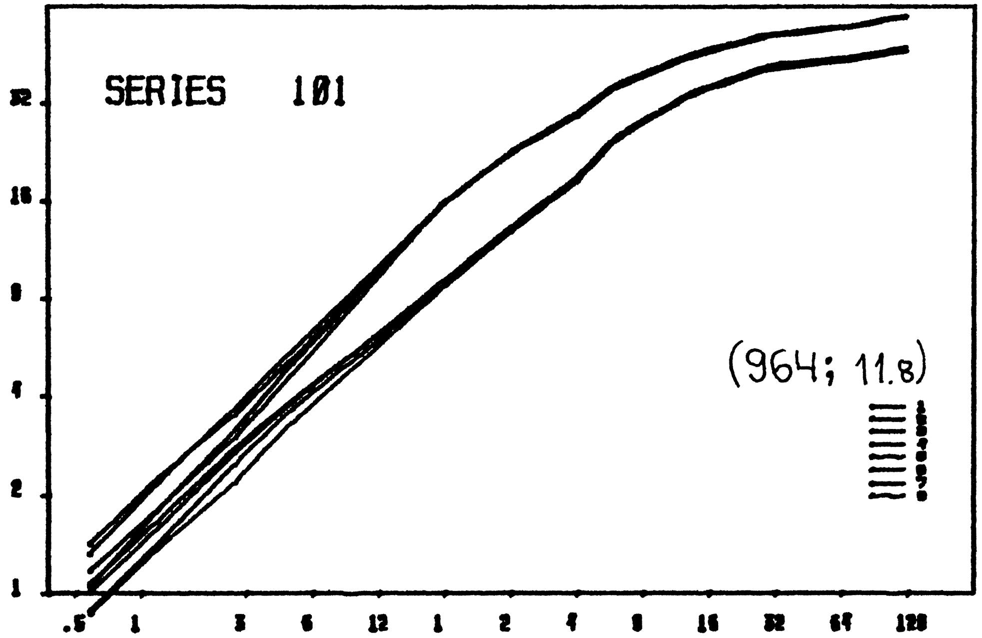
80

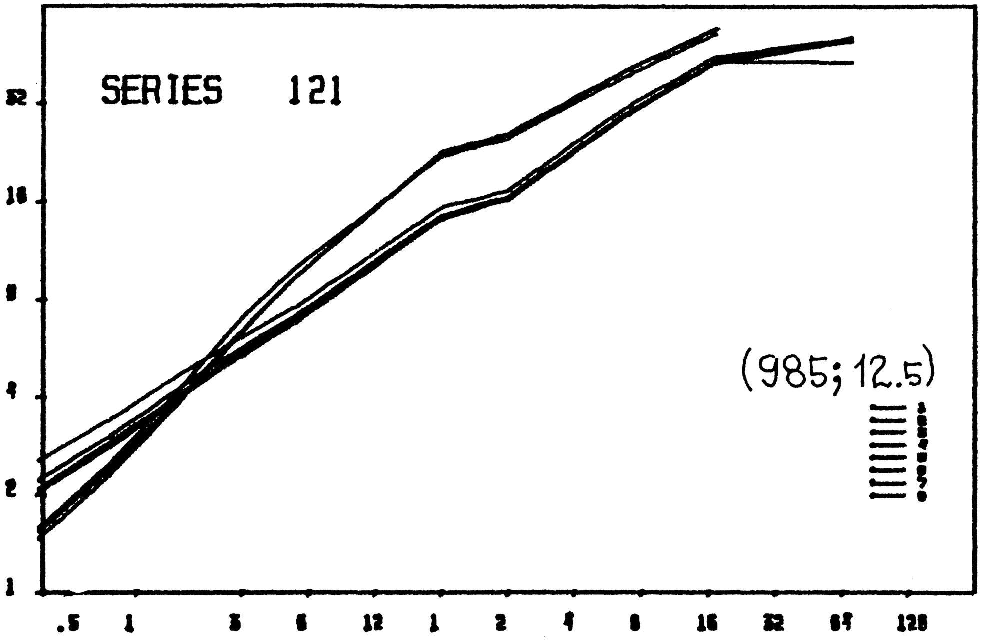

SERIES 091
80
40
20
10
5
2.5
.5
1
3
6
12
1
2
4
8
16
32
64
128
(3982;38.2)

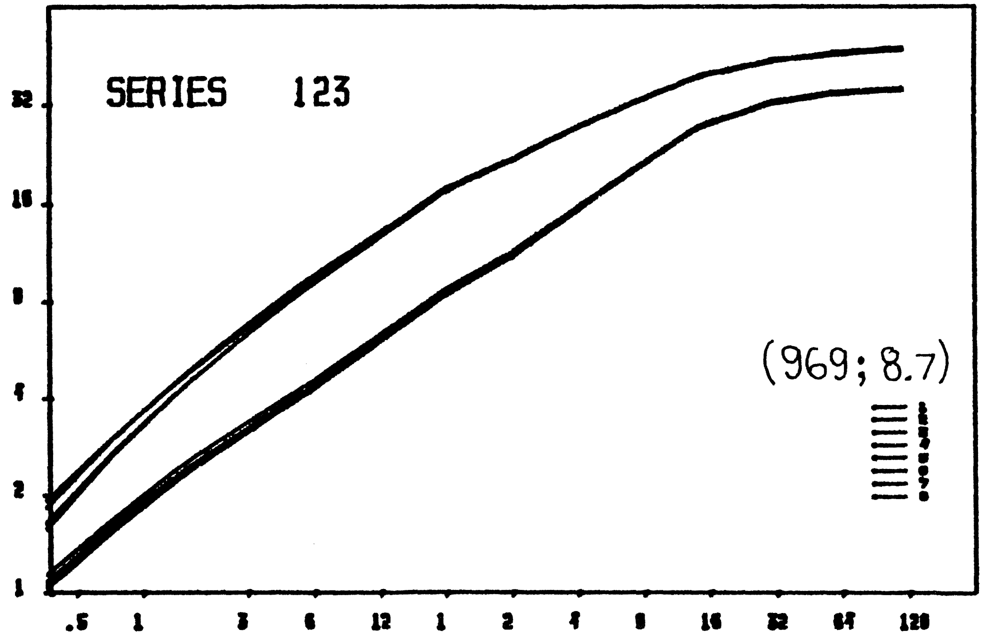

SERIES 092
80
40
20
10
5
2.5
.5
1
3
6
12
1
2
4
8
16
32
64
128
(4106;25.1)

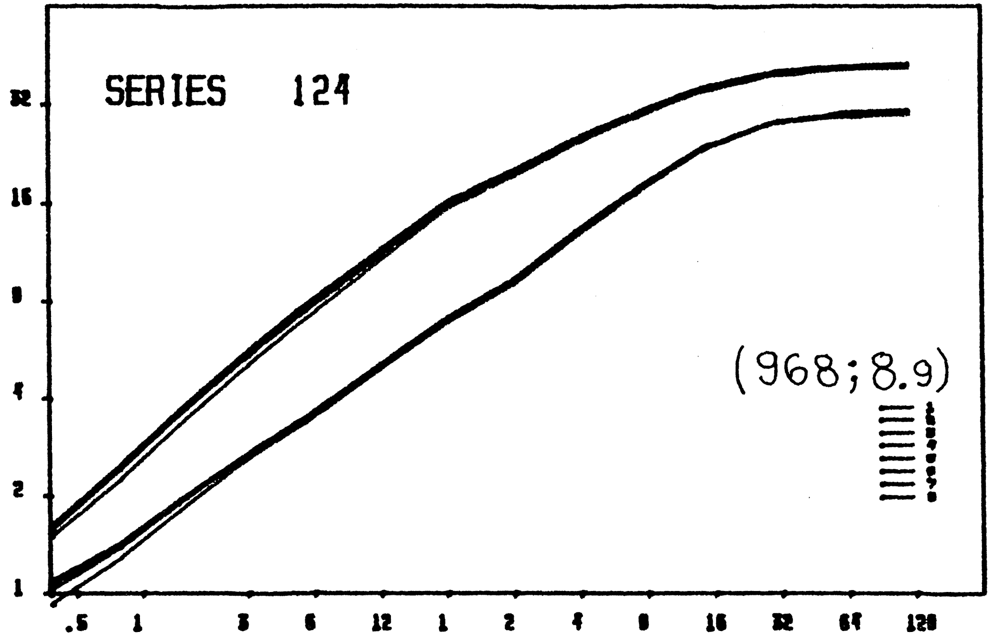

SERIES 093
80
40
20
10
5
2.5
.5
1
3
6
12
1
2
4
8
16
32
64
128
(4107;24.6)

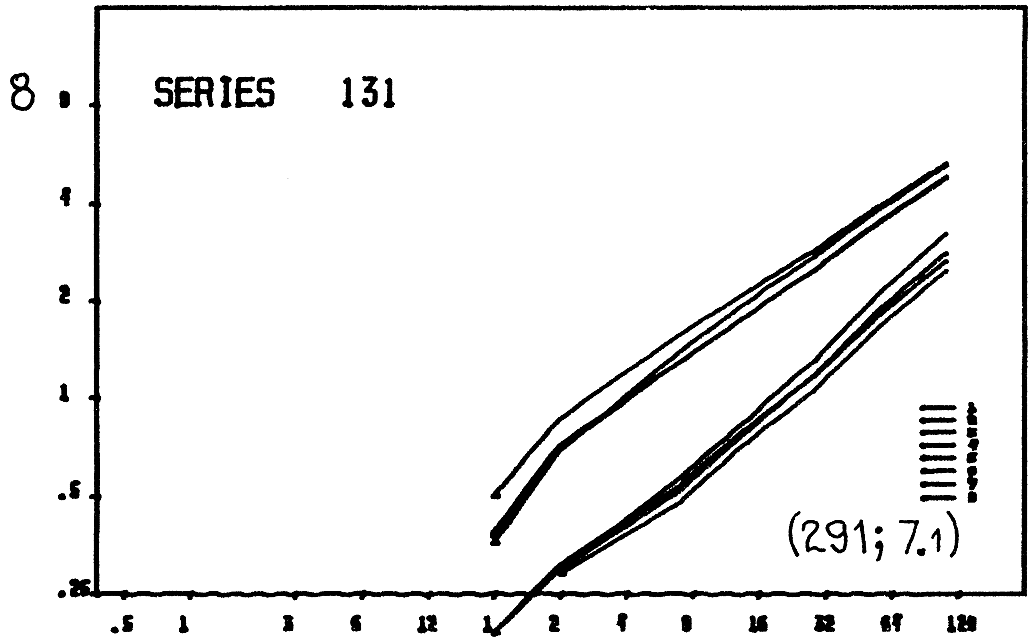

SERIES 094
80
40
20
10
5
2.5
.5
1
3
6
12
1
2
4
8
16
32
64
128
(4180;25.3)

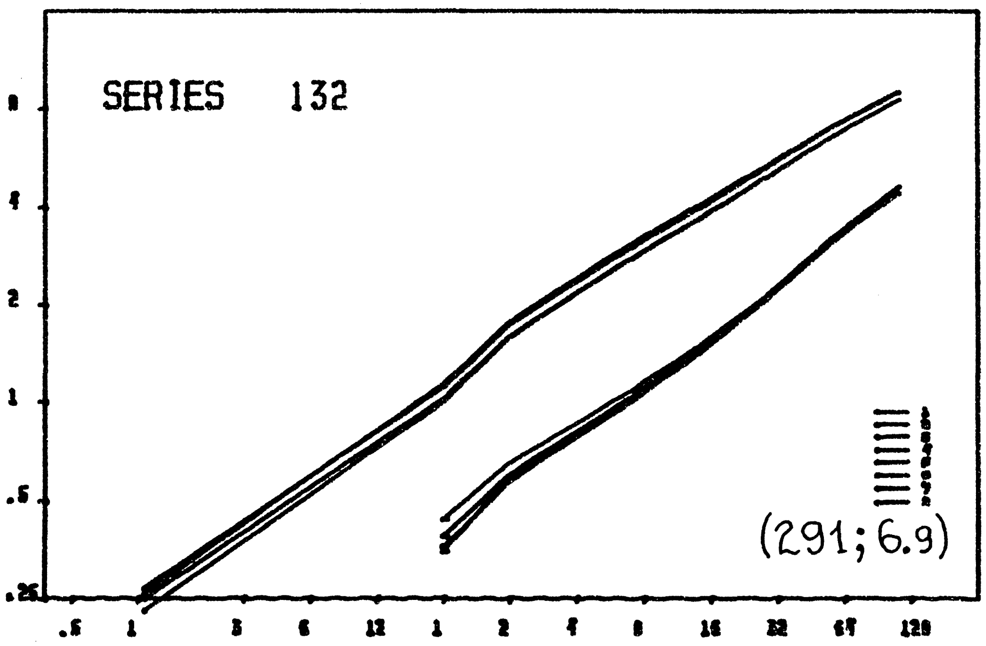

SERIES 101
(964; 11.8)
1
2
3
4
5
6
7
8
32
16
8
4
2
1
.5
1
3
6
12
1
2
4
8
16
32
64
128

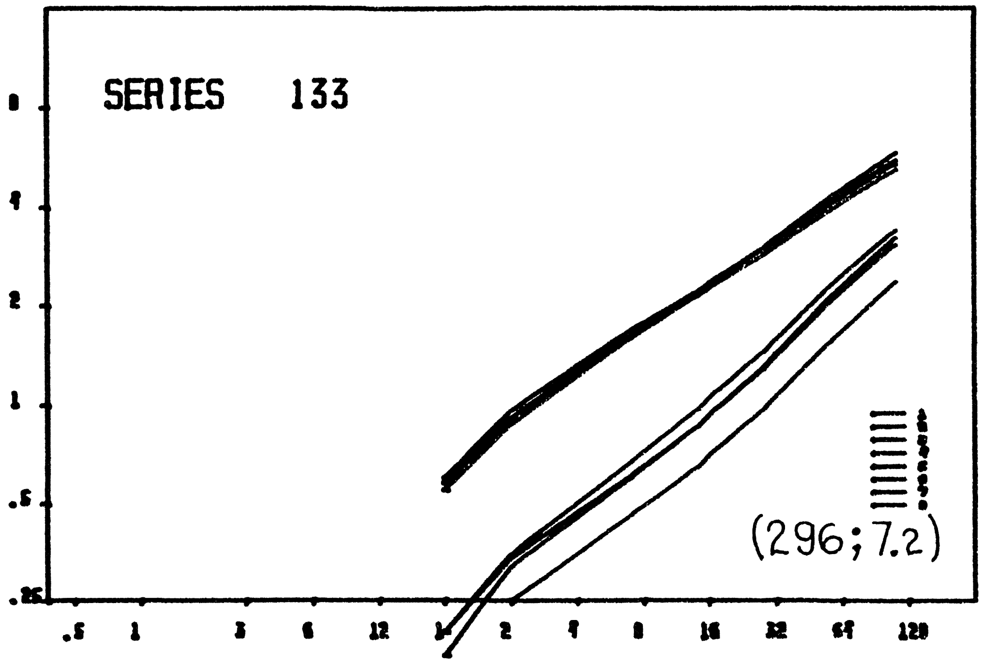

SERIES 121
(985; 12.5)
1
2
3
4
5
6
7
8
32
16
8
4
2
1
.5
1
3
6
12
1
2
4
8
16
32
64
128

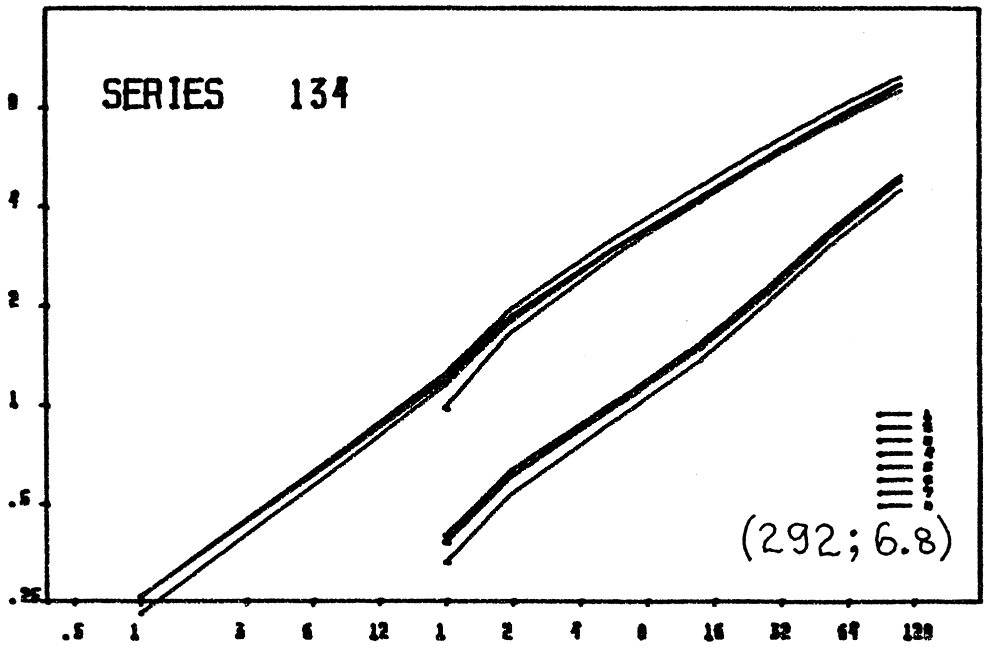

SERIES 123
(969; 8.7)
1
2
3
4
5
6
7
8
32
16
8
4
2
1
.5
1
3
6
12
1
2
4
8
16
32
64
128


SERIES 124
(968; 8.9)
1
2
3
4
5
6
7
8
32
16
8
4
2
1
.5
1
3
6
12
1
2
4
8
16
32
64
128


8
SERIES 131
8
4
2
1
.5
.25
.5
1
3
6
12
1
2
4
8
16
32
64
128
(291; 7.1)


SERIES 132
8
4
2
1
.5
.25
.5
1
3
6
12
1
2
4
8
16
32
64
128
(291; 6.9)


SERIES 133
8
4
2
1
.5
.25
.5
1
3
6
12
1
2
4
8
16
32
64
128
(296; 7.2)


SERIES 134
8
4
2
1
.5
.25
.5
1
3
6
12
1
2
4
8
16
32
64
128
(292; 6.8)