

VALTION TEKNILLINEN TUTKIMUSLAITOS  
STATENS TEKNISKA FORSKNINGSANSTALT  
THE STATE INSTITUTE FOR TECHNICAL RESEARCH, FINLAND

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JULKAISU 100 PUBLICATION

ON THE MAIN FEATURES AND METHODS  
OF INVESTIGATION OF DRYING AND  
RELATED PHENOMENA IN CONCRETE

S. E. PIHLAJAVAARA

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY  
University of Helsinki  
Philosophical Faculty  
Division for Mathematics and Natural Sciences

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## FOREWORD

Since 1961, the author has been engaged in a research project entitled the "Drying of Concrete". The diminution phenomenon, or more generally the change in the moisture content, can be said to constitute the principal factor in the main technical properties of concrete, that is to say its strength and dimensional stability. The strength, its development, and the deformation properties of concrete, such as hydration, drying-strengthening, wetting-weakening, drying-shrinkage and creep, depend essentially upon the moisture content or moisture-content field and the alternations which occur in it. The conclusion can thus be drawn that water plays a vital role in concrete technology.

The work of research has been pursued along two main lines, of which one is an attempt to clarify the drying phenomenon, and the other elucidation of the effects exerted by drying on the properties of concrete. More generally, the principal objects in view are concerned with elucidation of both the variations in moisture and their effects, including closely related phenomena.

During a number of years of activity in research work connected with concrete, later chiefly in concrete physics, it became clear to the author that although a great deal of research had been done to clarify concrete deformations, too few attempts were concerned with elucidation of the basic factor, the moisture-content field in concrete. Subsequently, it became apparent that this observation was not unique, because this subject matter has been accorded ever-increasing international recognition, and the growth in interest has also led to research activity in several countries [1].

Notwithstanding the relatively minor research potential and traditions of the physical research concerned with concrete in Finland, the author started the project, as remarked above, in 1961, has published a number of reports and reviews on the subject [1] ... [10] and has also presented his results to the international conferences held in Paris 1964 [4] and in Helsinki 1965 [7], [8]. The present contribution accordingly represents the author's most recent publication on this subject matter, and will probably not be the last. It may be necessary to stress that this publication is not independent of the former reports, as many of the central ideas, the definitions, and the terminology have been presented in the earlier publications.

The author has been fortunate enough to receive considerable support, both financial and otherwise, from the State Commission for Technology, as well as from different persons at home and abroad with respect to the drying studies on concrete in general. The author wishes to express his gratitude to the Cultural Foundation of Finland for the personal grant given for this publication in particular.

Participation in the international conferences mentioned provided great stimulation, and information on the subject.

Thanks are especially due to my assistant, Mr Esko Pihlman, whose keen interest and assistance proved to be of vital importance to the successful progress of the study.

Aknowledgement is also due to Professor Arvo Nykänen, director of this laboratory, and Dr Viljo Kuuskoski, Professor of Building Technology at the Institute of Technology, who have supported this work in many ways.

The author takes this opportunity to express his deep gratitude to his tutors, Dr P.E. Tahvonen and Dr N. Fontell, professors in the Institute of Physics at the University of Helsinki, for the concern they showed in the author's efforts at the State Institute for Technical Research in general, and in this work in particular.

The preliminary linguistic checking was made by Mrs RakeI Toivola M.A., and the final revision by Mr Fred A. Fewster. Mr Jorma Nyman carried out the major portion of the numerous experimental procedures. Aid was also received in particular determinations from Mr O. Sarlin, student of Technical Physics at the Institute of Technology (gravity experiment, temperature dependence of sorption isotherms), Mr R. Makkonen Lic.Sc. (eng.), research engineer of the Laboratory of Metallurgy in this Institute (carbon dioxide determination with tube furnace), Mr L. Kinnunen, M.Sc., research engineer of the Laboratory of Building Technology in this Institute (determination of porosity with mercury porosimeter). The figures were drawn by Mrs Irja Tennberg.

The author wishes to express his sincere gratitude to all those who assisted him at the different stages of this work.

September, 1965

STATE INSTITUTE FOR TECHNICAL RESEARCH  
Laboratory of Concrete Technology  
Physics Section

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## GLOSSARY

For understanding of some parts of the test there should be borne in mind the author's definitions of a few terms, which are given below. Additional information is contained in [2].

### PART 1

The list is in accordance with the glossary presented by Dr T.C. Powers [20].

**Capillaries, or, Capillary spaces:** in fresh cement paste, the space occupied by water; in mature paste, the pore space in a specimen of paste in excess of about 28 per cent of the volume of the specimen. These spaces are regarded as discontinuities in a mass of cement gel.

**Capillary cavities:** capillary spaces that are isolated by cement gel.

**Cement:** portland cement in the initial, practically anhydrous state.

**Cement gel:** the cohesive mass of hydrated cement in its densest state. It includes gel pores, and has a porosity of about 28 per cent. The solid material is composed mostly of colloids, but non-colloids, particularly calcium hydroxide, are included in this definition. Its overall specific volume is about  $0.57 \text{ cm}^3/\text{g}$  dry weight; when prepared at room temperature its specific surface area is about  $200 \text{ m}^2/\text{g}$  dry weight.

**Cement paste:** the term is applied at any stage of hydration. As applied to fresh paste, it is the mixture of cement and water, exclusive of air bubbles, if any; as applied to hardened paste, it is the rigid body produced by cement and water, composed of cement gel, capillary spaces, if any, and residual cement, if any. When there is neither capillary space nor residual cement, cement paste and cement gel are identical.

**Colloid:** a substance in such physical state that its chemical and physical properties are influenced to a significant degree by the surface energy of the substance. A solid colloidal substance may be amorphous or crystalline, but, if crystalline, the crystals are apt to be imperfectly organized. A colloid is characterized by a high specific surface area. In cement gel calcium hydroxide, and perhaps some other components are not colloidal.

**Gel:** a cohesive mass of colloidal material. (Compare with cement gel).

Gel pores: the pores in cement gel.

Hydrated cement: a collective term for all the chemical species produced by the reactions between cement and water, except transient products of initial reactions.

Pore (in cement paste): space in cement paste that is, or can be, occupied by evaporable water. Its definition, quantitatively, involves a standard method of drying the sample.

## PART 2

Basic-drying: drying process of a fine-porous solid obeying the following conditions 1) surface or surfaces of the body are at constant moisture equilibrium controlled by ambient constant humidity (usually air humidity) during the whole process 2) drying process is isothermal 3) initial moisture content is uniform at the start of drying.

Dehydration: removal of water held to a material by chemical or strong physical forces by heat or by other means of process.

Fixation-drying: water does not escape from the examined body, but drying is caused by the strong fixation of water chemically, and by strong sorption.

Fixed water, or non-evaporable water: consists of the water fixed chemically during the hydration of cement, and of the water fixed by hydration products by strong sorption, which does not evaporate when oven-dried at 105°C, but escapes gradually when heated from 105°C to 550°C in a furnace. It is thus believed that after the ignition at 550°C all fixed water has been released.

Evaporable water, non-fixed water, or free water: the water which escapes from concrete under normal pressure conditions and at an air temperature of 105°C, or in "oven drying" at 105°C, when the temperature and the relative humidity of the ambient air are 20°C and 40 % respectively (Photo 1, Appendix 1).

Evaporation-drying: water escapes from the body under examination into the ambient space, usually into the air, by evaporation (as water vapour).

Moisture, moisture content, or moisture concentration: the amount of evaporable water, generally expressed as its ratio to the volume or weight of concrete dried at 105°C (kg/m<sup>3</sup>, kg/kg), the latter often being expressed also as a percentage.

Mortar, cement mortar  $\equiv$  concrete mortar, a mixture of cement paste and sand (Cf. Standard cement mortar).

Non-evaporable water: see fixed water.

Ovendry (adjective), Oven-dry (verb): dried, or drying, in an oven the temperature of which has been previously fixed at 105°C (see Evaporable water).

Sealed curing: no water exchange between cement paste or concrete body and ambient space, no carbonation, normal air pressure. Specimens in a glass jar equipped with an elastic rubber lid are in practice in sealed curing.

Stable cement paste: scientifically and generally speaking no stable cement paste exists in accordance with present knowledge. For the sake of simplicity and to avoid complexity, however, cement paste may be assumed to be stable in some examinations and in some practical cases in fixed conditions and within limited time. Cf. Unstable cement paste.

Standard cement mortar: generally used for cement testing purposes in Finland; frequently used in making specimens for the experiments presented in this publication. Water-cement ration 0.56 by weight, cement paste-aggregate ratio 1:1.2 by volume, maximum particle size of the standard aggregate (quartz) 1.4 mm [91].

Semi-stable cement paste: "stable" cement paste in which only moisture content variations and related phenomena may cause changes in structure (practically no hydration, no carbonation, no ageing). Cf. Stable cement paste and Unstable cement paste.

Total water content of concrete (cement paste): the total amount of evaporable and fixed water in concrete.

Unstable cement paste: during its life-time cement paste is generally an unstable material. This is due to the continuous change in microstructure brought about by hydration, moisture content and temperature variations, ageing, carbonation. Cf. Stable cement paste.



## NOTATION

a	surface area covered by a gram of moisture ( $\text{m}^2/\text{g}$ )
$a_1$	surface area covered by a single molecule of water ( $\text{m}^2$ )
$a_1$	parameter of carbonation
$a_2$	parameter of carbonation
$a'$	parameter of BET-theory (slope)
$a/c_p$	aggregate to cement paste ratio by volume ( $\text{m}^3/\text{m}^3$ )
B	coefficient
$b'$	parameter of BET-theory (intercept)
b	parameter
C	moisture content (concentration of water that will escape under oven treatment: $t = 105^\circ\text{C}$ ; ambient air $t = 20^\circ\text{C}$ , $\varphi = 40\%$ ) ( $\text{kg}/\text{m}^3$ )
$C_0$	initial moisture content ( $\text{kg}/\text{m}^3$ )
$C_e$	equilibrium moisture content ( $\text{kg}/\text{m}^3$ )
$\bar{C}$	average moisture content in the whole body ( $\text{kg}/\text{m}^3$ )
${}^\circ\text{C}$	moisture content released by carbon dioxide take-up (carbonation) ( $\text{kg}/\text{m}^3$ )
${}^\circ\text{C}_e$	equilibrium or final water content released by the carbon dioxide take-up ( $\text{kg}/\text{m}^3$ )
${}^\circ\bar{C}$	average moisture content released by carbon dioxide take-up in whole body ( $\text{kg}/\text{m}^3$ )
$C^{cp}$	moisture content of cement paste ( $\text{kg}/\text{m}^3$ ), or in concrete as expressed for cement paste in concrete only ( $\text{kg}$ moisture in concrete/ $\text{m}^3$ cement paste in concrete)
$C_0^{cp}$	initial moisture content in cement paste ( $\text{kg}/\text{m}^3$ )
$C_e^{cp}$	equilibrium moisture content in cement paste ( $\text{kg}/\text{m}^3$ )
c	cement; basis: after ordinary storage in sacks (kg)
$c_0$	cement; basis: after ignition at $1000^\circ\text{C}$ (kg). On the average $1.05c_0 = c$
$c'_0$	cement, material insoluble in HCl excluded (kg)
D	carbon dioxide content (take-up) ( $\text{kg}/\text{m}^3$ )
$D_0$	initial carbon dioxide content ( $\text{kg}/\text{m}^3$ )
$D_e$	equilibrium carbon dioxide content ( $\text{kg}/\text{m}^3$ )
$\bar{D}$	average carbon dioxide content in the whole body ( $\text{kg}/\text{m}^3$ )
d	parameter; symbol indicating differentiation
e	parameter
G	gravity term in the drying theory ( $\text{kg}/\text{m}^3\text{s}$ )
h	time; also as dimension, hour

I	$\int_0^z u dz$
$\vec{i}_g$	unit vector in the direction gravitation
J	moisture flux (kg/m <sup>2</sup> s)
j	carbon dioxide take-up (kg)
j <sub>0</sub>	initial amount of carbon dioxide take-up (kg)
j <sub>e</sub>	equilibrium or final amount of carbon dioxide take-up (kg)
K	strength of concrete (kp/cm <sup>2</sup> )
k	moisture conductivity (m <sup>2</sup> /s)
k <sub>e</sub>	moisture conductivity at equilibrium (m <sup>2</sup> /s)
<sup>c</sup> k	carbonation conductivity (m <sup>2</sup> /s)
kg	gravitational mobility of moisture (m/s)
L	penetration depth of carbonation (m)
l	characteristic thickness (e.g. half-thickness of a slab drying on both surfaces in Fourier number) (m)
l'	length (m)
Δl'	change in l' (m)
M	mass (of a body) (kg)
M'	molecular weight (g/mole)
M <sub>0</sub>	initial mass of a body at the start of drying (kg)
M <sub>e</sub>	equilibrium mass of a body at the end of drying (kg)
<sup>c</sup> M	mass gained in carbon dioxide take-up (carbonation) (kg/m <sup>3</sup> )
<sup>c</sup> $\bar{M}$	average mass gain in the carbon dioxide take-up in the whole body (kg/m <sup>3</sup> )
<sup>c</sup> M <sub>e</sub>	mass gained when the carbon dioxide take-up has reached its ultimate value (equilibrium) (kg/m <sup>3</sup> )
M(h)	maturity factor
N	Avogadro's number (1/mole)
n	parameter, exponent
O(...)	order of magnitude
p	partial water vapour pressure in the air (mmHg)
p <sub>s</sub>	saturated partial water vapour pressure in the air (mmHg)
Q <sub>ag</sub>	aggregated content of concrete (kg/m <sup>3</sup> )
Q <sub>c</sub>	cement content used in making of concrete (kg/m <sup>3</sup> )
Q <sub>w</sub>	water content used in making of concrete (kg/m <sup>3</sup> )
q	parameter
RH	relative humidity of the air
r	= (D - D <sub>0</sub> )/(D <sub>e</sub> - D <sub>0</sub> ) relative carbon dioxide content (take-up) at a point of a body
$\bar{r}$	= ( $\bar{D}$ - D <sub>0</sub> )/(D <sub>e</sub> - D <sub>0</sub> ) the relative average carbon dioxide content (take-up) of a body
S	specific surface area (m <sup>2</sup> /g)

$S_{cp}$	specific surface area of cement paste ( $m^2/g$ )
$S_C$	source of moisture due to carbonation ( $kg/m^3s$ )
$S_H$	sink of moisture due to hydration (water fixation) ( $kg/m^3s$ )
$S'$	unrestrained linear shrinkage strain ( $= \Delta l'/l'$ )
$S'_{\infty}$	final shrinkage strain ( $S'$ at $h = \infty$ )
$s$	relative shrinkage ( $= S'/S'_{\infty}$ )
$t$	temperature ( $^{\circ}C$ ). Exception: $t = hk_g/l$ dimensionless time variable (in Table 1)
$u$	$= (C - C_e)/(C_0 - C_e)$ relative moisture content in a point of a body
$\bar{u}$	$= (\bar{C} - C_e)/(C_0 - C_e)$ relative average moisture content of a body
$V$	volume (of a body) ( $m^3$ )
$v$	air velocity (m/s); exception: equilibrium moisture content (Section 7.63) ( $kg/kg$ )
$v_m$	moisture content of monomolecular layer ( $kg/kg$ )
$w$	water used in making paste or concrete (kg)
$w_n$	non-evaporable water, fixed water (kg)
$w_f$	evaporable water, "free" water, moisture (kg)
$w/c$	water cement ratio ( $kg/kg$ ) used in making cement paste or concrete
$\Delta w$	decrease of moisture content due to hydration or fixation drying (kg)
$x$	coordinate (m)
$z$	dimensionless coordinate $z = x/l$
$\alpha$	$= k/k_g l$ dimensionless parameter
$\gamma$	parameter
$\delta$	parameter, conversion factor ( $kg \text{ water}/kg \text{ CO}_2$ )
$\partial$	symbol indicating partial differentiation
$\varkappa$	parameter
$\rho$	density ( $kg/m^3$ )
$\rho_0$	initial density at start of drying ( $kg/m^3$ )
$\rho_e$	equilibrium density at end of drying ( $kg/m^3$ )
$\rho_{ag}$	density of aggregate ( $kg/m^3$ )
$\rho_c$	density of cement ( $kg/m^3$ )
$\rho_w$	density of water ( $kg/m^3$ )
$\varphi$	relative humidity of the air, $\varphi = 100 \frac{P}{P_s}$
$\sigma$	stress ( $kp/cm^2$ )
$\nabla$	differential operator (nabla)
$\Delta$	symbol for difference
$\infty$	symbol for infinity
$\approx$	symbol for approximation (for example $C_1 \approx C_2$ )
$\#$	symbol for sieve
$Fo$	Fourier number of drying $= kh/l^2$ (dimensionless)
$^{\circ}Fo$	Fourier number of carbonation $= ^{\circ}kh/l^2$ (dimensionless)

## Subscripts:

ag	aggregate
c	moisture
c	cement
cp	cement paste
e	equilibrium
f	free water, moisture
g	gravitation
H	hydration
m	monomolecular
n	fixed water
0	initial state
s	saturation
t	temperature
w	water

## Superscripts:

c	carbonation
cp	cement paste
-	average

In the selection of symbols, Anglo-Saxon practice has been preferred. By reason of the limited number of Latin letters, which have been preferred, together with the usage of symbols in the author's previous publications on the same subject, the possibilities of selection have been limited. The units given in parenthesis (metre-kilogram-second system) are those most frequently used in accordance with international recommendations. As a rule, the dimensions of specimens have been given in centimetres.

The literature references have been indicated with [number].

## 1 INTRODUCTION

The title of this publication expresses its general scope and range. The list of contents provides a more detailed description.

The publication is concerned with the behaviour of individual, isothermal and relatively mature cement pastes and cement mortars, exposed to more or less unsaturated air after the curing period under sealed conditions.

The making and the pouring of the cement pastes and cement mortars used in the experiments were carried out under "normal" conditions (in the air,  $t = 20^{\circ}\text{C}$ ,  $\varphi = 70\%$ ,  $v < 0.5\text{ m/s}$ ) and with the avoidance of moisture loss. A period of long curing under sealed conditions (in glass jars or desiccators, to preclude the existence of practically any moisture exchange between specimens and the air in bulk) was preferred before the cement pastes or concrete mortars were subjected to drying. Such a long curing period ensures a high degree of hydration or high maturity. Attention was paid to a carbon dioxide attack in the air. By virtue of the relatively little influence exercised by carbon dioxide on an ordinary, thick concrete structure owing to the slow carbonation process, the elimination of carbon dioxide from the test air was often favoured.

Study of the evaporation drying was made within the second falling-rate period only under forced convection conditions, because of the primary importance of this period (see report 2, Section 6.2). This implies that the basic-drying conditions, as defined in the Glossary, have been assumed to be valid.

The main aim of the publication has been that of deepening the general understanding of the drying and related phenomena of concrete. An attempt has been made here to cover all aspects of the concrete drying phenomenon. Such an attempt easily leads to lengthy discussions, especially when there is a scarcity of earlier literature on the subject. This is what happened in the preparation of this publication. The effort to acquire a general idea of the drying phenomena has proved more valuable to the author than thorough investigation of some restricted details, of which the value may even be unknown. Thus the published work is not a presentation of "detailed" final results or "detailed" definite conclusions. The accumulation of results over a period of several years made it necessary to collect and evaluate them in order to clarify ideas, and not result in confusion originating in the abundance of data compiled in numerous experiments. Success was not achieved as regards improvement in research to a level which would justify statistical treatment of the results. The general features, along with the order-of-magnitude values in respect of the drying of concrete and related phenomena, do not seem sufficiently well known to validate the investigation and testing of a large number of specimens

with variable, but within each population fixed properties, especially when consideration is given to the facilities available in this laboratory. Consequently, the study presented below seeks to throw more light on the main features and investigation methods of the phenomena involved, and is intended as a basis for subsequent detailed studies. Finally, two additional points support the fundamental conception adopted and outlined above: as portland cements are not strictly standardized, they may give variable properties to concrete, and too little is known about the significant ageing processes of cement paste. Furthermore, the slowness of the drying process has often been a great obstacle; experiments with concrete made of normal aggregate must be performed with specimens of relatively large dimensions.

The author's previous report: "Notes on the drying of concrete" [2] must be regarded as a basic work on the subject, presenting many central ideas, definitions and terminology, used, and assumed as being known when the publication in hand is examined. It is evident that the works of numerous other authors [1], along with the other reports on the subject by the present author [3 ... 10] play a vital role in clarification of the author's opinions in this respect.

Finally, stress must be laid on the results in this publication having been obtained for cement pastes and for standard cement mortars (see Glossary) with dense quartz aggregate and made of Finish portland cements. Strictly speaking, the results apply to these alone. Although the various properties of aggregate, and the variable properties of portland cements, are factors which exert an influence on examination of the material being studied, common knowledge of the general similarity of all portland cement pastes and concretes appears to provide justification for the assumptions that the general features determined here are sufficiently true, and that the methods of investigation are applicable to cement pastes and concretes in general.

It should be pointed out that repetition of some of the subject matter in what follows below was unavoidable for the sake of clarity, and also because the reader of a lengthy paper seldom reads it thoroughly and systematically from first page to the last.

## 2 STRUCTURE OF CONCRETE AND MODELS FOR MOISTURE TRANSFER IN CONCRETE

### 2.1 STRUCTURE AND STRUCTURAL MODELS

#### 2.11 Introduction. Macrostructure

The structure of concrete can be divided into three main parts:

- 1) Structure of cement paste
- 2) Structure of cement paste-aggregate boundaries
- 3) Structure of aggregate

As regards moisture transfer in ordinary portland cement concrete, the structure of cement paste is dominant. The main reason for this is that only the cement paste forms a continuous matrix through concrete [11]. In addition, its permeability is higher than or as low as that of most rocks [12], [13]. Furthermore, in general the properties of concrete depend chiefly upon the hardened cement paste, which consists principally of hydrated cement, pore space, and water.

However, it is evident that the aggregate in concrete must exercise certain structural influences and thus affect the moisture flow. For example, an increase in the fine aggregate content raises the capillary porosity of concrete [14], [15], [13]. The findings of Kroone and Crook [16] support this observation, showing that the total volume of the pores greater in diameter than 50 000 Å rose with increase in the sand/cement ratio. Moreover, they found that the cross section of the pores became more irregular with increase in the sand content. An investigation by Henry and Kurtz [17] indicated that the moisture transfer decreases with an increase in the maximum aggregate size. Additionally, in some cases the structure of the cement paste - aggregate boundaries may be of significance for moisture transfer [54], although a proportion of them must often be regarding as exceptional and/or "no-good-technique" cases. Such instances appear, for example, if shrinking and highly porous aggregate is used. Shrinking aggregate may show severe peripheral crack development around aggregate particles [18]. The role of aggregate in the moisture transfer is not treated here, partly because too little is known of this subject matter, and partly, as was mentioned above because currently it appears that the cement paste plays the leading role. Consequently some of following paragraphs are concerned only with the microstructure of cement paste and moisture transfer in cement paste. Since it is hardly possible to do so, the main aim is not that of giving a complete picture of the complicated matters involved, but rather some kind of introductory examination which may assist the reader to achieve a better comprehension of the nature of concrete and its flow

properties. The examination is restricted to cement paste of a high degree of hydration, and is based chiefly on the publications of the eminent concrete scientist, Dr T.C. Powers. To avoid additional complexity, it is generally assumed that cement paste is practically stable as a material, i.e., there is no virtual change in the microstructure of mature paste, at least within the period of examination in question.

Systematic study of the structure and of the properties of hardened portland cement, on a major scale at least, is relatively young. Studies were begun in the Portland Cement Association (U.S.A.) in 1936, and a series of reports of this was published in 1946 and 1947 by Powers and Brownyard [19]. These reports must be regarded as the most fundamental work in the science of concrete, especially in respect of concrete physics. The personal opinion - and a sad one - of the present author is that even as late as 1965 a considerable amount of the valuable information contained in these reports has not been fully digested internationally.

### 2.12 Structure of cement paste

Cement paste, as defined here in accordance with Powers [20], consists of

- 1) Cement gel
- 2) Capillaries (capillary space or pores), if any
- 3) Residue of anhydrous cement, if any.

Cement gel is the cohesive mass of hydrated cement in its densest state, and occupies about 2.2 times as much space as the cement from which it was derived. It includes gel pores, and has a porosity of about 28 per cent. The average width of the pores is about 18 Å, about 6 times the diameter of a water molecule. The porosity is a natural consequence of the growth of very small irregular crypto-crystalline particles (fibrous or acicular and flaky or floc-like [21]) in random directions from random-distributed starting points. The solid material is mostly composed of colloids, but non-colloids, chiefly calcium hydroxide, are included in its definition. The gel particles are in contact with each other at many points, and some of the points of contact are chemically bonded. A special characteristic of cement gel is its enormous specific surface area, which is of the order 200 m<sup>2</sup>/g dry weight. Its overall specific volume is 0.57 cm<sup>3</sup>/g dry weight.

Usually, the amount of cement gel is insufficient to fill all the space within the visible boundaries of a specimen of cement paste. The space not filled with cement gel (or unhydrated cement) is known as the capillary spaces or capillary pores. In a fresh cement paste, these spaces are occupied by water. In a mature paste, these spaces are, as defined, pores in excess of about 28 per cent of the volume of the specimen of cement paste. Capillary spaces are regarded as discontinuities in a mass of cement gel. (Capillary cavities are defined as being capillary spaces isolated by cement gel). The order of magnitude of capillary spaces is generally greater than that of gel pores, amounting to at least several

hundred Ångströms. The capillary porosity of a nearly mature cement paste, made originally with a weight ratio of water-to-cement (water-cement ratio) of 0.3, is small, of the order of some units of per cent. The corresponding porosity of the paste with a water-cement ratio of 0.5 is of the order of 10 per cent or so. The greater the water cement ratio the greater is the capillary porosity.

When there is neither capillary space nor residual cement, the cement paste and cement gel are identical. (The entrapped air, so-called macropores, within the boundaries or the cement paste specimens, is not included in the cement paste proper.)

As a result, the cement paste has a high capacity of evaporable water, upwards of 30 per cent by volume, as compared with 1 per cent, more or less, for typical rocks. However, the permeability can be as low as that of most rocks. Structural differences among pastes made from the same cement are primarily due to the differences in capillary porosity, which is in turn, mainly dependent upon the water-cement ratio, as stated above. However, the effect on general microstructure of variations in the water-cement ratio within the normal range (about 0.3 ... 0.7) appears to be slight. The electron microscopy studies show that old pastes, cured under saturated conditions up to 10 years, do not display a markedly higher degree of crystallinity than freshly hardened ones [21]. A considerable fraction, if not all, of the water contained in the minor pores of the cement paste is absorbed, that is, it falls within the range of mutual attraction between water molecules and a solid surface.

A study by Powers & Copeland & Mann [22] demonstrated that the capillaries in fresh paste are continuous, but if the specific surface area of the cement is 1800 cm<sup>2</sup>/g or greater (Wagner, corresponding to 3200 cm<sup>2</sup>/g Blaine; although there exists no definite ratio between the surface area of cement as determined by the Blaine and Wagner methods, an approximation of the Wagner values may be made by dividing the Blaine values by 1.8 [23]; nitrogen adsorption gives a much higher surface: division by 4.5 is necessary to obtain the Wagner values [24]), and if the water-cement ratio does not exceed 0.7, the production of cement gel during the period will eventually segment the capillaries, forming capillary cavities. If the specific surface area of cement is higher, the limiting water-cement ratio is also higher, and presumably the reverse is true.

### 2.13 Diagrams of the structure models of cement paste

The first widely reproduced (for example in publication [25]) simplified diagram of the structure of cement paste, as far as the author knows, was presented by Powers in 1956 [26]. In this article dealing with freezing, he stated that a body of hardened portland cement paste may be regarded as comprising many individual containers for water. Fig. 1 presents a simplified diagram of the model suggested by experimental data [19], [27]. The word "simplified" is understandable in this

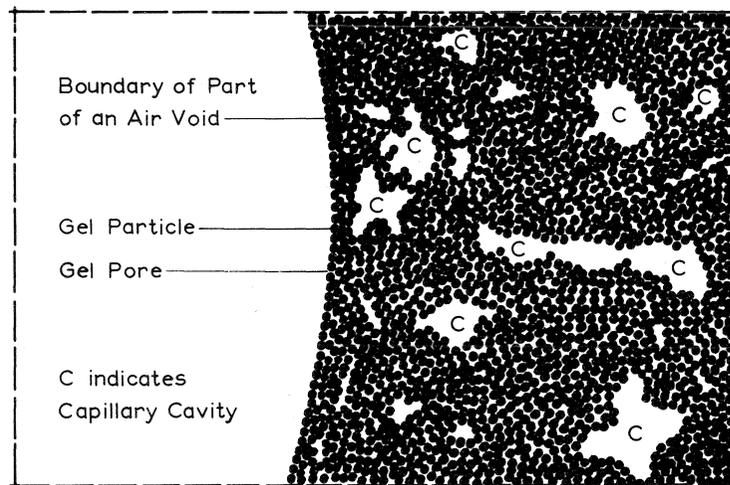


Figure 1. Simplified diagram of the structure of cement paste. Powers 1956 [26].

model chiefly in that the gel particles in Fig. 1 actually consist of gel particle systems. A diagram which demonstrated this improved feature was presented by Powers in the same year [28], and in a clearer form some few years later [29], [30], [20]. A simplified model which corresponds to those presented in [30], [20] is reproduced in Fig. 2 by the courtesy of Dr Powers, who sent the author a reproducible figure.

The electron-micrographs obtained by Grudemo during 1957 and later [20] showed that the gel particles proper are in the main slender ribbons and crumpled sheets or foils. In 1959, he also presented simplified models of cement paste [31]; Fig. 3 shows different particle shapes. As it is very difficult to illustrate the microstructure of cement paste by the aid of a few microphotographs, no attempt has been made to do so here. A collection of Grudemo's electron-micrographs is contained in [32], [21].

A simplified diagram which elucidates the structure of cement paste has also been presented by Taylor [33].

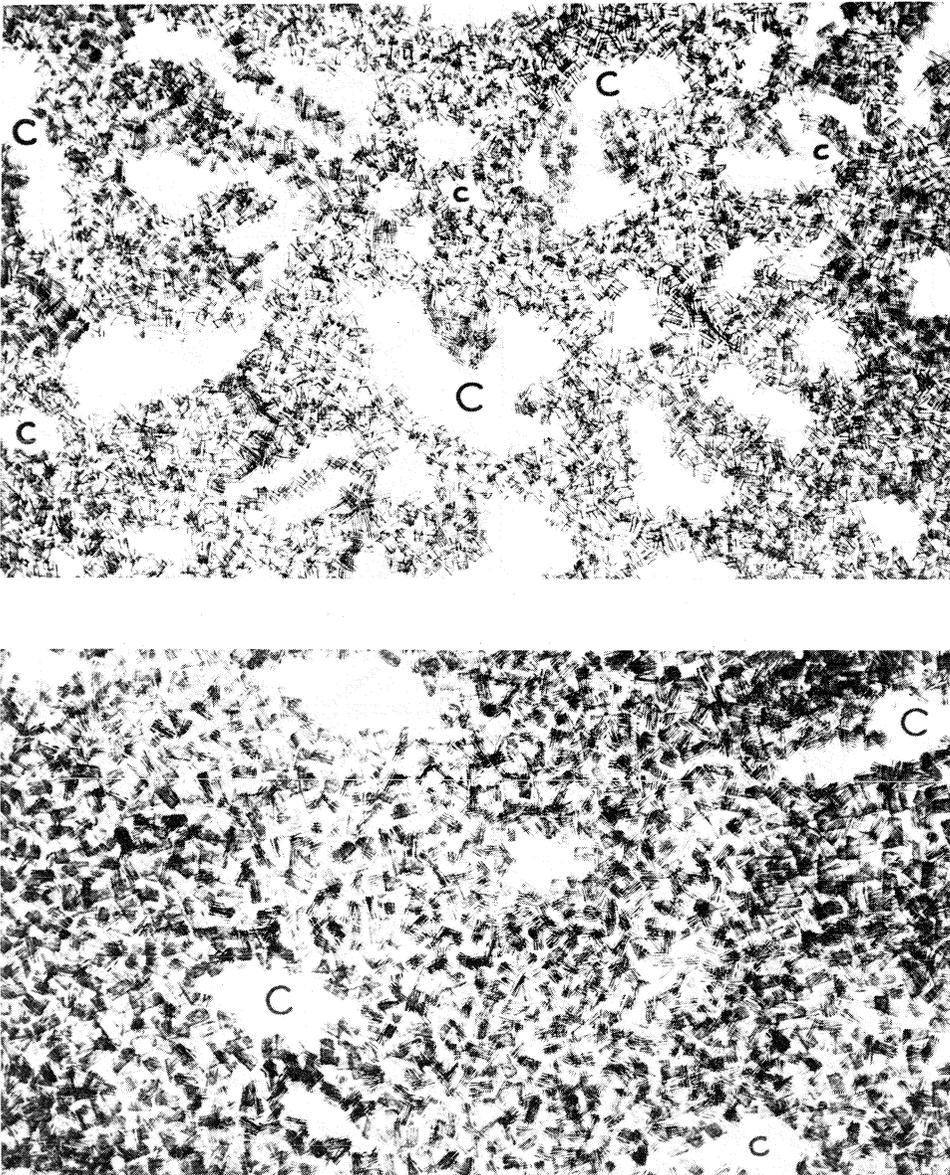


Figure 2. Simplified model of the structure of cement paste. Masses of randomly oriented groups of black lines represent cement gel. Spaces like those marked C represent capillary cavities. The upper drawing represents mature paste,  $w/c = 0.5$ , capillary porosity 20 %; the lower drawing represents nearly mature paste,  $w/c = 0.3$ , capillary porosity 7 %. Powers 1958 ... 1960 [20].

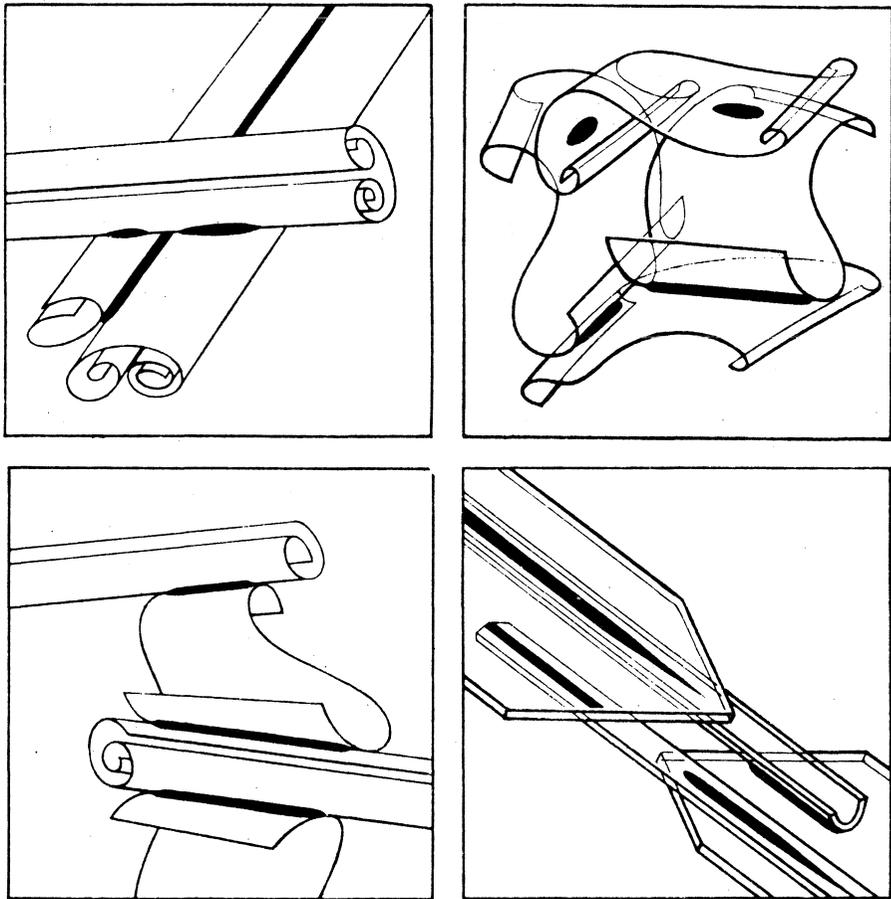


Figure 3. Models of the particle shapes of cement paste (cement gel). Grudemo 1959 [31].

## 2.14 Moisture flow models of drying

### 2.141 Basic facts and conceptions supported experimentally

Examination of the process of drying, or the moisture transfer in concrete, is based to great extent on the following facts or conceptions supported experimentally:

1. At temperatures above freezing point, chemically-free water molecules present in cement paste at any humidity below 100 per cent would be gaseous and negligible in amount, were it not for the adsorption forces which hold nearly all of them in a condensed state. As a rule, all the surfaces are covered with water molecules, and except at low humidities, capillary cavities contain water. [20].

2. The fracture stress of water is about -1200 atm. This is the negative pressure which gives a probability of unity for the nucleation of a vapour bubble spontaneous within about 1 second, by thermal fluctuation of the water molecules in the liquid [34], [20]. Under such a stress, water molecules are unable to cohere. The condensation of the water on the surfaces depends on the fracture strength and adhesion forces between water molecules and the underlying surface. If the surface belongs to a hydrophilic material, the effect of adhesion forces may extend through several layers of water molecules. If, as is normally the case, the effect of adhesion is restricted to the first molecular layer (an assumption of the BET-theory; adhesion theory: the weakest point of the junction between an adhesive and an adherend is likely to be located between the first and second layers of adsorbed molecules on the adherend [35]), capillary condensation cannot occur below a relative humidity of 40 per cent, at which the negative pressure on water molecules reaches the fracture strength value (-1200 atm; it is -1100 at 45 per cent). Cement paste seems to behave in accord within this conception, and consequently no capillary condensation occurs in it below RH 40 per cent [20].
3. Sorption isotherms, supported by sorption and capillary condensation theories, indicate the following. At lower humidities, say in the neighborhood of 0.2, the internal surfaces are covered with a monomolecular layer of water; below this humidity, the monomolecular layer is incomplete, and above it the surface is covered with two or more layers. At humidities of 0.45 ... 0.50, the surface has approximately two molecular layers of water. At these humidities, capillary condensation begins, as the "evaporation tension" is smaller than fracture strength, and the average radius of the gel pores is of the order of 3 diameters of water molecules (diam. 2.8 Å). [20], [19].
4. Below humidities of 0.45 ... 0.50, the film of water (thickness about one molecular layer or less) does not possess the properties of liquid water by reason of the adsorption forces. The mobility of the water molecules on the surface is restricted. By way of rough generalization, it is often assumed that the energy barrier for movement across the surface is about one quarter of that required to remove the molecule from the surface [35]. It is evident that the mobility of the first layer, with the strongest adhesive bond, is least. The tendency towards film transfer, i.e. water transfer along surfaces, is augmented with increase in the film thickness.
5. In a specimen saturated with water and surrounded by water or water-saturated atmosphere, there is no hydrostatic tension, and some of the water in the pores exhibits the normal properties of water [20].
6. Moisture transfer in porous solids generally occurs in the form of water vapour and/or liquid water. The moisture content determines the dominant type of flow. At low humidities, the moisture is attached to the internal surfaces by adhesive forces, and the only moisture transfer possible is than in the form

of vapour. Thus, it is obvious that moisture transfer is a function of moisture content, and often a complicated one [36].

7. Cement paste and concrete are capillary porous colloidal materials with a wide range of pore sizes, and accordingly all types of individual flow, such as vapour diffusion, unsaturated (film transfer) and saturated capillary transfer, are attributable to divergent driving forces which differ in origin. For the most part, the driving forces can be shown to be moisture gradients [36] ... [39].
8. The distribution of the pore sizes in concrete and in cement paste, ranging from a few Å to several hundred or thousand Å, seems to be relatively uniform, which indicates that there is no substantial concentration at any one size. No bimodal distribution has been obtained. [16], [40] ... [43], [20].
9. Capillary pores are mostly isolated, i.e., they are capillary cavities, especially at lower ratios of water to cement. Consequently the gel pore system with occasional capillary cavities constitutes a more or less continuous channel system for moisture flow. It is evident that the flow of moisture can occur only when there exists a sufficient number of permeable spaces connected to form paths. As has been proved in drying experiments, a continuous cement paste matrix, or a system of gel and capillary pores, possesses such paths [20], [22], [41].
10. The moisture flow in cement paste and concrete, the capillary porous colloid, can be considered to be a random motion, termed internal diffusion, consisting of several different types of vapour and liquid transfer [36]. This is one of the reasons which justify application of the diffusion theory as the mathematical model which governs the drying process in cement paste and concrete.
11. As regards ordinary cement pastes and concretes, the effect of gravitation seems in practice to be of minor significance. The effect of gravitation diminishes with a decrease in the moisture content, or in other words when there occurs an increase in the effect of internal forces [9].
12. As for concrete made with dense aggregate, it seems reasonable to conclude that aggregate particles form randomly distributed, discontinuous, and virtually impermeable solids in concrete [11].
13. Rose [38] has distinguished between six stages in the wetting of a porous medium, which he idealizes as a single pore with a neck at each end (Fig. 4). The model shows the wetting process, but the drying process can be understood as being similar in principle, despite the reverse sequence of the individual processes. At the first stage (a), there occurs the vapour adsorption, and no vapour flux cannot be transferred until this is complete. The second stage (b) is one of unimpeded vapour movement, in which the vapour behaves like an inert gas. In stage (c), the system is impervious to an inert gas, and pervious to water only by a process of distillation, which the necks of water acting as short-circuits for vapour movement. Rose describes this process as liquid-assisted vapour transfer, the assistance coming into being as a result of the liquid shortening the effective path length for vapour. His experiments

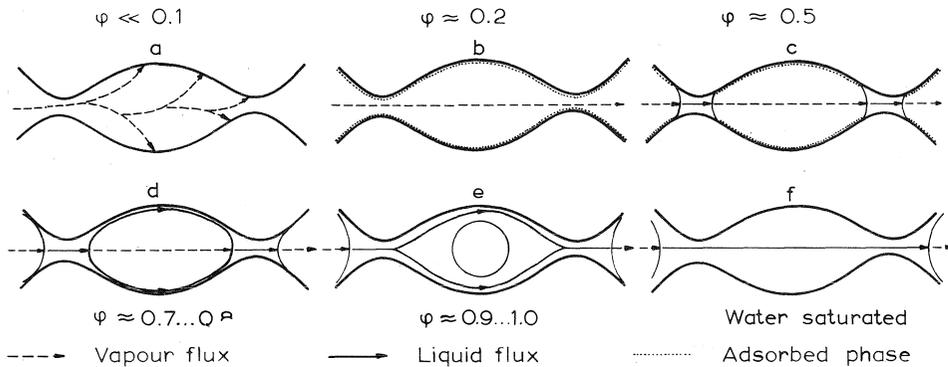


Figure 4. Schematic figure indicating moisture transfer types in porous solids. The figure is drawn in strict accordance with the figure presented by Rose [38]. The present author has added the estimates of relative humidities related to cement paste or concrete.

demonstrate that moisture conductivity increases by some tens of percentage in consequence of this assistance. In stage (d), the film transfer or surface creep, viz. the flow in thin surface films, begins in addition to the vapour transfer. Rose entitles this process "vapour assisted liquid transfer". Stage (e) shows unsaturated liquid flow, where vapour ceases to make a significant contribution to the total flux. Stage (f) indicates saturated liquid flow.

14. If an examination is made of the wetting or drying of a specimen of considerable size, it is evident that all the types of flows mentioned above occur in the specimen at the same time, if the specimen is completely dry at the beginning of wetting, or dries at zero humidity. Generally, if the "range of drying" is wide, the drying process involves several types of flow as presented above, point 13. In respect of the drying, for instance, it is therefore reasonable to expect that the drying process depends significantly upon the relative humidity of the ambient air, and the moisture content of the body, which determines the individual flow types in concrete.
15. Ageing phenomena have been obtained in many colloidal solids, including cement paste. Colloidal systems are unstable, and as time passes chemical and physical changes usually take place, which transform the system towards a more stable state [44], [20]. One of the changes normally associated with ageing is a diminution in surface area. This indicates that the equilibrium in moisture content at constant humidity of the ambient air is dependent upon ageing.
16. The carbon dioxide take-up of cement paste from ordinary air introduces an essential change in the microstructure of cement paste, and accordingly in its properties. However, carbonation in cement paste or in concrete is a slow process, and thus its effect is significantly dependent upon the body dimensions of the structure or specimen. Carbonation is examined in detail in Chapter 4.
17. The drying of an ordinary concrete in normal air can usually be regarded as an isothermal process [2].

2.142 Discussion of the isothermal drying of semi-stable cement paste:  
a tentative qualitative model for the drying process

In this paragraph, there is presented a qualitative model of the isothermal drying of individual cement pastes (or concretes). Cement paste is assumed to be practically "stable" (high maturity, no carbonation and ageing processes), i.e., semi-stable (Definition in Glossary).

In practice, the drying process of cement paste is essentially the displacement of moisture by the air in its pores. Consequently, the transfer of air may be a significant phenomenon in detailed explanation of the drying process. Nevertheless, the air transfer has as a rule been left out of consideration, as it is thought that from the phenomenal and quantitative aspects, its role does not assume primary importance. Indeed, the mass of air and also that of water vapour in the pores of the body is negligible as compared with that of liquid water. At any rate, the fact is that this neglect, mainly attributable to a lack of comprehension of the phenomenon, does not necessarily diminish the importance of the transfer of air in the drying process. It is noteworthy in this connection that air and water are partly miscible, and that the changes in internal forces and in the concentration of moving water solution exercise an effect upon the concentration of soluble air in water. It is also possible that in some cases the air acts as a carrier gas.

As was discussed in the previous section (2.141), the drying process is essentially affected by the relative moisture content of the body, or, in other words, by the relative water vapour pressure in the body or at the point of the body under examination.

In lower humidities, below the point or regime at which the capillary condensation begins, moisture is transferred in the form of water vapour alone. The author is unaware of the role played by the air transfer, and thus this topic, although very interesting, must be omitted from this discussion.

In the main, the capillary condensation begins within the humidity range of 0.45 ... 0.50, and makes a proportion of the pores impervious to water vapour. The theory of capillary condensation shows that this water vapour pressure exists on curved water menisci in capillaries with diameters of the order of  $30 \text{ \AA}$ . This means that at least one half of the gel pores, of which the average diameter is of this order, are subjected to capillary condensation. At higher humidities, say between 0.5 ... 0.7, the pore system of cement paste is impervious to gas and water vapour, and pervious to water only by a process of distillation in which the necks of water act as short circuits for air and water vapour movement. In accordance with Rose [38], as was mentioned in the previous section (2.141), this is termed liquid assisted vapour transfer.

At high humidities, say between 0.7 and 0.9, the film transfer begins to dominate (see Fig. 4), which indicates that the liquid-assisted vapour transfer turns to vapour-assisted liquid transfer, and further to unsaturated liquid transfer. If the cement paste has been cured under sealed conditions, the drying process begins with

unsaturated liquid transfer, or in other words with film transfer. It is worthwhile mentioning that a concrete structure or specimen of considerable body size (of the order of several centimetres) is very seldom completely water-saturated [6], even when stored in water.

When a wet concrete body begins to dry, there is in practice justification for the assumption that its surface relatively quickly attains moisture equilibrium with the ambient air [2]. Dependent on the humidity of the ambient air, several types of moisture flow occur in the body. As a result of the carbon dioxide attack and the ageing phenomenon, moisture equilibrium in a concrete body does not necessarily exist. As the ageing and carbonation proceed, the microstructure changes involved lead the cement paste towards a state in which both the equilibrium moisture (free water) content and the fixed water content are very small. Practically speaking, this implies that cement paste and concrete dry continuously in the scale of the span of human life. At the current stage of knowledge, however, and in this publication, it is reasonable to assume that there exists a kind of practical equilibrium moisture content. Acceptance of the ageing phenomena of cement paste implies that a very significant reevaluation of many of the essential parts of concrete theory and practice is necessary.

The discussion entered into above indicates that the drying of cement paste at relatively high humidities must be accounted for on the basis of water transfer as a film, although it seems probable that the bubble formation [20], and air transfer as a gas and on dissolution, play important roles in a particularized description of the flow process.

There is a great need for a detailed study of the microflow process during drying in cement paste and concrete (Cf. [45] and [38]).

## 2.2 MATHEMATICAL MODELS

### 2.21 Introduction

One of the main aims of Section 2.1 was that of providing a quantitative, detailed picture of the structure of cement paste and concrete. This leads to the conception that, particularly as a result of the complicated physico-chemical microstructure, it is impossible, at least in the light of present knowledge, to formulate a detailed kinetic mathematical description of the drying process in cement paste and concrete; this means that mathematical prediction of the drying of cement paste and concrete will to a varying extent be phenomenological. It should be mentioned that this problem has already been examined in Report [2].

It is also known internationally that although we have a number of theories which are capable of application to flow problems of limited nature, the structure of porous colloidal media is so complicated that practically all kinds of simultaneous individual flows are inherently feasible in them. Furthermore, it has been widely accepted that the diffusion theory is adequate, and even good for mathematical

treatment of the drying process in most porous solids. Thus the problems posed appear mainly to be: the finding of numerical values for the parameters of the theory, and the formulation of some refinements of the theory with a view to taking into account the special nature of the drying medium under examination. However, some observations, although few in number, seem to invalidate the diffusion theory [46], which implies in any event that the diffusion theory is not necessarily the only possible theory with respect to the drying process.

The research carried out during the course of years on the drying of concrete, although relatively small in extent, demonstrates that the views of the governing drying theory presented above also hold good for cement paste and concrete. The diffusion theory is one of the most advanced theories in mathematical or theoretical physics, and consequently it is definitely worthwhile to make a thorough examination of all the possibilities it offers before introducing any basic changes in the theory of drying (of a particular porous solid). However, even at this comparatively early stage of knowledge of the drying of concrete, or perhaps because of it, some experimental mathematical theories or formulae suitable, as it appears, for limited cases, have been proposed [47], [48]. This kind of research is valuable, although no attempt has been in this direction in the current publication.

## 2.22 Mathematical theory of the drying of cement paste and concrete

A review of the theory of drying, with special reference to concrete, including the basic ideas on which rests the theory to be presented, has already been presented by the author in Report [2]. Moreover, the mathematics of the drying of concrete, including also the effect of gravitation, has been elucidated in reports by the author and his co-workers [9], [10]. The more general analytical theory of heat and mass (moisture) transfer in porous media has been put forward in a condensed form by Luikov [49], [50], [51] and Lebedev [52], [53]. It may be necessary to mention that the general theory does not take the special features of cement paste and concrete into account.

Although the most dependable conception of the drying process of concrete is that it is a non-stationary hydrothermal process in an unstable material, it has here been accepted, in order to get an applicable mathematical theory, that the diffusion theory with certain refinements and additions applies to the drying process of concrete. The diffusion theory is basically a statistical theory which examines a large number of individual processes, but which gives only the integral main features and total results of the individual processes. Here, this means that the drying theory gives information only of such quantities as the statistical moisture content or statistical average moisture content of the body during the course of drying. The ordinary diffusion theory is believed to be valid at least as regards a quasi-isotropic and quasi-homogeneous medium. It is reasonable to assume that concrete, apart perhaps

from some concretes which contain aggregate of large maximum particle size, is a quasi-isotropic and quasi-homogeneous material, or in other words, that it is assumed to be a macroscopically isotropic and homogeneous material.

The analytical theory of the drying of cement paste and concrete presented below, and applied in what follows, is essentially limited to isothermal individual concrete, in which the temperature is below the boiling point of water, and above its freezing point. In addition, examination is confined to the second falling-rate period of drying, by reason of its primary role in the drying process of concrete [2]; as a boundary condition, use is made of the reasonable assumption that the surface is at moisture equilibrium with the ambient air, in accordance with Reports [2], [7]. These conditions are here briefly termed the basic-drying conditions (see Glossary).

A review of the differential field equations which govern the isothermal drying process of individual cement pastes and concretes is presented in Table 1. Explanation of the terms "stable", "unstable" and "semi-stable" is given in the Glossary.

Equation I represents the general form of the mathematical isothermal drying of an individual concrete which contains unstable cement paste. The word "analytical" is here employed only in its apparent meaning, as it is hardly feasible to find the general solutions of the equation. The first term on the right side of the equation is the ordinary diffusion term for the isotropic and homogeneous (at least quasi-isotropic and quasi-homogeneous) medium. The detailed analytical forms of the gravitation term,  $G$ , the sink term due to fixation,  $S_H$ , and the source term due to carbonation,  $S_C$ , are generally unknown. Term  $S_H$  is mainly dependent upon the hydration process, and term  $S_C$  on the decomposition of the hydration products in cement paste caused by a carbon dioxide take-up. The integral of term  $S_H$  valid for sealed conditions, and with gravity ignored, is presented in Chapter 6; term  $S_C$ , valid also for a special case, is presented below in Section 4.3. These presentations give an idea of the nature of the sink and source terms,  $S_H$  and  $S_C$ . The terms in Equation I are generally complicated and mutually dependent.

Only very restrictive assumptions can simplify Equation I and permit of calculations in practice at the present stage of knowledge. The assumptions are mainly: 1) cement paste is a stable material, 2) the individual processes do not occur concurrently, 3) the individual processes are mutually independent, 4) the geometry of the body under examination is simple, and 5) the initial (and final) and boundary conditions are simple. It should be pointed out that in the concrete drying studies assumptions 1), 2) and 3) have to a greater or lesser extent been tacit in nature.

Equation II a) (Table 1) relates to the simplest form of the isothermal drying of an individual concrete. It is obvious that the largest number of numerical solutions exist for this equation, covering various geometrical forms of the drying body, and various initial and boundary conditions. Perhaps the most critical assumption involved in the equation, is that relating to the constancy of moisture conductivity  $k$ . It is obvious that in practical computations use will be made of the reasonably selected average value of  $k$ . Equation II b) indicates the one-dimensional

Table 1. Mathematical theory of isothermal drying of concrete: Differential field equations.

unstable cement paste:

$$I \quad \frac{\partial C}{\partial h} = \text{div}(k \text{ grad } C) + G + S_H + S_C \quad (1)$$

stable cement paste:

$$II \text{ a) } \frac{\partial u}{\partial h} = k \text{ div grad } u \equiv k \nabla^2 u \quad (2)$$

$$b) \quad \frac{\partial u}{\partial h} = k \frac{\partial^2 u}{\partial x^2} \quad \text{or} \quad \frac{\partial u}{\partial Fo} = \frac{\partial^2 u}{\partial z^2}, \quad (3)$$

$$\text{when } z = \frac{x}{l}; \quad Fo = \frac{kh}{l^2}$$

$$III \text{ a) } \frac{\partial u}{\partial h} = k \nabla^2 u - k_g \text{ div}(u \vec{i}_g) \quad (4)$$

$$b) \quad \frac{\partial u}{\partial t} = \alpha \frac{\partial^2 u}{\partial z^2} - \frac{\partial u}{\partial z}, \quad (5)$$

$$\text{when } z = \frac{x}{l}, \quad \alpha = \frac{k}{k_g l}, \quad t = \frac{hk_g}{l}, \quad (Fo = \alpha t)$$

(z-axis in the direction of gravitation)

semi-stable cement paste:

$$IV \text{ a) } \frac{\partial u}{\partial h} = \text{div}(k \text{ grad } u); \quad k = f(u) \quad \text{or} \quad k = f(u, \dots) \quad (6)$$

$$b) \quad \frac{\partial u}{\partial Fo} = \frac{\partial}{\partial z} \left[ (1 + bu) \frac{\partial u}{\partial z} \right], \quad (7)$$

$$\text{when } k = k_e(1 + bu), \quad z = \frac{x}{l}, \quad Fo = \frac{k_e h}{l^2}$$

case, and also a convenient dimensionless form. Equations II, where moisture conductivity  $k$  is assumed to be constant, relative moisture content  $u$  unambiguous, and gravitation, hydration, carbonation and ageing negligible, have been treated in the author's Reports [2] and [7], and particularly in Report [7]. In Report [7], there were further introduced some simple methods for taking variable  $k$  and the other parameters,  $C_0$  and  $C_e$ , into account in the preliminary prediction of the drying of concrete.

Equations III show the cases in which an attempt was made to give consideration to the effect of gravitation. Equation III b) introduces the one-dimensional case in the dimensionless form. The theory of this case was presented in detail in Report [9].

Although the assumption that  $k$  is constant may be approximately valid in some limited cases, and in some preliminary or engineering predictions of drying, it is evident that  $k$  is a variable. Many divergent properties could be accounted for the variation of  $k$ , but a reasonable assumption seems to be to put down  $k$  as a function of moisture content alone, although it is in fact evident that this formal notation involves a great deal more, as described earlier in Report [2]. Equations IV elucidate the case which involves variable  $k$ , and further include a basic one-dimensional equation in the dimensionless form. The solutions of Equation IV b), in which the moisture conductivity depends linearly on moisture content only, have been presented in graphical form for slabs in Report [10]. Several other solutions and methods of calculation of the diffusion equation when the diffusivity is moisture-dependent have been put forward in literature [1], but not always in a form appropriate for practical application.

Apart from the moisture-content distribution obtainable direct from the solutions of the field equations, primary interest is also attached to the average moisture content of the body,  $\bar{u}$ .

Equation

$$\bar{u} = \frac{1}{V} \int_{\text{Body}} u dV \quad (8)$$

yields this vital information.

### 3 MOISTURE DEPENDENCE OF MOISTURE CONDUCTIVITY OF CONCRETE AND ITS DETERMINATION

#### 3.1 GENERAL

Equation

$$\frac{\partial u}{\partial h} = \frac{\partial}{\partial x} \left( k \frac{\partial u}{\partial x} \right); \quad k = f(u) \quad (9)$$

constitutes the mathematical basis of this chapter, and the task set is that of finding by experimental means the type of function  $k = f(u)$ , or more generally that of function  $k = f(C)$ . The experiment must accordingly be made with mature concrete ( $S_H = 0$ ) slabs (uniaxial drying), and preferably in air free of carbon dioxide ( $S_C = 0$ ). During determination of the moisture conductivity, the cement paste can be considered as a relatively stable or semi-stable material (Cf. Glossary). The effect of gravitation is taken to be insignificant. Basic-drying conditions are assumed to be valid (see Glossary).

On the basis of the discussion contained in Chapter 2, and previously in Report [2], it is obvious that the moisture conductivity of concrete,  $k$ , is in general a complicated quantity which depends upon the properties of the cement, the cement paste, on the history of hydration, the aggregate, the cement paste-aggregate ratio, the moisture concentration and the temperature. Moisture conductivity also varies in the same concrete, and the basic factors are: the conditions or history of hydration, the degree of hydration, the moisture concentration and the temperature. If the hydration history is standardized, the concrete is mature at the start of drying, and the drying occurs at a fixed temperature, it seems reasonable to begin studies on the assumption that moisture conductivity  $k$  of a certain concrete depends mainly upon the moisture concentration or the moisture content (Cf. Fig. 4). Although the relationship between the moisture conductivity and the moisture content of concrete appears to be of primary importance in drying studies where the diffusion theory forms the mathematical basis, no success has been gained in discovery of any published report on the subject. The relationship in respect of other materials, and the theory involved has been treated in several textbooks and papers on variable moisture diffusivity, for example [36], [55] ... [65].

In what follows, Sections 3.2 and 3.3, there are put forward two different methods of measurement, and the results of two test series, intended for elucidation of the general features of the relationship between moisture conductivity  $k$  and moisture content  $u$ .

## 3.2 EXPERIMENTAL METHOD BASED ON NARROW HUMIDITY-RANGE DRYING

### 3.21 Introduction

The most natural way of discovering the interrelationship of moisture conductivity and moisture content seems to be the making of experiments with plates within an extensive range of moisture content but with narrow humidity-range drying of the uniaxially drying specimens, proceeding gradually from a wet to a dry state. It is reasonable to assume that moisture conductivity  $k$  is approximately constant, if drying occurs within the narrow humidity range, and if the limited conditions outlined at the beginning of Section 3.1 are valid.

Concrete cured under sealed conditions is in moisture equilibrium with air of relative humidity amounting to about 95 ... 100 %. The test may accordingly be commenced by putting the specimens (plates drying from both main surfaces) first of all in a humidity chamber, in which the relative humidity of the air is less than 95 ... 100 %, say 85 %. Carbon dioxide must be removed from the test air to preclude carbonation during the test, and especially when the drying of small specimens is to be studied gravimetrically. When satisfactory, or preferably complete, moisture equilibrium has been attained, the test is continued by changing the relative humidity to 70 % (say). The test may be continued gradually in this way until zero humidity is reached. As is customary in drying experiments, the serious difficulty arises that the total drying time is of the order of a year or more, if the plates are about 1 cm in thickness. Concrete specimens made of coarse aggregate must be at least several centimetres thick. The lengthy test period imposes many demands on the test apparatus, and thus it appears advisable, on the basis of the author's experience, that the apparatus employed be as simple and reliable as possible to ensure its continuous, correct functioning. The narrow range of humidity between the individual drying periods may result in further difficulties, since the permissible variations in humidity (and temperature) of the test air must be rather small.

The test method described above apparently has a serious inherent defect. Within each narrow range of humidity, only limited types of moisture flow occur (Cf. Fig. 4). If the drying process occurs within the wide humidity-range, e.g. if initially wet specimens dry in the dry air, there simultaneously exists several, or all types of moisture flow, of which the interplay may be a significant factor in the drying phenomenon. Consequently the interrelation of  $k$  and moisture content in wide humidity-range drying may differ from that in narrow humidity-range drying.

### 3.22 Experiment, results, and treatment of results

A test series was begun with five "old" plates of standard concrete mortar (Cement Pa 6500), employing an automatic humidity chamber (Photo 4) furnished with a self-made carbon dioxide removal system (Photo 5). The test procedure was planned to proceed as follows: plates stored in water  $\rightarrow$  RH 85 % (equilibrium)  $\rightarrow$  RH 70 %  $\rightarrow$  RH 55 %  $\rightarrow$  RH 40 %  $\rightarrow$  RH 25 %  $\rightarrow$  RH 10 %  $\rightarrow$  RH 0 %  $\rightarrow$  105°C

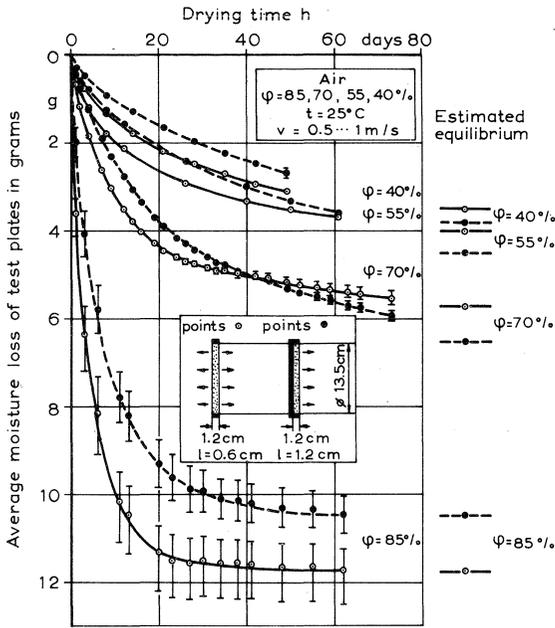


Figure 5 a. Moisture loss curves of uniaxially drying plates under different air humidities and basic-drying conditions (see definition in Glossary). The test was started with water-stored specimens of standard cement mortar (Cement Pa 6500), and the air humidity was lowered in steps from 85 % to 70 %, from 70 % to 55 %, and from 55 % to 40 %, after the test plates had attained sufficient moisture equilibrium at each humidity. The points represent the average values obtained from three plates dried on both main surfaces, and two plates dried on one main surface only. The segments of a line, if discernible, show the range of the individual measurement values.

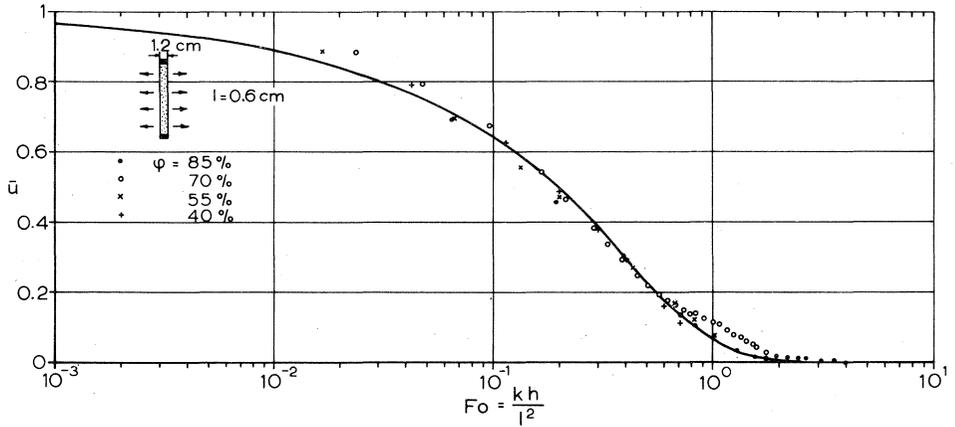


Figure 5 b. The experimental  $\bar{u} - h/l^2$  curves (points) fitted with the corresponding theoretical curve  $\bar{u} - Fo$  for uniaxially drying plates under basic-drying conditions at different air humidities. Each point represents an average value obtained from three plates; the results of the plates dried on both main surfaces are presented in this figure (Cf. Figs. 5 a and 5 c).

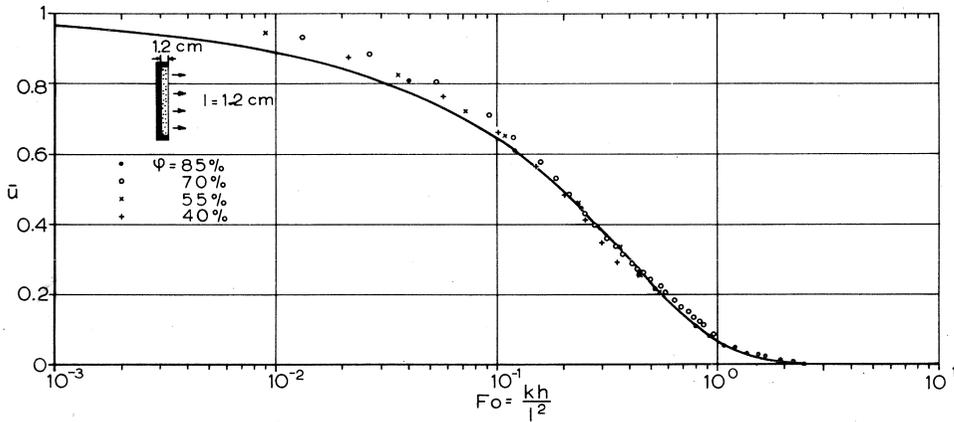


Figure 5c. The experimental  $\bar{u} - h/l^2$  curves (points) fitted with the corresponding theoretical curve  $\bar{u} - Fo$  for uniaxially drying plates under basic-drying conditions. Each point is an average value obtained from two plates; the results of the plates dried on one main surface only are presented in this figure (Cf. Figs. 5 a and 5 c).

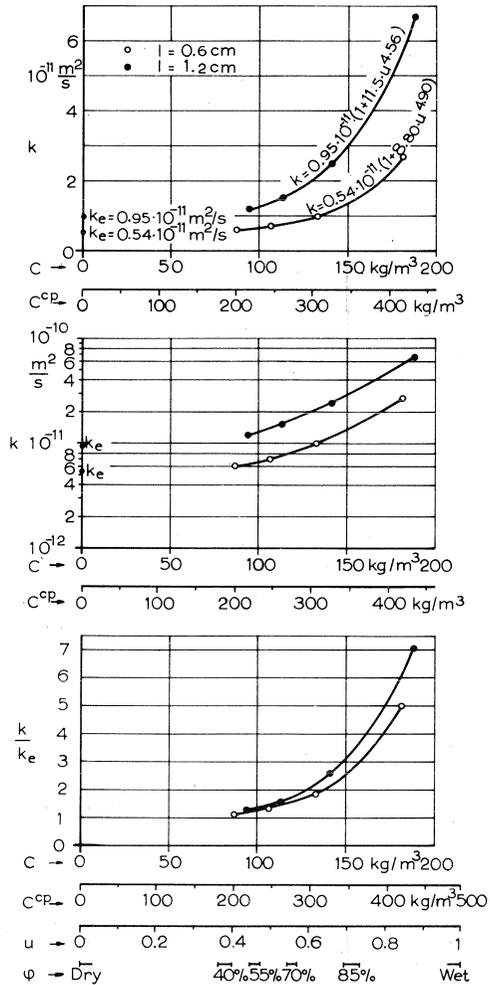


Figure 5d. The moisture dependence of moisture conductivity  $k$  obtained for uniaxially dried plates of standard cement mortar (Cement Pa 6500) under basic-drying conditions, with the aid of narrow humidity-range drying (Cf. Figs. 5 a, 5 b, 5 c). The same interrelation between  $k$  and moisture content has been presented in three different ways. The theoretical curves  $k = k_e(1 + bu^n)$  go exactly through the experimental points, as is observable in the uppermost part of the figure.

drying. However, only the tests down to RH 40 % are dealt with here. Although the chamber was new when the test was started, and the preliminary tests were made carefully it did not function properly. After 4½ months it was necessary to transfer the test specimens to a desiccator equipped with an electric fan to provide forced convection (Photo 9). To arrive at the relative humidity desired, H<sub>2</sub>SO<sub>4</sub>-water solution was put at the bottom of the desiccator. No removal of carbon dioxide from the test air seemed necessary, as the weight of the carbon dioxide in the air present in the desiccator used was of the order of 15 mg. Thus, if the desiccator contains 5 plates, the weight of each of which is several hundred grams, the maximum amount of the carbon dioxide take-up is virtually insignificant for each specimen, even if the desiccator is opened once or twice a week. The five plates used in the experiment had a thickness of 1.2 cm, and a diameter of 13 cm. Three of them dried from both main surfaces, but two had only one surface free; the other surfaces were isolated with glued metal sheets. A detailed description of the specimens and the experimental procedure is to be found in Appendix 3.

Fig. 5 a illustrates the average moisture loss of the test plates (standard cement mortar; Cement Pa 6500) at each RH (85 %, 70 %, 55 %, 40 %) of the ambient air at  $t \approx 25^\circ\text{C}$  and  $v \approx 0,5 \dots 1 \text{ m/s}$ . The plates had been stored continuously for several months in water prior to drying. As was mentioned above, the plates were first, at the start of second falling-rate period, put in a humidity chamber, in which the RH was 85 %. When sufficient moisture equilibrium had been attained, the humidity was changed to the next in order, 70 %. A similar process was continued down to 40 % RH.

The procedure for determination of the moisture conductivity with the aid of narrow humidity-range drying is as follows

- 1) Plot weight changes against time continuously during the test to obtain satisfactory or, preferably, almost complete equilibrium (Cf. Fig. 5 a).
- 2) Select three or two  $C_e$  values for each curve, and plot  $\bar{u} = (\bar{C} - C_e)/(C_0 - C_e)$  against  $h/1^2$ . If  $C_e$  is unambiguous, i.e. complete equilibrium had been attained, one  $C_e$  value is enough.
- 3) Select the best curve by comparison of the  $\bar{u} - h/1^2$  curves with the corresponding theoretical  $\bar{u} - Fo$  curve (uniaxially drying plates under basic-drying conditions). The best curve for each drying procedure of the present tests is reproduced in Figs. 5 b and 5 c. If the moisture equilibrium was complete, fit the only experimental  $\bar{u} - h/1^2$  curve with the theoretical  $\bar{u} - Fo$  curve. The fitting tends to be somewhat subjective. To avoid this, the fitting could be done by letting  $\bar{u} = 50 \%$  coincide, for example. As is indicated by Figs. 5 b and 5 c, the compatibility at the later ages has been preferred.
- 4) Take one pair of the numerical values of  $h/1^2$  (experimental curve) and  $Fo = kh/1^2$  for computation of a corresponding k-value.
- 5) Plot the k-values obtained against the respective average moisture content, preferably against  $(C_0^{cP} - C_e^{cP})/2$ . Fig. 5 d shows that this can be done in many ways.

The results (Figs. 5 b and 5 c) point to the relative humidity difference of the air used in the tests, 15 %, having been approximately correct, although it appears that the experimental curves would have been a better fit with the theoretical curve if the humidity range had been narrower, say 10 %.

Fig. 5 d clearly indicates the exponential nature of the interrelation of  $k$  and moisture content. The following relation between  $k$  and  $u$  seems to be in close coincidence with the experimental points:

$$k = k_e (1 + bu^n) \quad (10)$$

In accordance with the test results of the special cases,  $b$  and  $n$  are of the order of 10 and 5, respectively. Additionally, Fig. 5 d appears to indicate that  $k$  is a function of the thickness of the plates or, in other words, a function of the drying rate. A similar effect has also been observed in a number of shrinkage tests.

### 3.3 EXPERIMENTAL METHOD BASED ON THE DETERMINATION OF MOISTURE DISTRIBUTION CURVES: EGNER'S METHOD

#### 3.31 Introduction

Egner [55] derived from the equation

$$\frac{\partial u}{\partial h} = \frac{\partial}{\partial x} \left( k \frac{\partial u}{\partial x} \right); \quad k = f(u), \quad (11)$$

by simple integration under condition  $(\partial u / \partial x)_{x=0} \equiv 0$ , the relation

$$k = \frac{\frac{\partial}{\partial h} \int_0^x u dx}{\partial u / \partial x}, \quad \text{or if } z = x/l \quad (12)$$

$$k = l^2 \frac{\frac{\partial}{\partial h} \int_0^z u dz}{\partial u / \partial z} = l^2 \frac{\partial l / \partial h}{\partial u / \partial z}, \quad (\text{see Fig. 6}) \quad (13)$$

The last expression for  $k$  is the basic relation used in this section to determine the variation of  $k$  with moisture conductivity by means of uniaxially drying prisms. Egner used his method for determination of the relationship between  $k$  and moisture in spruce specimens. Several other scientists have applied Egner's method, but as far as the author knows it is here used in concrete research for the first time. Skaar [62] and Niskanen [63] have both published a review of the results, and instructions for application of the method.

EGNER'S METHOD FOR CALCULATION OF THE  
DEPENDENCE OF MOISTURE CONDUCTIVITY  $k$   
UPON MOISTURE CONTENT WITH THE AID OF  
MOISTURE DISTRIBUTION CURVES

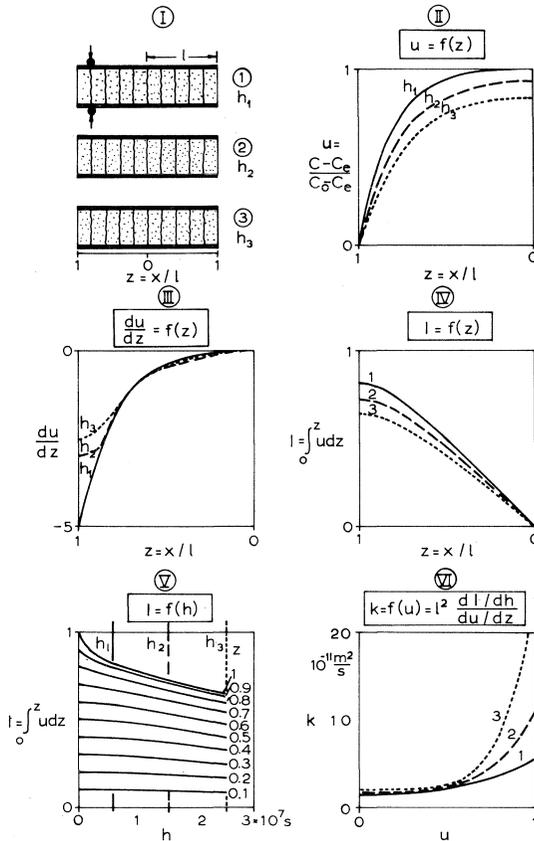


Figure 6. An example of the application of Egner's method to determination of the moisture dependence of moisture conductivity. (Cf. Figs. 7a, b, c, d, e.)

Egner's method requires knowledge of the moisture distribution in uniaxially drying specimens at various times during the drying process. The author solved the problem by splitting uniaxially drying prisms into ten pieces with the aid of a loading machine, and a device constructed especially for this purpose, after stated intervals of time. After splitting, the pieces were dried at  $105^\circ\text{C}$  to determine moisture content  $C$ . Crushed samples made of the pieces taken from similar prisms stored continuously under sealed conditions were used simultaneously to determine initial moisture content  $C_0$ , and equilibrium moisture content  $C_e$ . The relative moisture content  $u$  could then be calculated. The method, which needs graphical and/or numerical differentiation and integration, is presented in a simple form in a series of figures (Fig. 6).

Fig. 6 I shows three prisms split into ten pieces after drying times of  $h_1$ ,  $h_2$  and  $h_3$ .

Fig. 6 II indicates the moisture distribution curves drawn after the pieces had been dried at  $105^\circ\text{C}$  for the determination of  $C$ , and after determination of  $C_0$  and  $C_e$  effected with the aid of analogous crushed samples stored under the same climatic conditions.

Fig. 6 III represents the derivatives of the curves depicted in Fig. 6 II. The derivatives are needed in the computation of  $k$  in accordance with Equation (13).

Fig. 6 IV shows integral I as the function of  $z$ , arrived at (for example) with the aid of the trapezoidal rule from the curves shown in Fig. 6 II.

Fig. 6 V indicates integral I as the function of time  $h$ , drawn with the aid of Fig. 6 IV.

Fig. 6 VI finally represents the relationship between moisture conductivity  $k$  and moisture content. This figure was drawn on the basis of the information given in Figs. 6 II, 6 III and 6 V: first, moisture conductivity  $k$  is found with the aid of Figs. 6 V and 6 III, and then, by the aid of the fixed pairs of  $z$  and  $h$  values, the corresponding values for  $u$  are to be seen in Fig. 6 II. Derivative  $di/dh$  is obtained graphically.

A description of the experiments themselves is presented in the following section.

### 3.32 Experiment, results, and treatment of results

The specimens were standard cement mortar prisms (4 cm x 4 cm x 16 cm, cement Pa 7100) which were, after 6 months curing under sealed conditions, and covering with glued metal and plastic foils (Photo 14), exposed to uniaxial drying in two climate rooms (RH 40 %, 70 %;  $t = 20^\circ\text{C}$ ) (Photo 1 and 2; Appendix 1). The drying was effected under basic-drying conditions (see Glossary). One prism from each of two climate rooms was split after 68, 179, and 293 days of drying, to determine the moisture distribution. The corresponding average moisture content  $\bar{u}$  amounted to 0.82, 0.73, and 0.65 respectively. The experimental procedure is explained in detail in Appendix 3.

Figs. 7 a, 7 b, 7 c, 7 d, and 7 e illustrate the treatment of the results in accordance with the procedure explained in Section 3.31.

Fig. 7 e indicates that the results obtained by the application of Egnér's method, and the method of narrow humidity-range drying, are similar in principle, and obey the same type of equation,  $k = k_e(1 + bu^n)$ . The parameters  $b$  and  $n$  vary approximately within the ranges of 2.5 ... 11 and 2.5 ... 5 respectively. The curves are the same in  $u$ -scale (Cf. Fig. 7 a), although there are differences in absolute moisture content  $C$  ( $C$ -scales) as a result of the differences in storage conditions (RH 40 %, 70 %). The moisture conductivity is nearly constant, and of the order of  $2 \cdot 10^{-11} \text{ m}^2/\text{s}$  within lower moisture contents. The most abrupt change in moisture conductivity  $k$  occurs within  $C^{\text{CP}}$ -range 380 ... 300  $\text{kg}/\text{m}^3$ . Fig. 7 e further appears

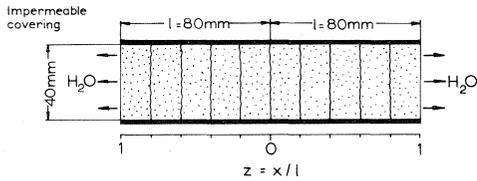
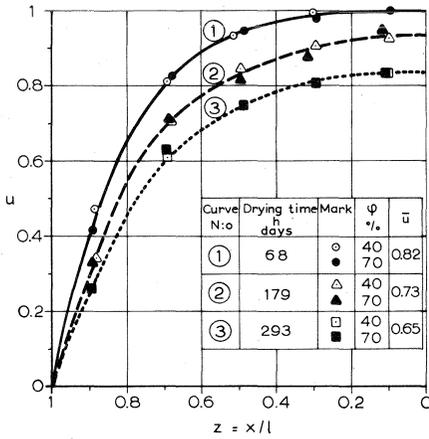


Figure 7a. Moisture distribution curves of prisms of standard cement mortar (Cement Pa 7100) dried uniaxially, obtained with the aid of the splitting test technique. Each point represents an average value of two respective pieces obtained from the two ends of one prism split at the ages of 68, 179, and 293 days respectively. (Cf. Fig. 6).

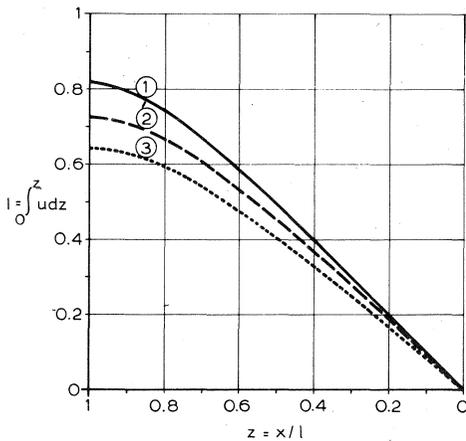


Figure 7c. The integral curves of the distribution curves presented in Fig. 7a (Cf. Fig. 6).

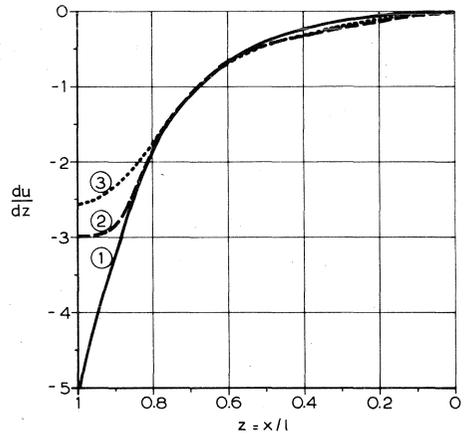


Figure 7b. The derivative curves of the distribution curves presented in Fig. 7a (Cf. Fig. 6).

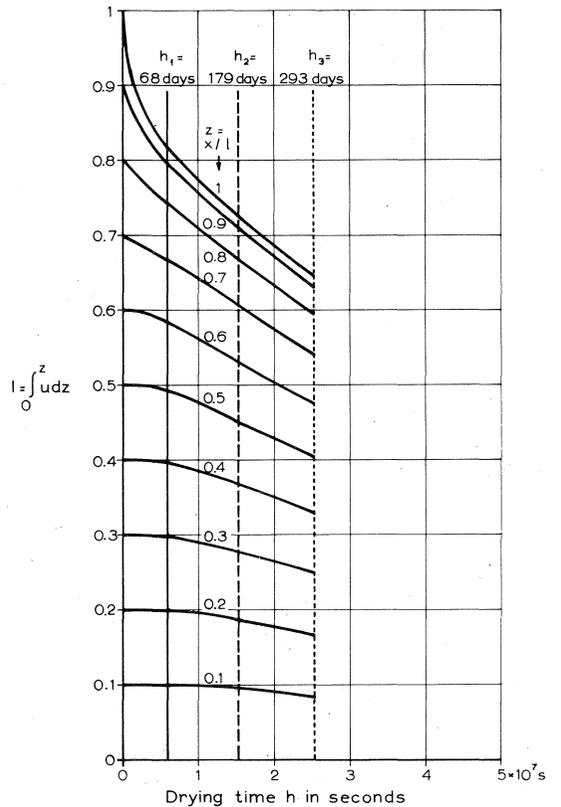


Figure 7d. Integral I as a function of time drawn with the aid of Fig. 7c. (Cf. Fig. 6).

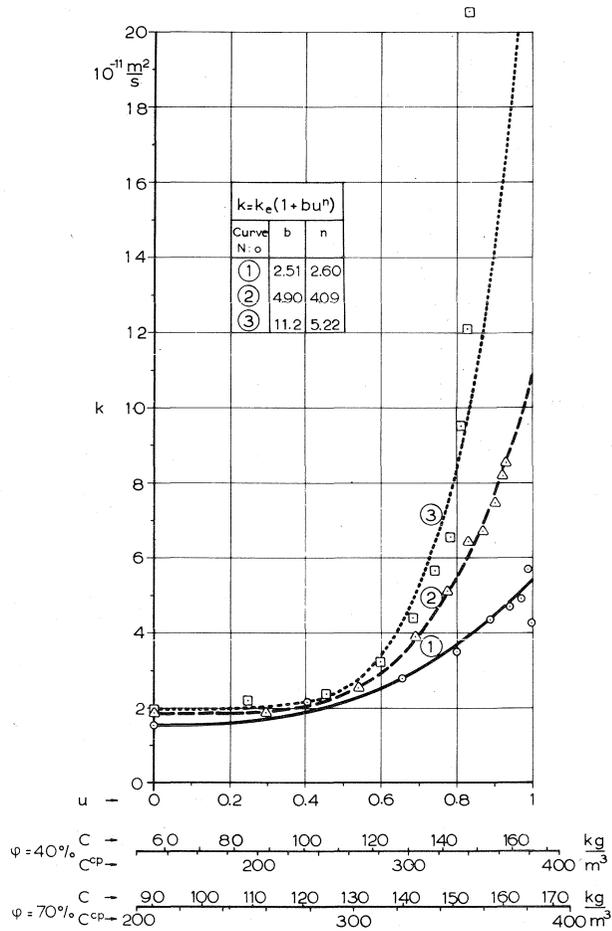


Figure 7e. The moisture dependence of moisture conductivity  $k$  obtained for uniaxially drying prisms of standard cement mortar (Cement Pa 7100) under basic-drying conditions, by means of Egner's method (Cf. Figs. 7a, b, c, d). Experimental points are fitted with equation  $k = k_e(1 + bu^n)$ .

to show that the relationship between moisture conductivity and moisture content is dependent upon drying time, or rather upon the time dependent factor or factors. Nevertheless, it is necessary to point out that determination of the derivative or tangent  $du/dz$  is somewhat subjective and unreliable at large  $u$ -values, and as a consequence the  $k - u$  relationship derived at large  $u$ -values is correspondingly unreliable. Moreover, carbonation could have exercised some effects on the results, although such effect is limited to the surface layer of the specimen (Cf. Figs. 17a and 17b).

### 3.4 GENERAL EVALUATION AND COMPARISON OF THE MOISTURE DEPENDENCE OF MOISTURE CONDUCTIVITY OBTAINED BY BOTH METHODS

The only difference in the original composition of the standard cement mortars used in the two experiments was that cement population Pa 7100 was used in making mortar specimens for the application of Egner's method, and Pa 6500 for that founded upon the narrow humidity-range. Nevertheless, there was a difference in the history and the initial moisture content at the start of drying for the two series of specimens. The specimens used in Egner's method were relatively dry at the start of drying because of the long period of sealed precuring, whereas those used in narrow humidity-range drying were dried at early ages at 105°C, and were very wet at the start of the test by reason of many years of storage in water. Additionally, there was divergences in the thickness or characteristic thickness  $l$  of the specimens used in the different determinations, and the number of the specimens was limited. All of these facts must be taken into consideration in evaluation of the results arrived at in the two experimental series. Thus it is unreasonable to draw conclusions which are too definite and detailed on the foundation of the results obtained.

Chapter 2 makes it obvious that moisture conductivity  $k$  generally depends upon absolute moisture content  $C$ , although under fixed conditions this dependence can also be expressed by means of relationship  $k - u$ . Fig. 8, which depicts relationship  $k - C$ , allows of some comparisons being drawn with the results obtained in the experiments described in Sections 3.2 and 3.3. The results arrived at in these special cases, supported by earlier findings [2] seem to provide a reasonably safe foundation for a preliminary conclusion that, for a certain concrete (cement paste, cement mortar, concrete) drying under fixed conditions, 1) relationship  $k - u$  can be adequately expressed by the equation

$$k = k_e(1 + bu^n), \quad (14)$$

and that 2) moisture conductivity  $k$  also depends upon another factor, or factors. Moreover, 3) the results indicate that the change in moisture conductivity occurs mainly within the high moisture range which corresponds roughly to the relative humidity range of the air 100 % ... 70 %, and that within the middle moisture range which corresponds approximately to the relative humidity range of the air 70 % ... 40 %, the moisture conductivity seems to be relatively stable.

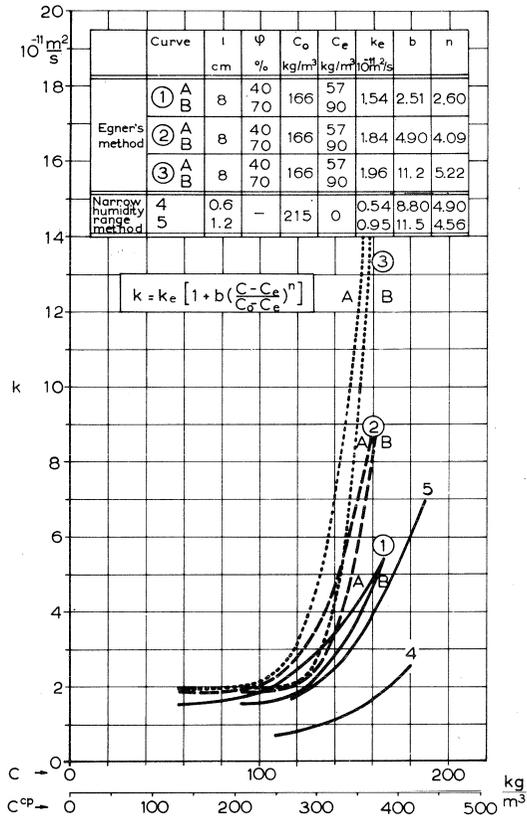


Figure 8. A comparison of the results obtained in the application of the narrow humidity-range method and Egner's method. The curves are similar in principle, obeying the same type of exponential equation.

The results obtained further indicates that for concretes drying only to equilibrium moisture content in air of about RH 70 %, the moisture conductivity seems approximately linearly dependent upon the moisture content. In these cases, the results presented in Report [10] are applicable.

As regards the behaviour of moisture conductivity, nothing certain can be said in respect of low moisture content on the basis of the results of the two methods presented above.

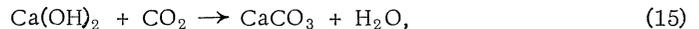
Future research on moisture conductivity as a function of moisture content, and the properties (water-cement ratio, cement paste-aggregate ratio, grading of aggregate), will provide a detailed conception of the subject.

## 4 CARBONATION: A SOURCE OF MOISTURE AND A SINK OF FIXED WATER

### 4.1 INTRODUCTION

The reaction between carbon dioxide gas and hardened portland cement pastes, mortars and concretes is of considerable practical and theoretical significance. The carbon dioxide take-up of concrete - the ultimate value of which can be of the order of 0.5 kg CO<sub>2</sub>/kg dry cement - changes the microstructure of cement paste, and therefore exercises, or may exercise, effects on the strength, the shrinkage, the corrosion, etc., in concrete and reinforced concrete structures, dependent upon the degree of carbonation of the structure [66].

The carbon dioxide taken up by cement paste or concrete exposed to the atmosphere, or to a stream of carbon dioxide, is present as calcium carbonate in the form of poorly crystallized minerals (vaterite, aragonite, and calcite). The calcium carbonate minerals have been formed from both calcium hydroxide, freed during the hydration of alite (3CaO · SiO<sub>2</sub>), and from the decomposition of hydrated cement minerals [67]. This general carbonation of cement paste deeply changes its chemical and physical properties. As has been remarked, not only the free carbon hydroxide in hydrated cement paste,



is transformed, but the other hydration products are decomposed by the action of carbon dioxide, principally as follows [68]



Consequently, if experimental concrete research is carried out, especially with relatively small or thin specimens or structures, the significant effect of the carbon dioxide take-up from the ambient air must be taken into consideration. This is principally because in practice concrete structures are normally much larger, and the slow carbon dioxide transfer may exert an insignificant, lesser or in any event different effect on them than on small or thin specimens or structures.

The effect may be extremely harmful in gravimetric examination of the desorption or adsorption processes in cement paste [2]. To achieve a reasonable duration for tests, small specimens or even crushed samples are necessary. This forces the investigator to perform tests at least partially in vacuum, or in air freed from carbon dioxide. However, in some cases, these methods are open to question, since

the air and its carbon dioxide are not necessarily irrelevant factors in sorption processes. As a consequence, a theory which would provide a computational method enabling the gravimetric effect of carbon dioxide to be taken into account, could be valuable.

As far as the author knows, no report has been made of an attempt to create a satisfactory mathematical model of the carbonation field, i.e., the penetration of carbonation, the gain in weight and the release of water attributable to carbonation in concrete bodies as a function of space and time. The penetration of carbon dioxide gas into concrete appears to be a diffusion process, and consequently the mathematical treatment of the phenomena mentioned will be based on the diffusion theory, one of the most advanced and used in the theoretical sciences. Therefore, this theory affords an excellent opportunity to study applications.

#### 4.2 ON DISTINGUISHING THE CARBON DIOXIDE TAKE-UP BY MEANS OF TEMPERATURE TREATMENT

The experiments made by Kroone & Blakey [69] with a mortar composed of an Australian cement clearly indicate that carbon dioxide taken up by hydrated cement paste is gradually freed above 100°C. The test samples were of crushed mortar, and the testing apparatus comprised a tube furnace and a train of bottles and u-tubes for take-up of the gases and vapours liberated at certain temperatures. The earlier, more or less indirect tests made in our laboratory [2], [70] seemed to indicate that the amount of carbon dioxide liberated between 105 ... 550°C was small. To make direct tests, a test series was begun, making use of a technique similar to that of Kroone & Blakey [69], with the exception that the carrier gas was oxygen (Kroone & Blakey used laboratory air). The carbonated cement paste specimens (average thickness of the order of 8 mm) belonged to the same series as those depicted in Report [2, p. 41, Photo 1]. Three cement paste specimens of different water-cement ratios were crushed into pieces of a maximum size of 7 mm, dried at 105°C, and utilized in the carbon dioxide determinations performed by a skilled thermochemist. Before the temperature treatment, the specimens had been 3 months in sealed curing, then dried at 105°C for determination of the moisture and the fixed water, and exposed to carbonation in a climate room (20°C, 70 % CO<sub>2</sub>-content about 500 ppm by volume) for a period of 29 months. In addition to carbon dioxide release, the total water content freed was determined. The results are presented in Table 2 and in Fig. 9, which also include the results arrived at with the same non-carbonated cement pastes after 3 months of sealed curing, and application of the same experimental technique.

The results of experiment agree in principle with the Australian ones mentioned above. It is also interesting to observe that approximately one mole or somewhat less of fixed water was released in the carbon dioxide take-up of one mole, as is indicated by the  $\delta$ -values in Table 2 (1 mole carbon dioxide 44 g, 1 mole water

Table 2. Carbon dioxide take-up and diminution in fixed water during 29 months of carbonation of three cement paste specimens (pillow-shaped, average weight 40 g, average thickness 8 mm) with water-cement ratios 0.3, 0.4, 0.5. The specimens were 3 months under sealed conditions and dried at 105°C before carbonation in a climate room (20°C, 70 %, CO<sub>2</sub>-content a. 500 ppm by volume). Cement: Pa 6800. In the measurements (tube furnace)  $w_n + j$  determined separately (soda asbestos, magnesium perchlorate) divided by total weight loss of the crushed samples amounted to about 0.999.

w/c		0.3	0.4	0.5
		% at 1000°C		
$j/c_0$	3 months	5.5	5.5	5.5
$j/c_0$	32 months	20.9	34.6	35.9
$\Delta j/c_0$	29 months	15.4	29.1	30.4
$w_n/c_0$	3 months	13.1	15.9	17.4
$w_n/c_0$	32 months	6.8	5.4	6.7
$\Delta w_n/c_0$	29 months	6.3	10.5	10.7
$\frac{\Delta w_n/c_0}{\Delta j/c_0} = \delta$		0.41	0.36	0.35

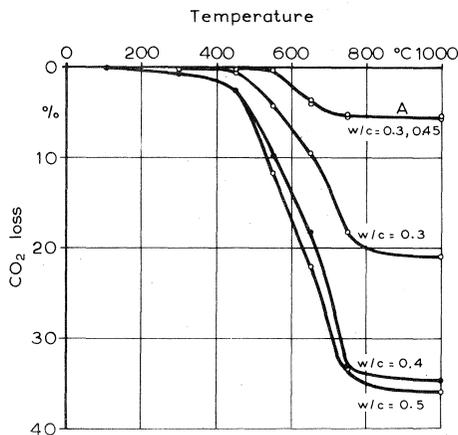


Figure 9. Carbon dioxide loss of cement pastes (Cement Pa 6800) as percentages by weight at 1000°C as a function of temperature, Curve A indicates the amount of carbon dioxide in the small cement paste specimens immediately after 3 months of sealed curing. Other curves show additionally the amount of carbon dioxide taken up by cement during 29 months of storage in a climate room (20°C, 70 %, CO<sub>2</sub>-content a. 500 ppm by volume). (Cf. Table 2).

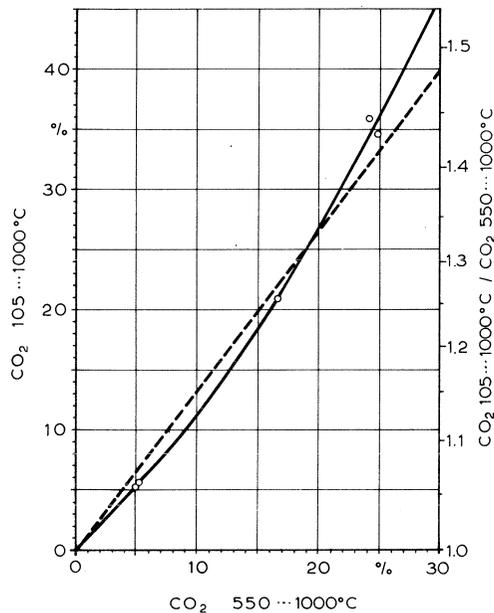


Figure 10. Conversion of CO<sub>2</sub> liberated within temperature range 550°C...1000°C into CO<sub>2</sub> liberated within range of 105°C...1000°C, drawn with the aid of the results presented in Fig. 9. The broken line indicates a simple linear relationship, 4/3.

18 g: 18/44 = 0.41). This is in accord with the theoretical consideration presented in Section 4.1.

To avoid the rather complicated tube-furnace analysis described above, an endeavour was made to create a simple system for determination of the total carbon dioxide content of cement paste with the aid of a normal muffle furnace (Photo 11) taking the carbon dioxide content released between 550...1000°C as a basis, and relying on the reasonable assumption that only carbon dioxide will be liberated within this temperature range. Fig. 10, arrived at with the assistance of the results presented in Fig. 9, serves this purpose. Fig. 10 seems to indicate that the carbon dioxide content liberated within the temperature range of 550...1000°C can be satisfactorily transformed into the total carbon dioxide content liberated between 105...1000°C.

#### 4.3 MATHEMATICS OF THE CARBONATION PROCESS AND TRANSFER

The basic assumption of the mathematical description of carbonation presented below is that the process of the transfer of carbonation in cement paste and concrete is a diffusion process. No attempt will be made at description of the carbonation potential of the transfer, since the carbonation transfer is a combination of a number of phenomena such as the diffusion of carbon dioxide gas, the dissolution of carbon dioxide gas into water, and the chemical reaction between dissolved carbon dioxide and hydration products of cement paste. Thus the apparent carbonation potential

to be presented and applied involves pressure and chemical potentials, and is complicated in nature.

There are three major interests with respect to carbonation

- 1) The quantitative field of the carbon dioxide take-up, including the average carbon dioxide take-up of the specimen or construction under examination
- 2) The water released due to the action of carbon dioxide in the body
- 3) The gain of mass (carbon dioxide take-up minus the water released) in the body.

The examination is restricted to cases in which no hydration occurs. This restriction can be assumed to be valid when the carbonation of the concrete takes place in air of a humidity below 80 per cent [2], or generally that the degree of hydration is very high before exposure to carbon dioxide. However, the carbonation brings about changes in the microstructure, and for this reason the cement paste must be regarded as being an unstable material during the process of carbonation. In spite of this, it will be assumed in the forthcoming applications that carbonation conductivity  $^{\circ}k$  employed in the theory is constant, and refinement of the theory will be left for later studies.

A review of the differential equations which govern the subject matter of carbonation discussed above is presented in Table 3. Equation I a) has the reasonable assumption that carbonation conductivity  $^{\circ}k$  is not generally a constant, but depends, inter alia, upon carbon dioxide take-up  $r$ . At this stage of development, examination will be restricted to the case in which  $^{\circ}k$  is taken to be a constant, in practical computations a reasonably selected average  $^{\circ}k$  (see Equation I b). Equation II represents the water released in the body as a result of the action of carbon dioxide. The carbonation process in normal air is very much slower than the moisture flow

Table 3. Mathematics of the carbonation process in concrete: Differential field equations.

Carbon dioxide take-up:	
I a) $\frac{\partial r}{\partial h} = \text{div } (^{\circ}k \text{ grad } r); \quad ^{\circ}k = f(r, \dots)$	(17)
b) $\frac{\partial r}{\partial h} = ^{\circ}k \text{ div grad } r \equiv ^{\circ}k \nabla^2 r$	(18)
Water released in the body:	
II $\frac{\partial ^{\circ}C}{\partial h} = ^{\circ}k \nabla^2 ^{\circ}C; \quad ^{\circ}C = \delta r (D_e - D_0)$	(19)
Mass gain when water released has been escaped:	
III $\frac{\partial ^{\circ}M}{\partial h} = ^{\circ}k \nabla^2 ^{\circ}M; \quad ^{\circ}M = (1 - \delta) r (D_e - D_0)$	(20)

Table 4. Solutions of the equations presented in Table 3 for one-dimensional cases: slab with initial uniform zero content and surface at equilibrium content of unity; Figs. 11 and 12. (Functions are presented in detail, e.g. in [58], [89]).

Carbon dioxide take-up field:

$$r = f\left(\frac{^{\circ}kh}{1^2}, \frac{x}{1}\right) \equiv f\left(^{\circ}Fo, \frac{x}{1}\right) \quad (21)$$

Average carbon dioxide take-up of the body:

$$\bar{r} = f(^{\circ}Fo) \quad (22)$$

Water released in the body:

$$\frac{^{\circ}C}{^{\circ}C_e} = f\left(^{\circ}Fo, \frac{x}{1}\right); \quad \frac{^{\circ}\bar{C}}{^{\circ}C_e} = f(^{\circ}Fo); \quad ^{\circ}C_e = \delta(D_e - D_0) \quad (23)$$

Mass gain when water released has escaped:

$$\frac{^{\circ}M}{^{\circ}M_e} = f\left(^{\circ}Fo, \frac{x}{1}\right); \quad \frac{^{\circ}\bar{M}}{^{\circ}M_e} = f(^{\circ}Fo); \quad ^{\circ}M_e = (1 - \delta)(D_e - D_0) \quad (24)$$

or drying, as was indicated by the preliminary examination [2]. There accordingly seems justification for the assumption that the water released in the body owing to carbonation escapes from the body without causing any significant change in its moisture content. This assumption also makes Equation III more reasonable. In Equations there is a parameter, denoted by  $\delta$ ; this equals the water released divided by the carbon dioxide take-up. Estimation of this parameter is discussed later.

Table 4 exhibits the well-known simple solutions of the diffusion equations I b), II, and III presented in Table 3. The assumption used is that the thin surface layer of the body immediately attains the equilibrium carbon dioxide content at the start of the carbonation process. This means that the boundary condition  $r = 1$ , and respectively  $^{\circ}C/^{\circ}C_e = 1$  and  $^{\circ}M/^{\circ}M_e = 1$ , have been employed. The numerical solutions are given in Figs. 11 and 12. Some practical examples of the theory, using the estimates given in Section 4.4, are to be found in Appendix 4.

To connect the mathematical formulation of the moisture released by the carbon dioxide take-up presented in Table 3, Equation II, with the formulation given in Table 1, Equation I, there is obtained for the approximately fixed and uniform moisture content of the body, with gravity being neglected,

$$\frac{\partial C}{\partial h} = S_c \quad (\text{Special case, Equation I, Table 1}) \quad (25)$$

or

$$\frac{\partial ^{\circ}C}{\partial h} = S_c; \quad \frac{\partial ^{\circ}C}{\partial h} = ^{\circ}k \nabla^2 ^{\circ}C; \quad ^{\circ}C = \delta r (D_e - D_0) \quad (26)$$

It should be emphasized that the equations and solutions to be found in Tables 3 and 4, with the exception of Equation (17), are based on the constancy of the properties of concrete. This implies that concrete is assumed to be stable, and that its moisture content is at least approximately uniform and constant. Estimation of the necessary parameters for the prediction of carbonation and related phenomena, in accordance with the formulae and solutions presented in Tables 3 and 4 (Figs. 11 and 12), is presented in Section 4.4.

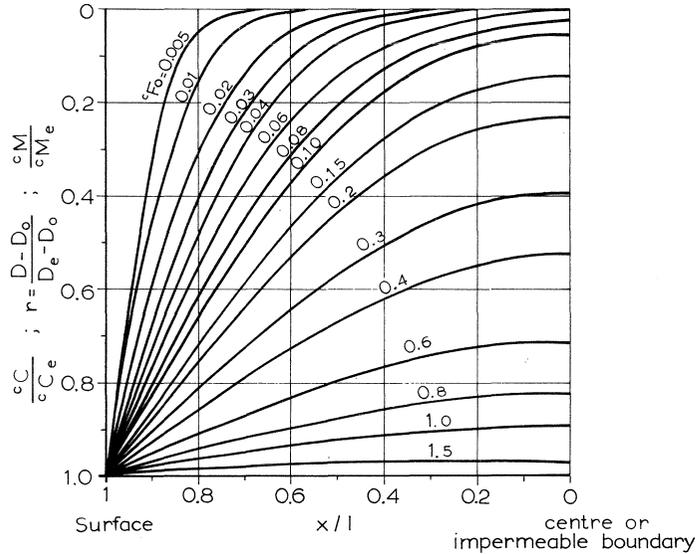


Figure 11. The distribution of relative carbon dioxide take-up,  $r$ , relative water content released during this action of carbon dioxide,  $cC/cC_e$ , and relative mass gain, if water released has escaped,  $cM/cM_e$ , at various times in a wide (infinite) slab of initial uniform carbon dioxide content  $D_0$  and of surface carbon dioxide content  $D_e$  = equilibrium carbon dioxide content. The initial water release and mass gain are zero. The figure indicated on the curves relate to the values of Fourier number  ${}^{\circ}Fo = {}^{\circ}kh/l^2$ . - The curves are theoretical curves of the diffusion theory [2].

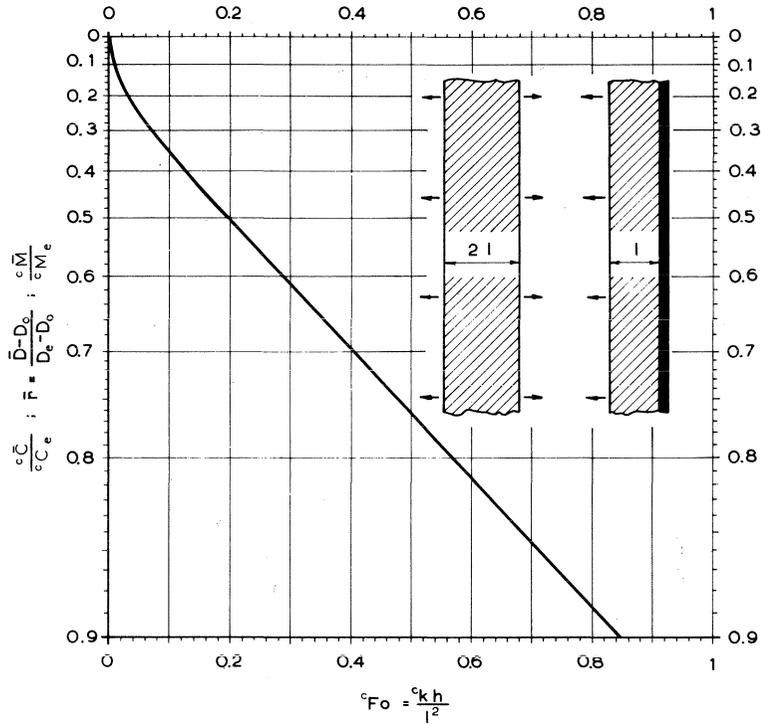


Figure 12. Relative average carbon dioxide take-up,  $\bar{r}$ , corresponding relative water release,  $^{\circ}\bar{C}/^{\circ}C_e$ , and relative mass gain, if water released has escaped,  $^{\circ}\bar{M}/^{\circ}M_e$ , of an (infinitely) wide slab as a function of Fourier number  $^{\circ}Fo = ^{\circ}kh/l^2$ . Initial uniform carbon dioxide content  $D_0$ , and surface carbon dioxide content  $D_e$  (= equilibrium carbon dioxide content). The initial water release and mass gain are zero. - The curve is a theoretical curve of the diffusion theory [7]. (Cf. examples in Appendix 4).

#### 4.4 ON ESTIMATION OF THE PARAMETERS FOR THE PREDICTION OF CARBONATION TRANSFER

##### 4.41 Parameter $D_0$

It is known that cement in storage gradually takes up water and carbon dioxide. In addition, there occurs some carbon dioxide take-up from the ambient air and also from mixing water during the weighing and mixing of concrete and cement paste.

Here,  $j_0$  is defined as the total amount of carbon dioxide taken up by cement during storage and cement paste during mixing under fixed conditions; in this publication, usually in air of a  $\text{CO}_2$ -content of about 500 ppm by volume. It is assumed that this initial amount of carbon dioxide  $j_0$  is uniformly distributed in cement paste.

Table 5 contains the determinations of  $j_0$ , including the other entities obtained during the course of the tests. All five of the cements were portland cement populations used also in the other tests presented in this publication. Numerous other similar tests made earlier, although not for this purpose, support these results, giving the magnitude of  $j_0$  expressed as  $j_0/c_0$  ( $\text{CO}_2$  kg/cement kg). Consequently, and without entering upon any detailed statistical examination, it can be established that in preliminary predictions,  $j_0/c_0$  is of the following order of magnitude:

$$\frac{j_0}{c_0} = (6 \pm 2) \text{ per cent,} \quad (27)$$

with the approximate range included.

For concretes, there is easily found

$$D_0 = Q_c \frac{j_0}{c} = Q_c \frac{j_0}{1.05 c_0} \left( \frac{\text{CO}_2 \text{ kg}}{\text{concrete m}^3} \right) \quad (28)$$

or with the average  $j_0/c_0 = 0.06$  inserted, and without taking strict account of the small correction (1.05),

$$D_0 = 0.06 Q_c \left( \frac{\text{CO}_2 \text{ kg}}{\text{concrete m}^3} \right) \quad (29)$$

Table 5. Temperature treatment of cement pastes made from 5 Finnish portland cements, with water-cement ratios of 0.3 and 0.45, for determination of the initial carbon dioxide content  $j_0$  in cement pastes. Curing prior to test 8 ... 9 months under sealed conditions. The moisture content (freed between 20 ... 105°C) and fixed water content (freed between 105 ... 550°C) is also given. In accordance with Fig. 10, no correction for the carbon dioxide content obtained in temperature treatment was necessary.

	Temperature range °C	Material liberated	Symbol	3 different factories marked Lo, La, Pa				3 different cement populations of factory Pa			
				7300 Lo %	7600 La %	7800 Pa %	average %	6800 Pa %	7100 Pa %	7800 Pa %	average %
w/c = 0.3	20 ... 105	moisture	$w_f/c_0$	19.4	19.8	18.2	19.1	19.2	18.4	18.2	18.6
	105 ... 550	fixed water	$w_n/c_0$	10.8	11.2	11.7	11.2	11.5	11.5	11.7	11.6
	550 ... 1000	CO <sub>2</sub>	$j_0/c_0$	5.1	8.2	4.1	5.8	6.0	5.0	4.1	5.0
Cement	550 ... 1000	CO <sub>2</sub>	$j/c_0$	2.6	5.9	2.5	3.7	4.3	3.6	2.5	3.5
	550 ... 1000	CO <sub>2</sub>	$\frac{j_0}{c_0} - \frac{j}{c_0}$	2.5	2.3	1.6	2.1	1.7	1.4	1.6	1.5
w/c = 0.45	20 ... 105	moisture	$w_f/c_0$	29.7	31.7	29.3	30.2	30.0	31.2	29.3	30.2
	105 ... 550	fixed water	$w_n/c_0$	14.0	14.4	14.8	14.4	14.3	14.3	14.8	14.5
	550 ... 1000	CO <sub>2</sub>	$j_0/c_0$	4.8	7.9	4.8	5.8	6.3	6.3	4.8	5.8
Cement	550 ... 1000	CO <sub>2</sub>	$j/c_0$	2.6	5.9	2.5	3.7	4.3	3.6	2.5	3.5
	550 ... 1000	CO <sub>2</sub>	$\frac{j_0}{c_0} - \frac{j}{c_0}$	2.2	2.0	2.3	2.1	2.0	2.7	2.3	2.3

4.42 Parameter  $D_e$ 

As defined here, parameter  $j_e$  is the equilibrium carbon dioxide take-up of more or less hydrated cement paste under fixed conditions, for the purposes of this publication usually in air of a  $\text{CO}_2$ -content amounting to about 500 ppm by volume.

The carbon dioxide content required for total carbonation of fully hydrated portland cement paste at a pressure of  $\text{CO}_2$  in ordinary air will be estimated with the aid of the following simple formula

$$\frac{j_e(\text{max})}{c_0} = 0.78 \cdot \text{CaO } \% \text{ (kg CO}_2\text{/kg cement),} \quad (30)$$

modified from the formulae presented by Steinour [71]. The content of total CaO in cement can be arrived at by means of ordinary cement analysis. When the CaO is of the order of 60 per cent in portland cements, the theoretical ultimate carbon dioxide take-up in fully hydrated portland cement pastes proves to be of the order of 0.45 kg  $\text{CO}_2$ /kg cement. Thus,

$$\frac{j_e(\text{max})}{c_0} = 0.45 \text{ (kg CO}_2\text{/kg cement)} \quad (31)$$

The maximum value observed experimentally by Kroone & Blakey [69] was 0.45 kg  $\text{CO}_2$ /kg cement.

As a general rule,  $j_e$  is a variable entity which depends upon the hydration degree or maturity of concrete, and on the moisture content of the body. The potential of the take-up of carbon dioxide as a function of hydration is assumed in Fig. 13. As the unhydrated cement also carbonates, an endeavour has been made to take this effect into account as well. The figure illustrating the principle (Fig. 13) may be employed in preliminary predictions of the problem in the absence of any more satisfactory solution. Further research is thus needed for clarification of this problem.

Verbeck [72] came to the practical conclusion that the maximum carbonation further depends upon the moisture content of the carbonating cement paste. When carbonation proceeds slowly, as it does in normal air, moisture resulting from carbonation can escape from the specimen, thereby maintaining the moisture content controlled by the humidity of the ambient air. This indicates that the effect exerted by moisture content on carbonation can be expressed in terms of the relative humidity of the ambient air. With the support of Verbeck's data [72], there was drawn Fig. 14, which depicts the main features of the problem. The presence of a substantial amount of free water in the pores of concrete prevents the diffusion of carbon dioxide gas into the specimen, and the absence of sufficient water on the pore surfaces hinders the reaction with carbon dioxide. As Verbeck [72] has already pointed out, it is not entirely clear whether the maximum carbonation depends upon moisture. Another, and perhaps theoretically more conceivable

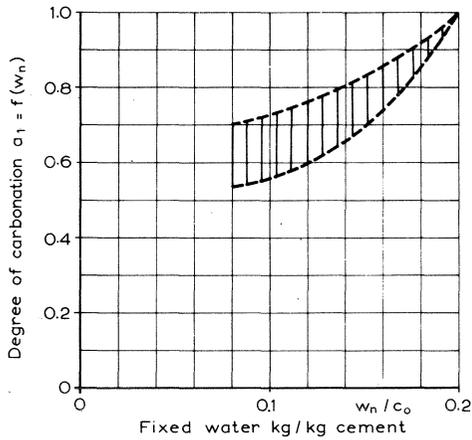


Figure 13. The possible maximum relative carbon dioxide take-up, or the potential degree of carbonation,  $a_1$ , of cement paste or concrete as a function of hydration or fixed water content at middle humidities of the ambient air ( $a_2 = 1$ , Cf. Fig. 14). The points of this relationship obtained in several experiments are in the hatched area. A figure of principle is involved.

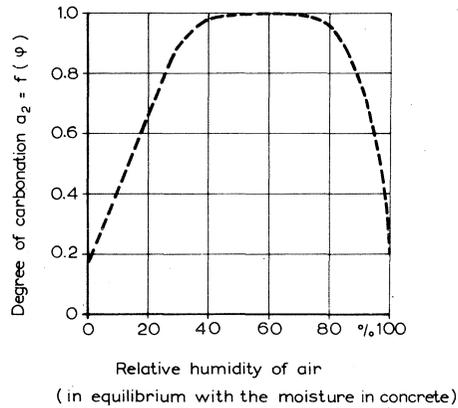


Figure 14. The possible maximum relative carbon dioxide take-up, or the potential degree of carbonation,  $a_2$ , of mature cement paste or concrete ( $a_1 = 1$ , Cf. Fig. 13) as a function of moisture content, which is assumed to be in equilibrium with the humidity of the ambient air. A figure of principle is involved. (Refer to the discussion in the text on the validity of the figure.)

possibility, is that under both wet and dry conditions the carbonation proceeds very much more slowly than is the case with middle moisture content. Thus  $\tau_k$  could be significantly smaller at both ends of the humidity range than at mid-range.

As Figs. 13 and 14 indicate,  $j_e$  can be estimated from the following equation

$$j_e = a_1 a_2 j_e(\max), \quad (32)$$

or when cement paste or concrete is drying in the middle humidities ( $\varphi \approx 40 \dots 80 \%$ ) where  $a_2 \approx 1$ :

$$\frac{j_e}{c_0} = a_1 \frac{j_e(\max)}{c_0} \quad (33)$$

The formula for concretes is

$$D_e = Q_c \frac{j_e}{c} = Q_c a_1 a_2 \frac{j_e(\max)}{1.05 c_0} \quad (34)$$

in analogy with Equation (28) for  $D_0$ , given in Section 4.41.

Table 6. Experimental determinations of  $\delta$  with temperature treatment. Crushed cement paste specimens ( $w/c = 0.3, 0.45$ ) cured, prior to 4 months carbonation in climate chamber,  $4\frac{1}{2}$  months under sealed conditions. The  $CO_2$ -figures arrived at in the experiment was corrected with the aid of the curve in Fig. 10. The fixed water was corrected by subtraction of the  $CO_2$ -increase from the value obtained in the experiment.

$\frac{w}{c}$	Temperature °C		7300 Lo		7600 La		7800 Pa	
			Ignited %	Cor- rected %	Ignited %	Cor- rected %	Ignited %	Cor- rected %
0.3	105 ... 550, fixed water $w_n/c_0$	Air	8.9	6.5	9.8	4.2	9.8	7.2
		Sealed	10.8	10.5	11.2	10.4	11.7	11.5
		$\Delta_1$		-4.0		-6.2		-4.3
	550 ... 1000, carbon dioxide take-up $j/c_0$	Air	13.5	15.9	18.4	24.0	13.8	16.4
		Sealed	5.1	5.4	8.2	9.0	4.1	4.3
		$\Delta_2$		+10.5		+15.0		+12.1
	$\delta = \frac{\Delta_1}{\Delta_2}$		0.38		0.41		0.36	
0.45	105 ... 550, fixed water $w_n/c_0$	Air	11.8	7.8	14.2	4.0	13.0	6.9
		Sealed	14.0	13.7	14.4	13.7	14.8	14.5
		$\Delta_1$		-5.9		-9.7		-7.6
	550 ... 1000, carbon dioxide take-up $j/c_0$	Air	16.2	20.2	23.9	34.1	18.9	25.0
		Sealed	4.8	5.1	7.9	8.6	4.8	5.1
		$\Delta_2$		+15.1		+25.5		+19.9
	$\delta = \frac{\Delta_1}{\Delta_2}$		0.39		0.38		0.38	

Finally, it is perhaps necessary to stress that Figs. 13 and 14 will or should be reconstructed once further knowledge of the subject has been gathered.

#### 4.43 Parameter $\delta$

Parameter  $\delta$  indicates the relation between the amount of fixed water turned into moisture (free water) as a result of carbonation and the amount of carbon dioxide taken up by hydrated cement paste, or, in other words, the relation between the water released and the carbon dioxide taken up during the carbonation process.

A brief discussion of parameter  $\delta$ , and some of its numerical values, has already taken place in Section 4.2 (Table 2). Verbeck's [72] findings indicate that the water released per mole of carbon dioxide might vary from 0 to 1 mole of water, closely approximating to 1 mole water released during most of the carbonation period, but approaching 0 moles during the advanced stages. The results to be found in Table 2 show that approximately 1 mole of water per 1 mole of carbon dioxide was released during carbonation ( $18/44 = 0.41$ ). In addition there is clearly discernible the tendency toward smaller ratios in accordance with Verbeck.

The values of  $\delta$  presented in Table 2 were for cement pastes ( $w/c = 0.3, 0.4, 0.5$ ) made of cement Pa 6800. Table 6 shows additional  $\delta$ -values obtained for cement pastes ( $w/c = 0.3, 0.45$ ) made of cement populations Lo 7300, La 7600, Pa 7800, but by application of a simplified method (muffle furnace, Photo 11) described at the end of Section 4.2 and in Fig. 10. The cement pastes were cured for  $4\frac{1}{2}$  months under sealed conditions (small plastic bags in sealed glass jars); after the curing period they were crushed, and samples of particle size of  $\approx 0.25 \dots 0.5$  mm (Photo 13) were stored for 4 months in the air (in the climate chamber, Photo 4) the carbon dioxide content of which varied from 50  $\dots$  500 ppm in volume, mostly amounting to 50 ppm, and of which during the 2 first months the relative humidity was 85 per cent, following by 2 months at 70 per cent.

The  $\delta$ -values taken from Tables 2 and 6 yield

$$\delta = 0.38 \pm 0.03 \quad (35)$$

#### 4.44 Carbonation conductivity $^{\circ}k$

In his Report [72] Verbeck stated that "the moisture content (relative humidity) of hydrated paste has a considerable and an important influence on the rate and ultimate extent of carbonation". Nevertheless this statement on the effect of the moisture content on the ultimate extent is somewhat open to question, although it was accepted in Section 4.42 for want of anything more satisfactory. The effect of moisture content on the rate of carbonation should be described with the aid of non-constant carbonation conductivity  $^{\circ}k$ . By reason of the slowness of the carbonation process, carbonation proceeds virtually only in those layers of concrete which are

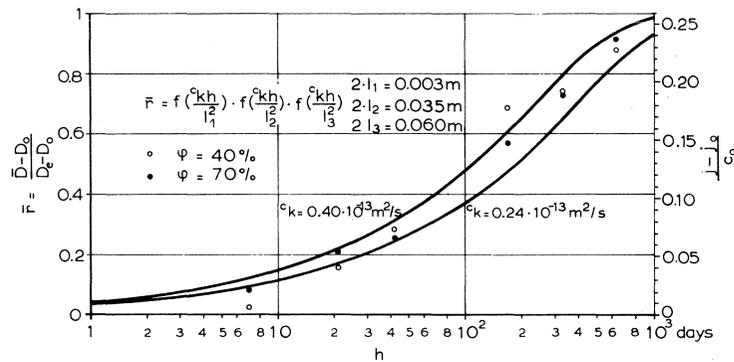


Figure 15. Carbon dioxide take-up of small cement paste specimens ( $w/c = 0.4$ ; cement Pa 6800) during drying in climate rooms ( $t = 20^\circ\text{C}$ ,  $v < 0.5$  m/s,  $\text{CO}_2$ -content a. 500 ppm by volume, RH 40 %, 70 %). Precuring 7 days sealed prior to  $\text{CO}_2$ -exposure.  $\text{CO}_2$ -take-up is the substance freed in  $550 \dots 1000$   $^\circ\text{C}$  ignition, corrected with the aid of the solid curve in Fig. 10. Each point represents the average value obtained from three specimens. Ultimate carbon dioxide take-up during exposure is fixed at 0.26. ( $j_0/c_0 = 0.06$ ,  $j_e/c_0 = 0.32$ ,  $(j_e - j_0)/c_0 = 0.26$ ). The curves of diffusion theory with constant  $^c k$ -values have been fitted in both cases of three-dimensional [7]  $\text{CO}_2$ -exposure.

in moisture equilibrium with the moisture in the ambient air. The preliminary examinations [2] gave the following order of magnitude, which is probably appropriate in the middle humidities of ambient air, and for mature concretes:

$$^c k = O(10^{-13} \text{ m}^2/\text{s}) \quad (36)$$

The basic formula for penetration depth used in Report [2] was  $L = 2(^c k h)^{1/2}$ , corresponding to  $r = 0.16$ . If  $r = 0.89$  is chosen,  $L = 0.2(^c k h)^{1/2}$  is arrived at, and the respective estimation is  $^c k = O(10^{-12} \text{ m}^2/\text{s})$ .

The tests made by Verbeck [72] clearly indicate that the thickness of the specimens exercised a considerable effect on the carbonation transfer when the tests were carried out at different humidities. In Verbeck's tests, the effect could be attributable to the accumulation of the water released in concrete, which changes the internal humidity in the specimens, in view of the relative rapidity of the carbonation process by virtue of the rather high carbon dioxide pressure, 1 atm.

If the carbon dioxide transfer were slower, as in normal air, a similar effect might be possible, but would primarily be due to the microstructure changes in concrete brought about by carbonation. This effect affords strong support for the opinion that  $^c k$  cannot be a constant during carbonation at a stated humidity.

In the same concrete,  $^{\circ}k$  is probably a function of 1) hydration degree, 2) hydration conditions, 3) degree of carbonation, 4) moisture concentration, and 5) temperature. If the concrete is relatively mature, and has been hydrated under average conditions, it seems reasonable to assume that  $^{\circ}k$  is to all intents and purposes a function of the degree of carbonation.

In what follows a further examination is made of the determination of the order of magnitude of carbonation conductivity  $^{\circ}k$ . Although  $^{\circ}k$  cannot be a constant, an endeavour is made at this stage of development of the subject to find average values for  $^{\circ}k$  for preliminary predictions of carbonation. It is evident that further research is greatly needed if the problem is to be elucidated more satisfactorily.

Fig. 15 illustrates the carbonation of small specimens of cement paste with an initial rather small degree of hydration. The amount of fixed water after 7-day sealed curing or at the beginning of exposure was about 0.08 kg fixed water/kg cement, increasing at a somewhat more advanced age to 0.09 as a consequence of the additional hydration during drying and carbon dioxide exposure. The concept that the diffusion theory provides a satisfactory description of the carbonation transfer is verifiable from this figure. Even the assumption of the constancy of carbonation conductivity  $^{\circ}k$  seems to provide satisfactory agreement between the theory and the experiments. These experiments give an average  $^{\circ}k$  of the order of  $0.3 \cdot 10^{-13} \text{ m}^2/\text{s}$ .

Fig. 16 shows the carbonation of another series of small specimens of cement paste. The values of  $w_n/c_0$  were determined immediately after precuring, and thus before  $\text{CO}_2$  exposure. The scattering of the experimental points is rather large, and is presumably chiefly ascribable to the comparatively large variations in the size of the specimen. The tests were not originally designed for carbonation determinations, and accordingly no special attention was paid to the exact dimensions. Nevertheless, the results afforded support for the observation that  $^{\circ}k$  for small specimens (or for two-year-carbonation for larger specimens) is of the order of  $10^{-13} \text{ m}^2/\text{s}$ . Further, the results give no evidence that carbonation is a function of the water-cement ratio, or of relative humidity at middle humidities (40 %, 70 %), in accordance with Fig. 14.

The two test series presented above were in respect of cement paste alone, and no study was made of the distribution of carbonation. Figs. 17 a and 17 b show the carbonation of standard cement mortar specimens (4 cm x 4 cm x 16 cm). The cement used was Pa 7100. The specimens were covered tightly with glued metal membrane (two layers) and with glued plastic sheet (one layer). The covering work was done after 223 days of sealed curing in desiccators. The sealed condition was maintained continuously during the curing period of 290 days, after which the end surfaces of the mature specimens were cut open to allow of uniaxial carbonation only (Fig. 17 a) in the two climate rooms at respective relative humidities of 40 % and 70 %. The measured carbon dioxide content in the climate rooms was about 500 ppm by volume. No significant effect of the differences in relative humidities was observable after 293 days of exposure, after which two specimens (one from

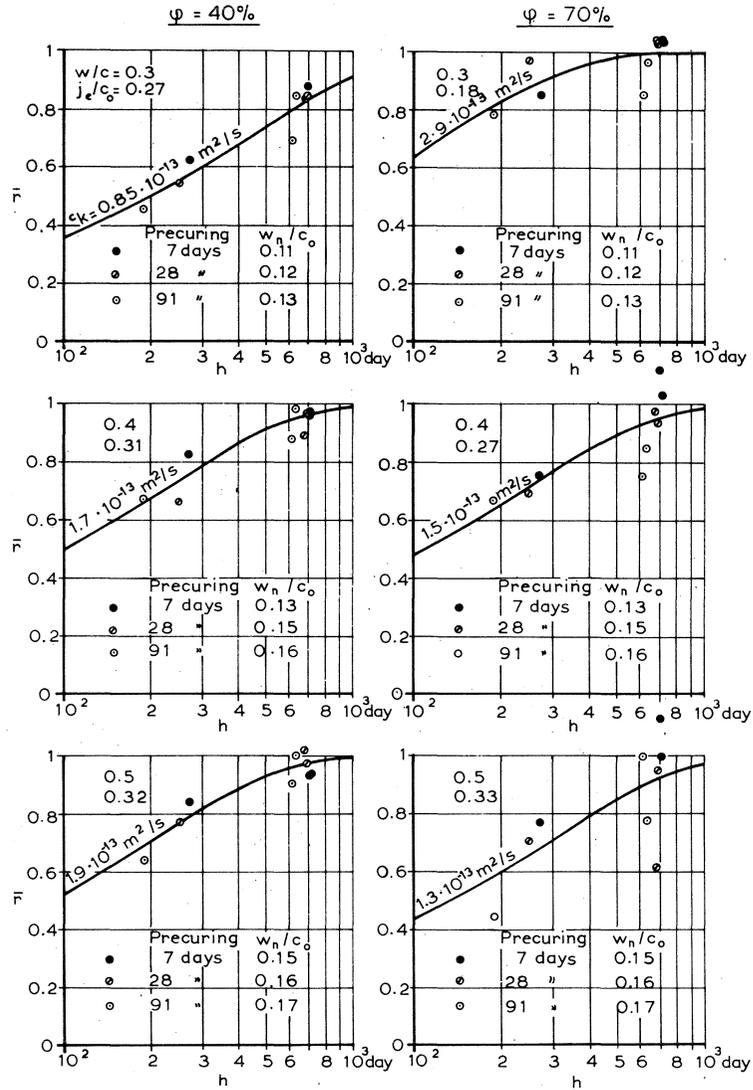


Figure 16. Carbon dioxide take-up of small cement paste specimens (pillow shaped, average size 6 cm x 6 cm x 0.6 cm, Cement: Pa 6800) during drying in climate rooms ( $t = 20^\circ\text{C}$ ,  $v < 0.5$  m/s,  $\text{CO}_2$ -content a. 500 ppm by volume, RH 40 %, 70 %). Precuring 7, 28, or 91 days almost sealed (wrapped in plastic sheets) before  $\text{CO}_2$  exposure.  $\text{CO}_2$  is the substance freed in  $550 \dots 1000^\circ\text{C}$  ignition, corrected with the aid of the broken line in Fig. 10. ( $j_0/c_0 = 0.06$ ). Each point represents a result obtained from one specimen. The curves of the diffusion theory with constant  $k$ -values (three-dimensional cases) have been fitted.

Figure 17a. 293-day distribution of carbonation in the prisms of mature standard cement mortar in air ( $\text{CO}_2$ -content a. 500 ppm by volume) of two climate rooms ( $t = 20^\circ\text{C}$ , RH 40 %, 70 %). Each point represents the average value obtained from two pieces (RH 40 %, 70 %). No significant difference was found in the carbonation of the two prisms kept at the different relative humidities mentioned. Each of the two prisms was split into ten pieces, and determination of the carbon dioxide content of each piece was effected with the aid of temperature treatment.

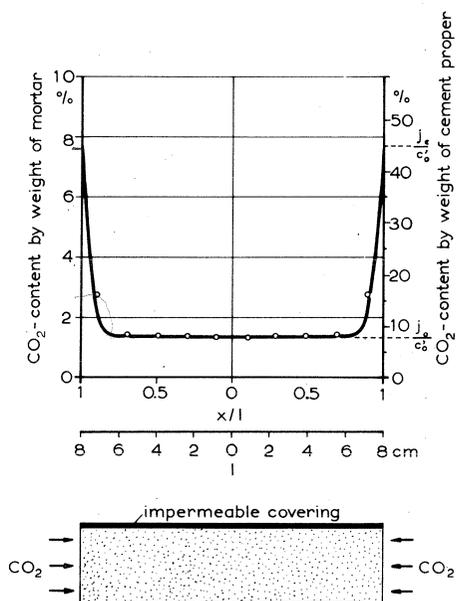
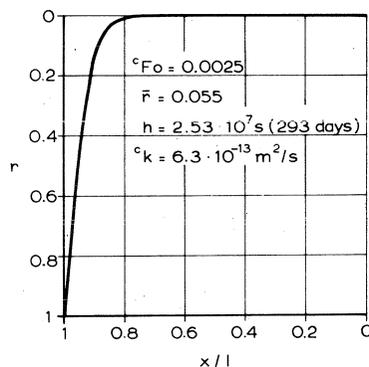


Figure 17b. 293-day distribution of carbonation in the mature concrete mortar prisms. In Fig. 17a, the results were presented in another form. The curve was drawn with the aid of Thorne's tables [73].



RH 40 % and one from RH 70 %) were split and tested. The specimens were split with the aid of a specially constructed device (see Photos 16 and 17) into ten pieces about 1.6 cm in length. The carbon dioxide content was taken to be the amount released between  $550^\circ\text{C}$  ...  $1000^\circ\text{C}$ , corrected with the aid of the broken line in Fig. 10. The amount of the "insoluble" (HCl) material (common in Finnish portland cement) was also taken into account (in this special case only) as a reduction in the amount of the cement content. In Fig. 17a, the reduced cement is termed "cement proper". (The correction is presented in detail in Appendix 5.) Fig. 17b, drawn on the basis of the experimental data presented in Fig. 17a, and using Thorne's tables [73], shows that carbonation conductivity  $^c k$  for a cement mortar is  $6.3 \cdot 10^{-13} \text{ m}^2/\text{s}$ , and is thus of the order of  $10^{-12} \text{ m}^2/\text{s}$ .

The results of the above examinations, although of preliminary nature, show that

$${}^c k = O(10^{-12} \dots 10^{-13} \text{ m}^2/\text{s}) \quad (37)$$

for the cement pastes and cement mortars concerned.

#### 4.5 ESTIMATION OF PENETRATION DEPTH OF CARBONATION IN CONCRETE STRUCTURES

When estimations are made of the penetration depths of carbonation in practical concrete structures, the concrete structures can be regarded as semi-infinite bodies, as the carbonation process is very slow. If this reasonable assumption is accepted, there must be selected the degree of carbonation of the moving boundary of carbonation under examination. This selection involves some arbitrary decisions, although help may be obtained from physical and chemical considerations which take practical aims into account. It seems, however, that the interesting carbonation degree  $r$  of a mature concrete (cement paste) kept at the middle humidities of the air is between 0.1 ... 0.9.

If the surface of the concrete structure is continuously maintained at a constant carbon dioxide atmosphere, then in accordance with the diffusion theory for semi-infinite media, the following well-known formula [93] is derived:

$$r = \operatorname{erfc} \left( \frac{L}{2} {}^c k^{-\frac{1}{2}} h^{-\frac{1}{2}} \right), \quad (38)$$

where  $L$  is the penetration depth of carbonation during time  $h$  when the carbonation conductivity is  ${}^c k$ . If the value  $r = 0.16$  is inserted in Equation (38), there is obtained [93]

$$L_{0.16} = 2 ({}^c k h)^{\frac{1}{2}} \quad (39)$$

Equation (39) was earlier given in Report [2]. If, instead, value  $r = 0.89$  is inserted in Equation (38), then

$$L_{0.89} = 0.2 ({}^c k h)^{\frac{1}{2}} \quad (40)$$

It is interesting to note that

$$L_{0.16} : L_{0.89} = 10 : 1 \quad (41)$$

In the application of Equations (39) and (40) there are required the values of carbonation conductivity  ${}^c k$ . Section 4.44 is devoted to this end.

If an average value of  ${}^c k = 10^{-12} \text{ m}^2/\text{s}$  is inserted in Equations (39) and (40), and  $h$  is expressed in years, then

$$L_{0.16} = h^{\frac{1}{2}} \text{ cm} \quad (42)$$

$$L_{0.89} = 0.1 h^{\frac{1}{2}} \text{ cm} \quad (43)$$

## 5 ON THE INTERRELATION OF THE EVAPORATION DRYING, FIXATION DRYING, AND CARBONATION OF CEMENT PASTE

### 5.1 INTRODUCTION

A knowledge of the interrelation of the different, principal substances in cement paste, or that of their changes, is of major importance in concrete research and practice, as the properties of concrete have a vital dependence on the amounts of fixed water, moisture or free water and carbon dioxide take-up. This is especially true as regards research concerned with the moisture, or its changes in cement paste or concrete. In this connection the main substances are defined as follows:

- 1) Moisture (evaporable or free)
- 2) Fixed water (non-evaporable or bound)
- 3) Fixed carbon dioxide (adsorbed or bound)

The substances mentioned are in general mutually dependent. There can occur no gain in the fixed water content when the moisture content is lower than a certain limit (approximately the amount of moisture on a sorption isotherm at a relative humidity of 80 per cent). Further, as has already been shown in Chapter 4, the carbon dioxide take-up is dependent on the moisture content, and in turn the carbon dioxide take-up decomposes fixed water and is therefore a source of moisture. It is evident that at this stage of development there exist no possibilities of analytical treatment of the moisture changes in concrete, if there are not, or cannot be found any reasonable assumptions, or restrictions imposed on the chaos originating in this mutual dependence. Fortunately, adequate restrictive assumptions of this type can be made in accordance with the general lines presented in Section 2.22. One reasonable assumption, appropriate for numerous practical situations, was made in Section 4.3:

- I The carbonation process in normal air is very slow in comparison with the moisture flow or drying. It seems therefore justified to assume that the water released in the body due to carbonation escapes from the body without causing any significant change in its moisture content. (Carbonation occurs in concrete at places in moisture equilibrium controlled by the humidity of ambient air. It is evident that microstructure changes brought about by carbonation will induce changes in the equilibrium moisture content).

Further, it is reasonable to assume:

- II The carbonation usually occurs at lower humidities in which occurs no significant gain in fixed water content.

Assumption I and II provide a possibility of treating the carbonation process analytically as an independent process, as was put forward in Chapter 4 (although the changes in equilibrium moisture content, as mentioned in parentheses above may bring about difficulties).

The relation of the diminution of fixed water, or the generation of moisture due to carbonation has already been discussed in Section 4.43.

To ensure the conversion of unhydrated cement paste into hydrated cement paste, or, in other words, the conversion of a concrete mass into concrete proper, it is necessary to keep it under conditions in which there occur no practical moisture exchange between the body and the surroundings (sealed condition by definition in this publication). This leads to the following reasonable assumption:

- III The major part of the hydration or fixation of water occurs at ordinary temperatures during the early days, during which concrete as a construction material is converted into concrete proper, and kept under conditions which are virtually sealed. (Cf. Report [2], Section 7.3.).

Further, it is known that

- IV The hydration process or fixation of water virtually ceases when the moisture content of cement paste is in equilibrium with air of a relative humidity of 80 %.

Assumptions III and IV, if accepted, allow of the treatment in numerous cases of fixation drying as an independent process (Cf. Report [2], Section 7.3).

If it is accepted that there are numerous cases in which hydration or fixation drying occurs before evaporation drying starts, and in which carbonation is essentially a slower process than evaporation drying, in those cases the evaporation drying can be regarded as an independent process.

In the following section of this chapter (Chapter 5) an examination is made of some experimental results on the subject matter expressed in the heading, and obtained for Finnish cement paste (Cement: Pa 6800).

## 5.2 EXPERIMENTS AND RESULTS

The mutual relations and amounts of different substances in some cement pastes made of cement Pa 6800 under different humidity conditions at 20°C are examined experimentally below. The substances have been divided into different categories by means of temperature treatments at 105°C, 550°C and 1000°C, using the information (solid curve) to be found in Fig. 10 as additional facts. At 105°C, by definition, only evaporable water or moisture is lost, between 105°C ... 550°C mainly fixed water is lost, and between 550°C ... 1000°C mainly carbon dioxide is lost [2]. However, the carbon dioxide content liberated within the temperature range of 105°C ... 550°C is so substantial that correction is necessary (Fig. 10). Some preliminary evidence also exists that a small amount of fixed water is

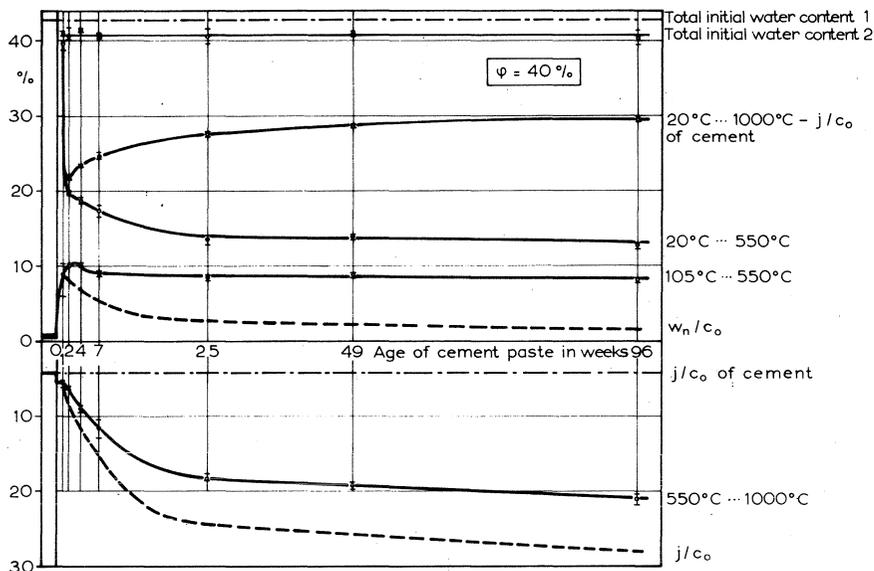


Figure 18. Thermal analysis of cement paste specimens ( $w/c = 0.40$ , Cement: Pa 6800) indicating the mutual relationship and changes in different substances during evaporation drying, fixation drying, and carbonation in a climate room ( $t = 20^\circ\text{C}$ , RH 40 %,  $\text{CO}_2$ -content about 500 ppm by vol.). Basic weight at  $1000^\circ\text{C}$ . Each experimental point represents an average value obtained from three specimens. The segments of lines indicate the range of individual values. (Cf. Fig. 19.)

liberated at a temperature somewhat above  $550^\circ\text{C}$ , probably between  $550^\circ\text{C} \dots 650^\circ\text{C}$ , but as this effect needs further investigation no attempt has been made at correction.

Figs. 18 and 19 relate to the general features of the moisture, fixed water and carbon dioxide content, and their changes during curing in two climate rooms ( $\phi = 40\%$ ,  $70\%$ ); they were arrived at with the aid of two series of cement paste specimens ( $w/c = 0.40$ , 39 pillow shaped specimens poured in small plastic bags, average weight 11 g, and average size  $0.3\text{ cm} \times 3.5\text{ cm} \times 6\text{ cm}$ ), precured under sealed conditions for one week before "exposure". Total water content 1 was obtained by use of the nominal water-cement ratio, but with the moisture, fixed water and carbon dioxide content in cement ( $0.4 \cdot 105.1 = 42.0$  (water added);  $42.0 + 0.4$  (moisture)  $+ 0.4$  (fixed water)  $= 42.8$ ) taken into account. Total water content 2 is the relative initial weight of the specimens, minus the weight of cement ignited at  $1000^\circ\text{C}$  ( $= 100$ ), minus the weight of  $\text{CO}_2$  ( $= 4.3$ ). Thus the total water content 2 = the initial weight of the paste in units used -  $104.3$  (or "true" total water content). The solid curves were found experimentally, each segment of a line representing the results and range of the results arrived at for three specimens. The broken curves indicate the effect of carbonation, or in other words the carbon

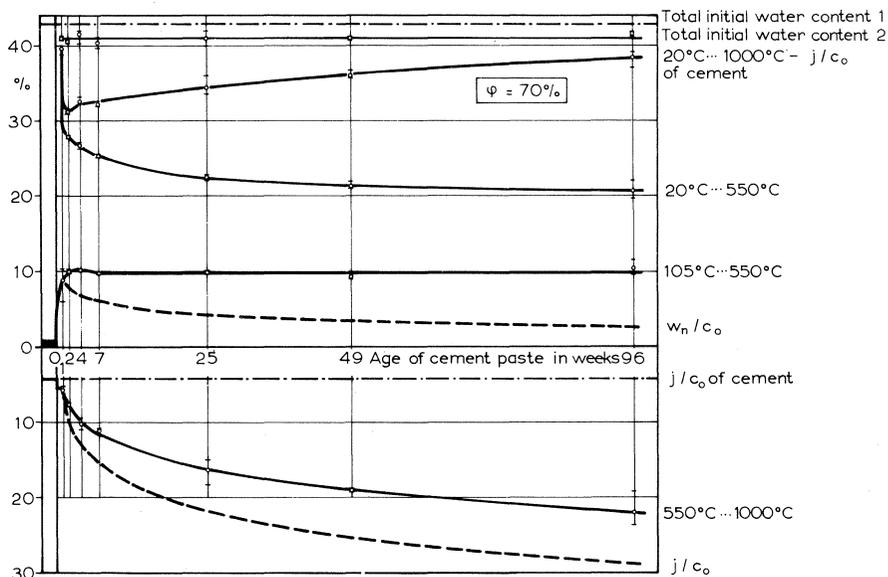


Figure 19. Thermal analysis of cement paste specimens ( $w/c = 0.40$ , Cement: Pa 6800) indicating the mutual relationship and changes in different substances during evaporation drying, fixation drying, and carbonation in a climate room ( $t = 20^{\circ}\text{C}$ , RH 70 %,  $\text{CO}_2$ -content about 500 ppm by vol.). Basic weight at  $1000^{\circ}\text{C}$ . Each experimental point represents an average value obtained from three specimens. The segments of lines indicate the range of individual values. (Cf. Fig. 18.)

dioxide take-up and the reduction in fixed water content induced by the carbon dioxide take-up; curves were prepared with the aid of the information afforded by Fig. 10 (solid curve).

Fig. 20 (a series of small figures) is concerned with additional tests on the same subject as that presented in Figs. 18 and 19 above. The specimens were similar to those used above, but variations had been introduced in the curing conditions: partial sealing was adopted (plastic bags wrapped in plastic sheets); the air had a RH of 100 % (in desiccator above water surface); they were in water. The precuring time under sealed conditions was 3 days (0.4 weeks). The differences in the curing conditions seem to have exercised an insignificant effect on the hydration process. Consequently, it is evident that the divergences between different "wet" curing conditions (sealed or nearly sealed, RH 100 %, water) exert an insignificant effect on the hydration process in practice (Cf. [6]). Moreover, the carbonation is very slight. It is possible that the changes in the curves  $550 \dots 1000^{\circ}\text{C}$  discernible in Fig. 20 are attributable to the fixed water liberated above  $550^{\circ}\text{C}$ . As has already been noted, this effect needs further study.

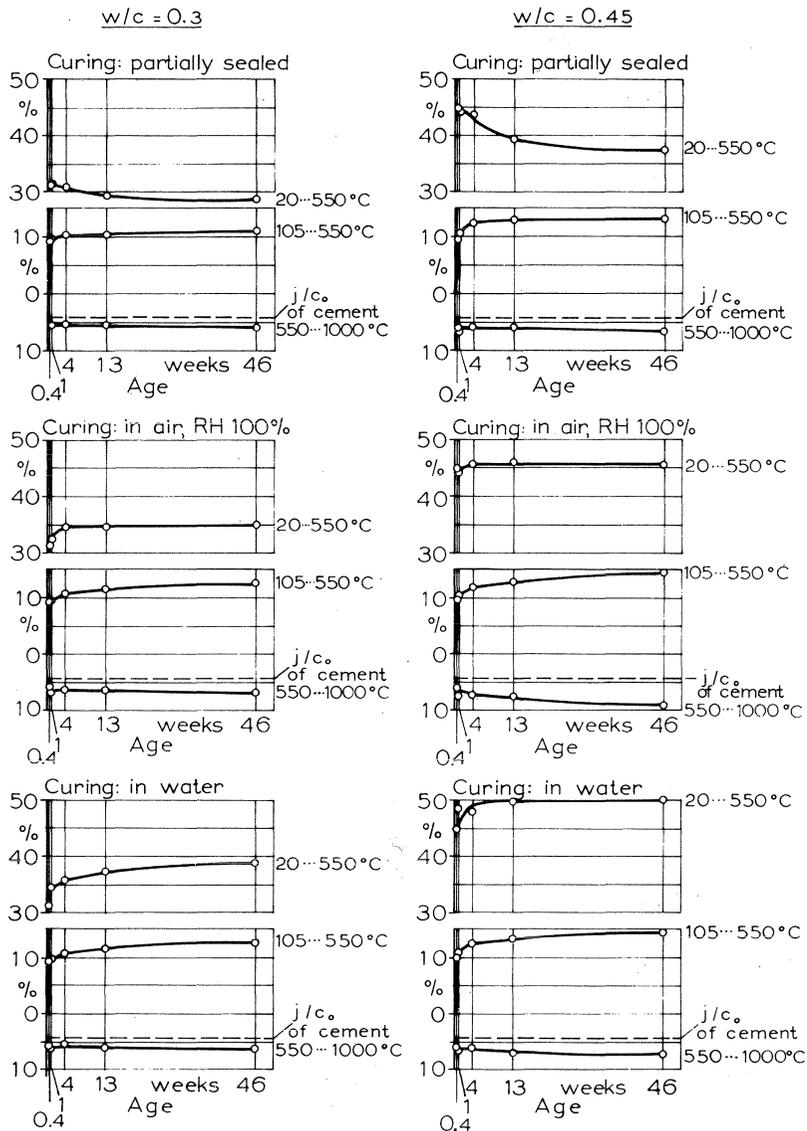


Figure 20. Thermal analysis of cement pastes ( $w/c = 0.3, 0.45$ ; Cement: Pa 6800) showing approximately the mutual relationship of total water content ( $20 \dots 550^\circ\text{C}$ ), fixation drying ( $105 \dots 550^\circ\text{C}$ ), and carbonation ( $550 \dots 1000^\circ\text{C}$ ) under different moist or wet-curing conditions. The amounts are given as percentages of the weight of cement paste ignited at  $1000^\circ\text{C}$ . Each experimental point represents an average value obtained from three specimens.

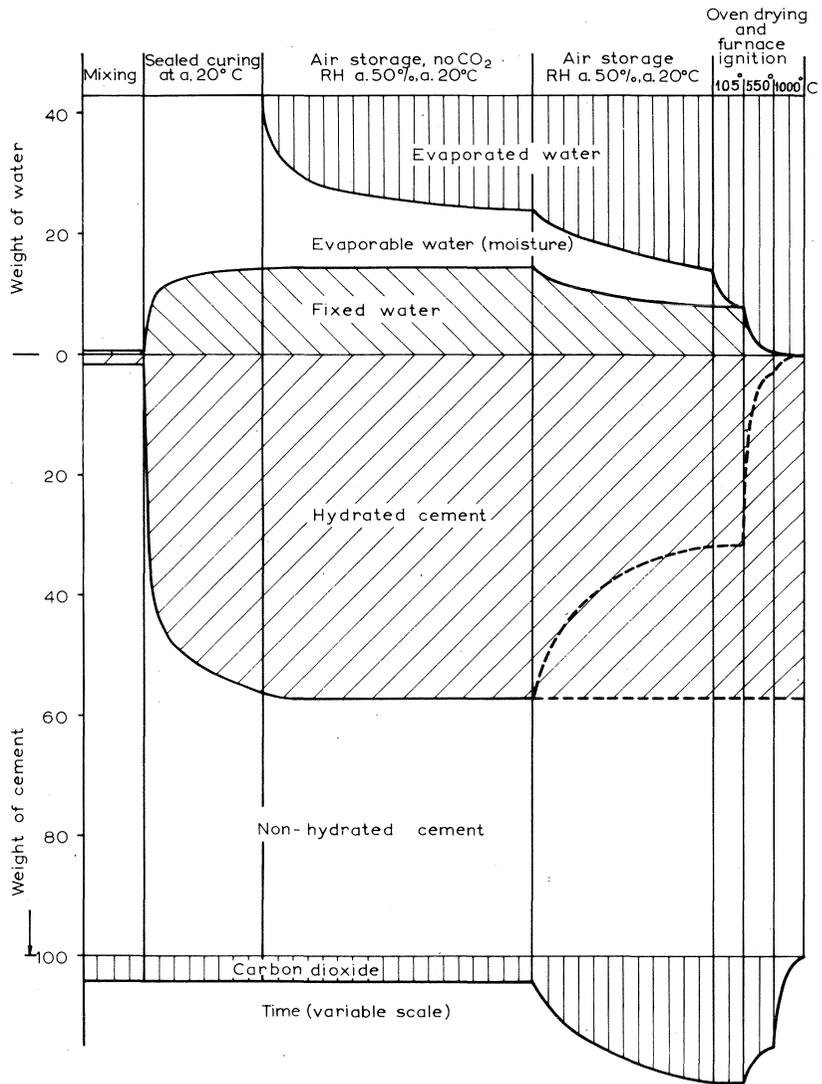


Figure 21. Schematic figure indicating the interrelations of the substances in cement paste (w/c about 0.4) under different conditions. The broken line indicates that hydrated cement undergoes transformation as a result of carbonation and temperature treatment. Vertical axis: weight (mass), horizontal axis: time. The weight of cement ignited at 1000°C has been fixed at 100. The figure is a revision of Fig. 3 presented in Report [2].

### 5.3 CONCLUSION. FIGURE OF PRINCIPLE

The interrelation or interplay of different substances in cement paste during its life-time is very considerable and significant. As Figs. 18 and 19 demonstrated, the carbonation frees fixed water so vigorously that its amount can be estimated as being virtually nil after complete carbonation. The question arises – what is concrete like in which practically speaking there is no hydrated water?

A schematic figure to indicate the mutual relations which exist between the substances in cement paste under selected conditions has already been presented in Report [2]. A similar but revised schematic figure is given here (Fig. 21). The broken curve within the area of the hydrated cement in Fig. 21 indicates the dehydration of the hydrated cement, first as a result of carbonation, and then of furnace ignition.

6 A BRIEF EXAMINATION OF FIXATION DRYING: A SINK OF MOISTURE AND A SOURCE OF FIXED WATER. ON THE ESTIMATION OF INITIAL MOISTURE CONTENT  $C_0$

The principles of the hydration of cement or the fixation drying have already been presented by the author in Report [2], and in the previous chapters of this publication. For the sake of completeness, a brief examination of fixation drying is given below.

In Report [2], as well as in Section 5.1 (Assumptions III and IV), there was reached a practical conclusion for the drying process of concrete. The major part of fixation drying occurs during the early days under sealed conditions, and virtually no fixation drying takes place during the subsequent evaporation drying process. This assumption, although not generally valid, is here employed as a guiding principle. Discussion of its weak points is to be found in the author's reports [2], [7], [8], and it is hoped that further research will throw more light on this subject.

Acceptance of the assumption presented above leads to the conclusion that in studying the drying of concrete, the initial determination should be the initial moisture content  $C_0$  as a function of the fixation drying which has occurred during the days immediately succeeding pouring, under sealed conditions:

$$C_0 = Q_c(w/c - \Delta w/c)(\text{kg/m}^3) \quad (44)$$

In the equation,  $Q_c$  is the cement content in concrete, kg cement/m<sup>3</sup> concrete,  $w/c$  is the original water-cement ratio corrected for bleeding, and

$$\Delta w/c = M(h)_t w_n(h = \infty)/c \quad (= \Delta w_n/c) \quad (45)$$

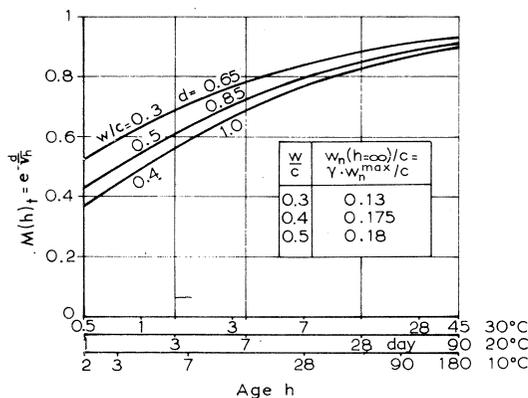


Figure 22. Experimental results of hydration or fixation drying for a Finnish portland cement Pa 6800: M-factor as the function of curing time (age) and temperature (10, 20, 30°C). Ultimate fixed water content  $w_n(h = \infty)/c$  is also indicated as a function of the water-cement ratio. For detailed description of the basis of the figure, see Report [2, Fig. 32 b].

Maturity factor  $M(h)_t$  as a function of time  $h$  at fixed hydration temperature  $t$ , and the ultimate value for  $w_n/c$  denoted by  $w_n(h = \infty)/c$ , are indicated for a Finnish portland cement (Pa 6800) in Fig. 22, reproduced from Report [2, Fig. 32 b]. The estimation of  $C_0$  has also been treated in Report [7].

For connection of the formulation presented above with that previously given in Table 1, for sealed conditions, and with gravity being ignored, (Cf. Table 1, Equation I) there is derived

$$\frac{\partial C}{\partial h} = S_H \quad (46)$$

$$\frac{1}{Q_c} \int_0^h S_H dh = \frac{1}{Q_c} \int_0^h \frac{\partial C}{\partial h} dh = M(h)_t w_n(h = \infty)/c \quad (47)$$

Begynnelse-fuktkont: (med "vårn" beteckningen)

$$U_0 = \frac{1}{\gamma} \cdot C \left[ \text{vct} - \left( \frac{w_n}{c} \right)_0 \right] = (w_0 - w_{n0}) \frac{1}{\gamma}$$

[vilets-%] kg/m<sup>3</sup>

$\gamma$  = betongens densitet [kg/m<sup>3</sup>]

$C$  = betongens cementhalt [kg/m<sup>3</sup>]

$w_0$  = betongens urspr. vattenhalt [kg/m<sup>3</sup>]

$w_{n0}$  = betongens hydratvattenhalt [kg/m<sup>3</sup>]  
vid uttorkningens början.

Kommentar: Vid höga vct och låg ålder  
kännes uttorkningen att starta med ett  
fuktillstånd som gör differensieringens  
användbarhet åtsaml.

## 7 SORPTION ISOTHERMS OF CEMENT PASTE: MOISTURE EQUILIBRIUM

### 7.1 INTRODUCTION

The following sections constitute a study of desorption and adsorption isotherms, or in other words of the moisture equilibrium of desorption and adsorption processes, and of the surface area of hardened portland cement paste, in this case particularly as regards hardened paste made of Finnish portland cements.

Knowledge of the moisture in the adsorbed state in cement pastes has gradually increased during the years, but the lack of information is still considerable. To acquire a complete quantitative description of the adsorbed state, there should be known not only the surface areas and sorption isotherms, but also how the adsorbed molecules interact with the surface and with each other. The area occupied by an adsorbed molecule and the number of molecular layers may be known, but knowledge of the "mobility" of the layers under the action of different driving forces (for instance pressure gradients, moisture gradients, and gravitation) is slight. Interest is also attached to the translational, rotational and vibrational motions of molecules on the surface. When these points are the object of study, difficulties are encountered by virtue of their all being functions of temperature and concentration, not to mention the complicated internal structure of cement paste.

In what follows, rather little new information is provided as regards the isotherms and surface areas of cement pastes in general. Nevertheless, this represents the first attempt to apply the principles involved to Finnish concrete research. Experimental information, new as far as the author knows, is contained in section 7.4 dealing with the temperature dependence of sorption isotherms. It is believed that the rapid development of surface science will furnish a valuable tool for concrete research.

Although the substantial differences which exist between desorption and adsorption isotherms are known, and have already been described in report [2], it seems worthwhile to repeat here that the amount of moisture held in equilibrium at any given relative humidity may vary substantially, dependent upon whether the material has lost moisture to ambient space (desorption) or has taken up moisture from ambient space (adsorption).

### 7.2 ZERO POINT OR DATUM POINT OF SORPTION ISOTHERMS: DISCUSSION

The amount of moisture held at equilibrium is a function of the final water vapour pressure and temperature only. When the pressure of vapour alone is varied,

and the temperature is kept constant, the plot of equilibrium moisture content against pressure is entitled a sorption isotherm. It is assumed that at zero pressure the equilibrium moisture content is also zero. It is known that the sorption isotherms of cement pastes rise very steeply from zero pressure point. The adsorption isotherms of cement paste are S-shaped, or of Type II according to the classification of Brunauer [74]. The type is most frequently formed in vapour adsorption in general. This run of the sorption isotherm near the zero point makes the isotherm very sensitive to the method of determination. As in actual measurement the zero pressure is not strictly attainable, the equilibrium moisture content varies in accordance with the determination method selected.

It is evident that from a scientific standpoint the correct datum point must be selected at the same temperature as the other points of equilibrium determinations. On investigation of cement paste, the vapour pressure of water at dry-ice temperature ( $-79^{\circ}\text{C}$ ),  $0,5 \cdot 10^{-3}$  mm Hg, has been used as a datum point in scientific papers since 1953 [75]. Previously, the water vapour pressure over magnesium perchlorate hydrates of  $0,8 \cdot 10^{-3}$  mm Hg was applied, in accordance with the practice of Powers & Brownyard [19]. Although the pressure difference is minor, it induces differences in equilibrium water content: the non-evaporable water determined by the old method may be approximated by multiplication by 1,084 of the non-evaporable water determined by means of the new method.

A new point of view concerning the selection of the datum point was introduced by Feldman & Sereda, when they selected a datum point based upon separation of the processes of desorption and dehydration [76]. Their results indicated that the relative vapour pressure in the region of the "transition point", referred to as the datum point, was less than  $10^{-2}$ .

Equilibrium moisture contents, or sorption isotherms, form a basis for study of the drying phenomenon. Up to the present time, an oven-drying process at  $105^{\circ}\text{C}$  (sometimes  $110^{\circ}\text{C}$ ) has been the internationally accepted and adopted basic method for the determination of moisture content in general. Although this non-isothermal method could be considered scientifically incorrect, it is also applied here in accordance with general international usage. The author has suggested some restrictions with respect to the properties of the ambient air, and therefore the equilibrium moisture or moisture in general is the water which escapes from concrete under normal air pressure and at an air temperature of  $105^{\circ}\text{C}$ , or in "oven drying" at  $105^{\circ}\text{C}$ , when the temperature and the relative humidity of the ambient air are  $20^{\circ}\text{C}$  and 40 % respectively [2]. - The state of equilibrium reached by concrete at  $105^{\circ}\text{C}$  roughly corresponds to the state of equilibrium of concrete at  $20^{\circ}\text{C}$  when the partial pressure of water vapour is about 0.001 mm Hg [19], [2].

It seems that the problem posed by the datum point requires further clarification.

## 7.3 SORPTION ISOTHERMS, DEPENDENCE OF CEMENT POPULATION IN FINLAND

One of the basic properties of a material subjected to drying is its equilibrium moisture content. In some preliminary examination of the drying process it may be sufficient to know the equilibrium moisture content as a function of the relative humidity of the air, i. e., the sorption isotherm of moisture.

When experimental data are being employed for estimation of the equilibrium moisture content, it should be noted that the curves arrived at are not necessarily valid for another cement and for another history, especially as the results depend upon the history of concrete, i. e., upon the way the concrete has reached the state of equilibrium [19]. In addition, the datum point selected may exercise a considerable effect upon the sorption isotherm. It is also necessary to make a clear distinction between the desorption and adsorption isotherms. In drying studies, the desorption isotherms are those mostly needed.

To get sorption isotherms for Finnish ordinary portland cements, and to arrive at an idea of their dependence on different cement populations, the following test series was made. The equilibrium moisture content of cement pastes (nominal w/c = 0.3, 0.45, some bleeding in the paste of w/c = 0.45) made of five different portland cement populations of three Finnish cement factories denoted by Pa, La and Lo, were determined for desorption and adsorption processes. Between desorption and adsorption, there was effected oven drying at 105°C. Cement pastes were precured under sealed conditions (poured in small plastic bags and stored in glass jars furnished with elastic rubber lids) for 8...9 months before testing. Hydration was thus virtually completed. Eighty crushed samples (about 1...1.5 g) of particle size  $\neq$  0.25...1 mm (Photo 13) were kept in desiccators at 25°C above H<sub>2</sub>SO<sub>4</sub> solutions (RH 20 %, 40 %, 70 %, 85 %) for three weeks, and weighings made once a week. Small electric fans were installed on the inside surface of the cover of the desiccator to ensure efficient forced convection (Photo 8). The carbon dioxide was removed (about 50 ppm by volume) from the air (about 500 ppm) by means of an especially constructed device, comprising a pump, a train of gas-washing bottles containing Ascarite, and gas-washing bottles holding salt solutions for remoistening the air pumped through the apparatus (Photo 6). The absolute amount of the carbon dioxide in the desiccator air was insignificant. Table 7 gives the average values obtained from two "identical" crushed samples. The results are of a very homogeneous nature for pastes made from different cement populations, especially as regards 0.45-paste. Nevertheless, large differences are discernible between the desorption and adsorption processes, as is clearly evident in Fig. 23. It is apparent that determination of the non-isothermal datum-point increases further divergences between desorption and adsorption isotherms than does the isothermal one [19]. Oven-drying at 105°C results in permanent shrinkage, clearly discernible in the reduction of the moisture content adsorbed after heat treatment. The results arrived at by Powers and Brownyard [19] indicate that the desorption and adsorption curves approximately coincide at 0.1 p/p<sub>s</sub> when use is made of isothermal

Table 7. Equilibrium moisture content of cement pastes (in percentages by weight) (nominal  $w/c = 0,3, 0,45$ ) made of different Finnish portland cements from three Finnish cement factories denoted by Pa, La and Lo, for the desorption and adsorption process.  $\varphi = 20\%$ ,  $40\%$ ,  $70\%$ ,  $85\%$ . Average values for different combinations of cement populations are also given, including average  $C_e^{cP}$ -values for all the pastes.  $t = 25^\circ\text{C}$ .

$\frac{w}{c}$		$\varphi = 20\%$		$\varphi = 40\%$		$\varphi = 70\%$		$\varphi = 85\%$	
		1. des.	1. ads.						
0.3	1) 7300 Lo	6.9	3.2	8.4	4.6	12.9	7.8	15.1	10.9
	2) 7600 La	6.9	3.2	8.2	4.5	12.4	7.8	14.4	10.5
	3) 7800 Pa	6.7	3.1	8.0	4.4	12.3	7.4	14.4	10.1
	4) 6800 Pa	6.5	3.1	7.5	4.3	12.6	7.7	14.9	10.8
	5) 7100 Pa	6.5	2.9	7.8	4.3	12.4	7.6	14.6	10.6
	(1+2+3+4+5)/5	6.7	3.1	8.0	4.4	12.5	7.7	14.7	10.6
	$C_e^{cP}$ kg/m <sup>3</sup>	120	55	143	79	223	138	263	189
(1+2+3)/3	6.8	3.2	8.2	4.5	12.5	7.7	14.6	10.5	
(3+4+5)/3	6.6	3.0	7.8	4.3	12.4	7.6	14.6	10.5	
0.45	1) 7300 Lo	7.4	4.0	9.3	5.8	15.2	9.4	19.0	13.1
	2) 7600 La	7.6	3.6	9.3	5.1	15.0	9.4	17.7	12.8
	3) 7800 Pa	7.5	3.7	9.3	5.5	14.9	9.0	18.9	12.8
	4) 6800 Pa	7.6	3.7	9.0	5.1	15.0	9.4	18.2	12.8
	5) 7100 Pa	7.7	3.6	9.5	5.3	15.1	9.3	18.9	13.1
	(1+2+3+4+5)/5	7.6	3.7	9.3	5.4	15.0	9.3	18.5	12.9
	$C_e^{cP}$ kg/m <sup>3</sup>	113	55	139	81	224	139	276	192
(1+2+3)/3	7.5	3.8	9.3	5.5	15.0	9.3	18.5	12.9	
(3+4+5)/3	7.6	3.7	9.3	5.3	15.0	9.2	18.7	12.9	

datum-point determination. The equilibrium moisture content, expressed as kg/m<sup>3</sup>,  $C_e^{cP}$ -values, is perhaps surprisingly independent of the water-cement ratio, a fact already recognised in report [2], and applied in report [7]. A reasonable explanation of this independence is that moisture is mostly held in gel pores, and gel porosity is independent of the water-cement ratio.

The findings reproduced in Table 7 and in Fig. 23 apparently indicate that the cement pastes made of different ordinary Finnish portland cements have almost equivalent sorption characteristics, which may mean that there exists little difference in their microstructures.

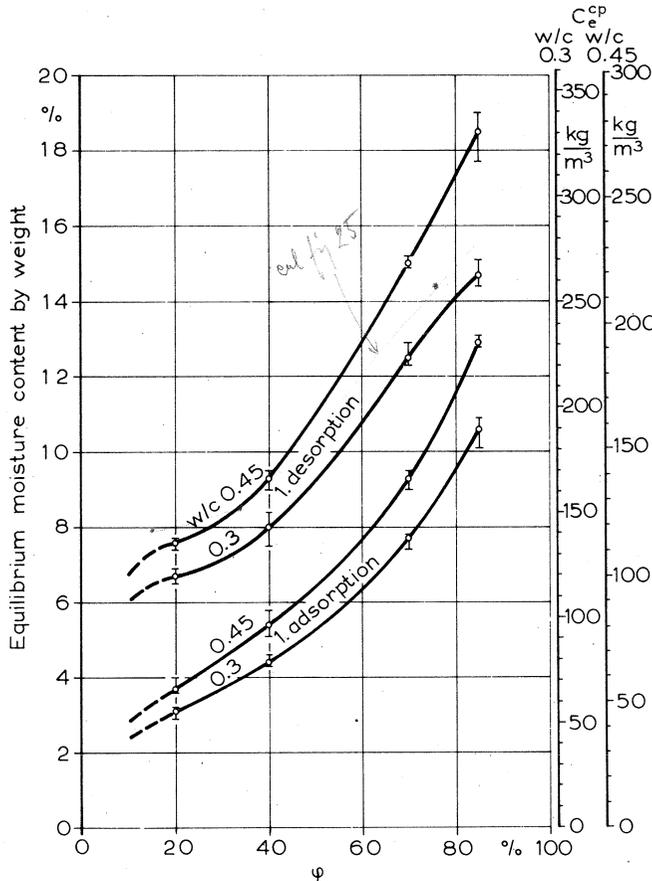


Figure 23. Average sorption isotherms of cement pastes ( $w/c = 0.3, 0.45$ ) made of five different Finnish portland cements (La 7600, Lo 7300, Pa 7800, Pa 6800, Pa 7100) and obtained in practically  $\text{CO}_2$ -free air. Data taken from Table 7. The segments of lines indicate the range of the individual values (Table 7). The sorption isotherms indicate that Finnish cement pastes made of different portland cement populations seem to have similar and equal sorption properties and microstructure.  $t = 25^\circ\text{C}$ .

#### 7.4 TEMPERATURE DEPENDENCE OF SORPTION ISOTHERMS

The equilibrium moisture content of porous materials at fixed relative humidities of the air depends to a rather minor extent upon temperature, at least as regards a range of temperature of the order of  $10^\circ\text{C}$  [36], [77], [78], [79]. Information on this point concerning concrete has been so scarce that no reports on it have been discoverable. Accordingly a test series was embarked upon with a view to acquiring experimental evidence in this respect, as is explained in detail in Appendix 6. Crushed samples of mature cement paste ( $w/c = 0.3, 0.45$ ) were kept above saturated salt solutions in desiccators placed in a water-bath thermostat furnished with cooling and heating (Photo 10). The air humidity above the salt solutions was almost independent of temperature. Fig. 24 illustrates the test procedure; virtual equilibrium was attained within three or four weeks, Figs. 25 and 26 indicate that the temperature-dependence of the desorption isotherms considerably exceeds that of the adsorption isotherms. The results given in Table 8 and in Figs. 25 and 26 confirm the statement that the sorption isotherms depend relatively little upon

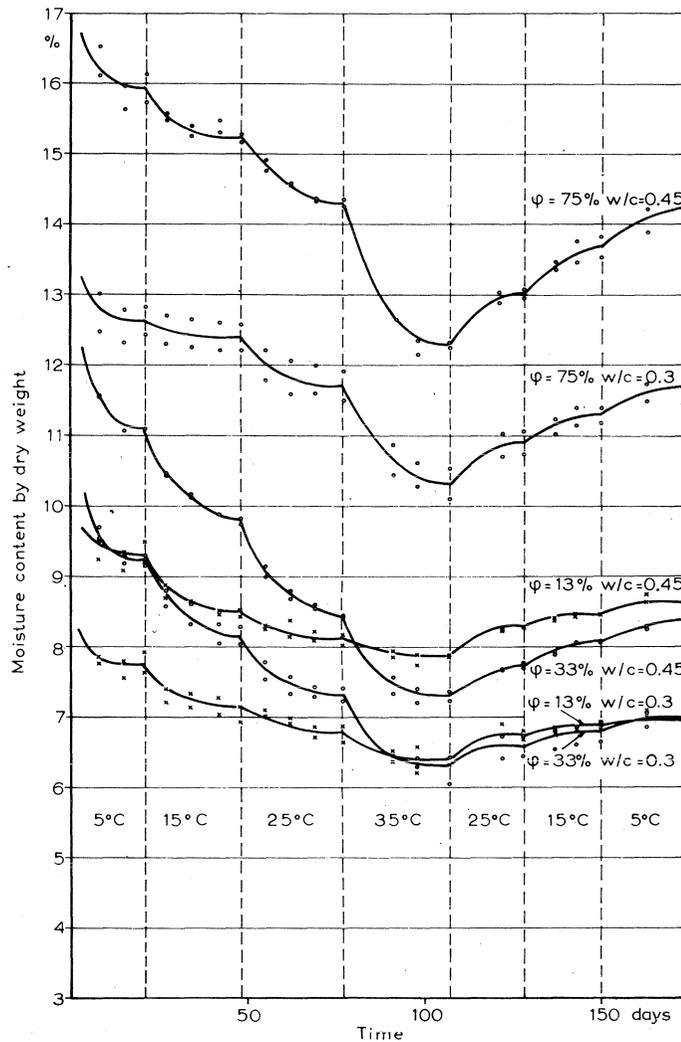


Figure 24. Weight change history of the cement paste samples used in determination of the temperature-dependence of desorption and adsorption at fixed relative air humidities. The samples were crushed mature cement pastes ( $w/c = 0.3, 0.45$ ; Cement: Pa 7100), and kept in desiccators above saturated salt solutions. The relative humidities of the air above the salt solutions (RH 13 %, 33 %, 75 %) were almost insensitive to the temperature changes within the range studied. The curves represent the average values of two samples as suggested by the experimental points observable. Sorption isotherms in Figs. 25, 26, 27 have been drawn on the basis of the equilibrium states reached in these tests.

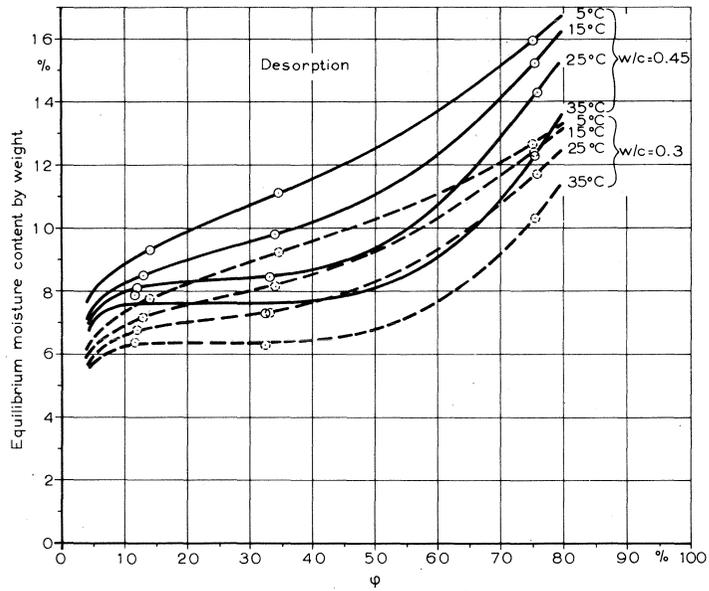


Figure 25. Temperature-dependence of desorption isotherms or desorption isotherms at 5, 15, 25, and 35°C for mature cement pastes, determined as shown in Fig. 24 (Cf. Fig. 26).

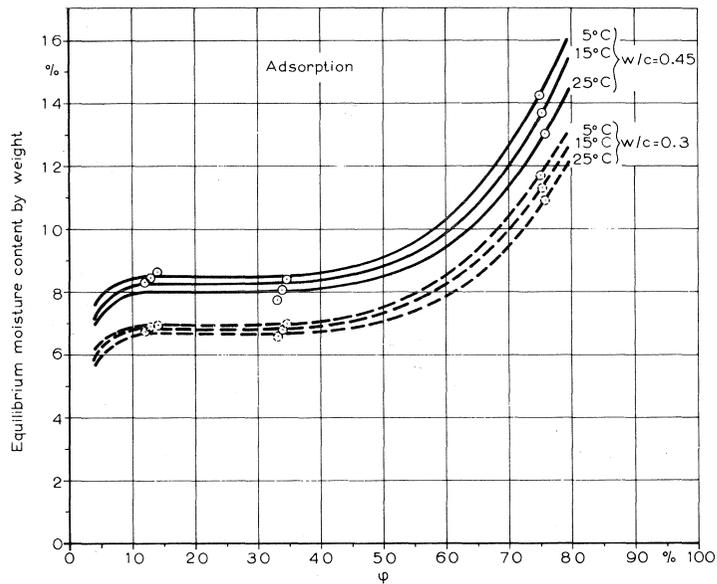


Figure 26. Temperature-dependence of adsorption isotherms or adsorption isotherms at 5, 15, and 25°C for mature cement pastes, determined as shown in Fig. 24 (Cf. Fig. 25).

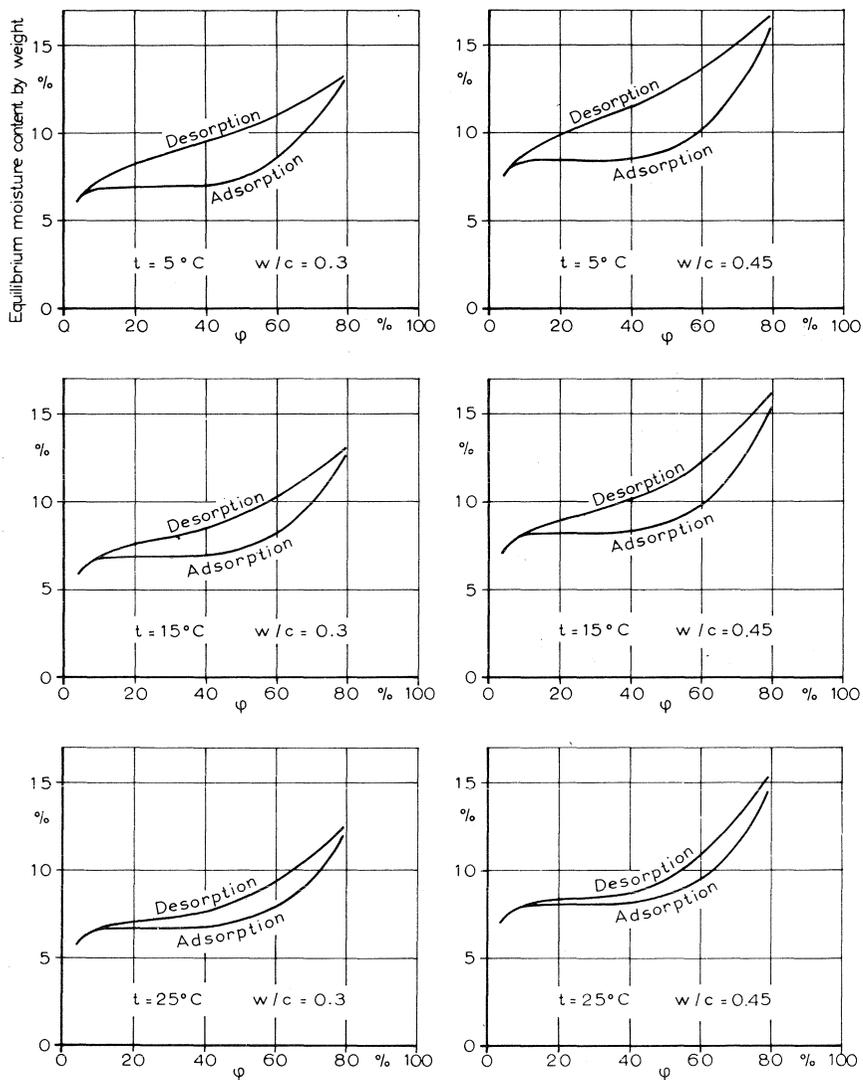


Figure 27. Sorption hysteresis at different temperatures determined with the aid of the test procedure and results presented in Fig. 24. (Cf. Figs. 25 and 26).

temperature within a range of temperature of the order of  $10^\circ\text{C}$ . This seems to be particularly true for adsorption isotherms.

A series of figures (Fig. 27), drawn on the basis of the information furnished in Figs. 25 and 26 clearly shows the well-known desorption - adsorption hysteresis as

Table 8. Temperature-dependence of sorption isotherms. Equilibrium moisture content as a percentage of dry weight.

w/c =	0.3			0.45		
$\varphi =$	13 %	33 %	75 %	13 %	33 %	75 %
Desorption						
5°C	7.8	9.2	12.6	9.3	11.1	15.9
15°C	7.2	8.2	12.4	8.5	9.8	15.2
25°C	6.8	7.3	11.7	8.1	8.4	14.3
35°C	6.4	6.3	10.3	7.9	7.3	12.3
Adsorption						
25°C	6.8	6.6	10.9	8.3	7.7	13.0
15°C	6.9	6.8	11.3	8.5	8.1	13.7
5°C	7.0	7.0	11.7	8.6	8.4	14.3

a function of temperature. The hysteresis loop clearly diminishes with a rise in temperature. This effect seems to suggest that sorption hysteresis disappears at higher temperatures.

## 7.5 ON THE STABILITY AND ESTIMATION OF THE MOISTURE EQUILIBRIUM OF THE DRYING PROCESS

### 7.51 Discussion

The existence of a state of equilibrium in drying is generally a basic property of the material being dried. If during drying the microstructure of the porous solid changes continuously, moisture equilibrium may be of ambiguous nature. Moisture equilibrium may then have apparent differences, dependent upon the dimensions of the specimen or structure being dried. Time-dependent or ageing phenomena have been observed in many colloidal solids, including cement paste [44], [20]. Colloidal systems are unstable, and with time, chemical and physical changes usually occur, transforming the system towards a more stable state. Investigations made up to the present time lead to the conclusion that mature cement pastes cured under conditions of saturation do not exhibit marked crystallinity variations up to 10 years [21], and that the greatest changes in microstructure occur in pastes from which part of the moisture (evaporable water) has been removed [44]. One of the changes associated with the ageing of cement paste is a decrease in internal surface area, which leads to a lower moisture capacity, and thus to a lower equilibrium moisture content. It is obvious that the ageing phenomenon complicates the theoretical treatment of drying.

The exponential nature of the drying phenomenon, theoretically presented in the form of a  $\bar{u} - F_0$  or  $\bar{u} - h$  relation as a solution of the diffusion equation, indicates that drying is very slow near the point of moisture equilibrium. If the drying process is followed by weighing, it is on occasion difficult to find a true equilibrium in practice, even under conditions free of disturbing effects. This difficulty may be a result of the limited reproducibility of the experimental procedure, but may also be attributable to the investigator's being too hasty.

Report [2] stated that the state of equilibrium is hardly to be found if the drying experiments are performed in the air, and the drying process is followed by weighing. This is mainly attributable to carbonation, but ageing effects may also play a part, apart from possible variations in climatic factors. Furthermore, gravimetric drying tests, even in a strictly controlled  $\text{CO}_2$ -free climate, at times appear to show that mature cement paste specimens do not reach constant weight, but rather a constant loss of weight is the case. As Feldman & Sereda [76] have pointed out, this type of drying process near equilibrium has been achieved for cement paste drying at almost zero humidity (in a vacuum system containing magnesium perchlorate dihydrate and tetrahydrate, or in a vacuum system containing "dry-ice"). If the drying time of the mature cement paste specimens in a strictly controlled  $\text{CO}_2$ -free climate has been relatively long, and the weights of the specimens do not gradually converge towards a constant weight, at least in rough accord with the prediction of the diffusion theory, it seems reasonable to assume that this condition might be the result of the slow internal change in microstructure, or, to put it briefly, of ageing.

#### 7.52 Experimental results of the stability of moisture equilibrium of Finnish cement paste

Lengthy experiments concerned with moisture equilibrium provide a possibility of following the time-dependent changes in the microstructure of cement paste. The changes in moisture equilibrium indicate changes in internal surface area, and thus changes in microstructure.

Figs. 28 and 29 indicate that moisture equilibrium for cement paste specimens made of an ordinary Finnish portland cement (Pa 6800) remained stable for a period of six months. The specimens were cured under sealed conditions for 7, 28 and 90 days before they were put in two desiccators, above  $\text{H}_2\text{SO}_4$ -solutions, and providing air humidity corresponding to 40 % and 70 % respectively. The specimens were kept continuously in the desiccators, although no more than the last part of the moisture loss curve is discernible in the figure. The desiccators were in a water-bath thermostat at  $25^\circ (\pm 0.1^\circ\text{C})$ , and the range of temperature variation was  $\pm 0.2^\circ\text{C}$ . The average size of the pillow-shaped specimens (poured into small plastic bags) was 6 cm x 6 cm x 0.6 cm. No appreciable time-dependent modification of the cement paste is discernible in Figs. 28 and 29, although closer examina-

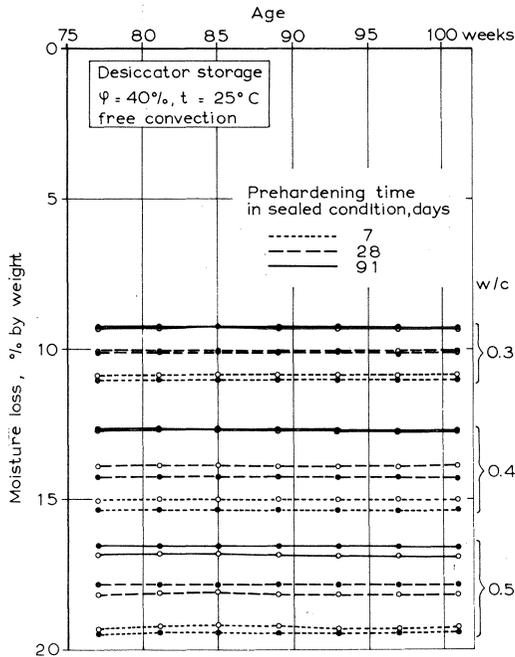


Figure 28. Shows that the weight of the cement paste specimens (6 cm x 6 cm x 0,6 cm, Cement: Pa 6800) was virtually permanent for about six months at fixed air humidity (40 %), and temperature ( $25^\circ\text{C}$ ), indicating that it is feasible to obtain a good moisture equilibrium for small cement paste specimens in air practically free from  $\text{CO}_2$ . (Cf. Fig. 29).

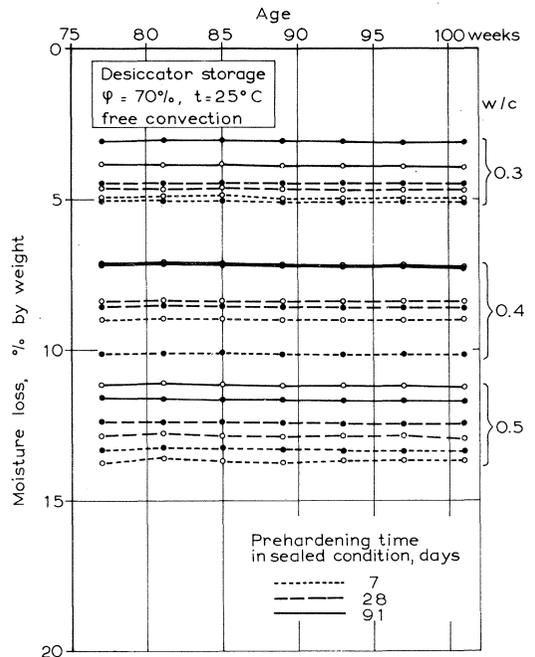


Figure 29. Shows that the weight of the cement paste specimens (6 cm x 6 cm x 0,6 cm, Cement: Pa 6800) was virtually permanent for about six months at fixed air humidity (70 %), and temperature ( $25^\circ\text{C}$ ), indicating that it is feasible to obtain a good moisture equilibrium for small cement paste specimens in air practically free from  $\text{CO}_2$ .

tion shows a slight trend towards lower moisture content in some cases. On the basis of this experiment, it seems safe to conclude that at least some small specimens of cement paste made of Finnish portland cements attain sufficient moisture equilibrium, in air almost free of  $\text{CO}_2$ , within a reasonable time. It is evident that many years of studies on the moisture equilibrium of cement paste, or in other words on the stability of sorption isotherms, are needed before final or definite conclusions can be drawn. The drying time of concrete structures can amount to some 10 years, and it is possible that the moisture equilibrium may change significantly during such a long time by reason of ageing effects. In addition, further clarification is urgently required in respect of the effect of the carbon

dioxide take-up on the moisture equilibrium and on the water content of concrete in general.

### 7.53 On the estimation and prediction of moisture equilibrium in a drying test with the aid of the simple drying (diffusion) theory

For those special cases in which the moisture conductivity is constant, the entity  $d\bar{u}/dFo$  furnishes an idea of how the drying process approaches moisture equilibrium. Fig. 30 indicates the numerical values of  $d\bar{u}/dFo$  for infinite slabs, infinite cylinders, and spheres [89] near moisture equilibrium and for the basic-drying conditions (See Glossary). As the drying is usually followed by weighing of

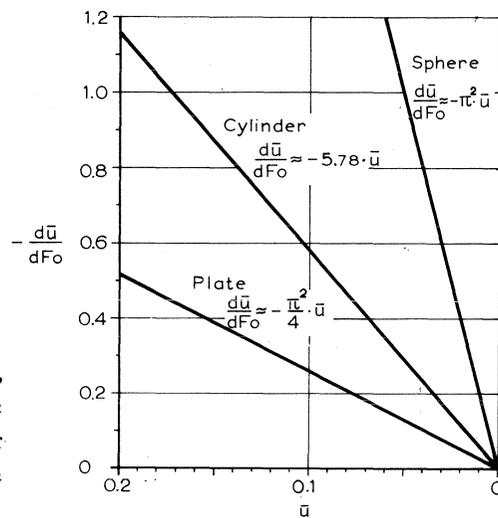


Figure 30. Drying rate of infinite slabs, infinite cylinders, and spheres under basic drying conditions (See Glossary) near equilibrium in accordance with simple diffusion theory [89].

the body subjected to drying, prediction of the relative weight or of mass changes during the drying process can be effected by application of the following simple equation

$$\frac{1}{M_0} \frac{dM}{dh} = \frac{k}{l^2} \left(1 - \frac{M_e}{M_0}\right) \frac{d\bar{u}}{dFo} \quad (48)$$

where  $M_0$  is the initial mass and  $M_e$  the equilibrium mass of the specimen. Values for  $k$  and  $M_e$  must frequently be estimated in practice. Near equilibrium,  $M_e$  can be estimated as the mass of the specimen at the last weighing. Equation (48) can be written in the following forms

$$\frac{1}{\rho_0} \frac{d\rho}{dh} = \frac{k}{l^2} \left( 1 - \frac{\rho_e}{\rho_0} \right) \frac{d\bar{u}}{dFo} \tag{49}$$

$$\frac{d\bar{C}}{dh} = \frac{k}{l^2} (C_0 - C_e) \frac{d\bar{u}}{dFo} \tag{50}$$

Equation (48) clearly indicates that the criterion for the attainment of moisture equilibrium often applied in drying tests depends, inter alia, upon the moisture conductivity and the dimensions of the specimens. No fixed value is generally valid for the estimation of  $dM/(M_0 dh)$  sufficiently near equilibrium, such as 0.1 %/week. Some illustrative examples in respect of slabs are presented in Fig. 31.

The most reliable method for finding the moisture equilibrium is undoubtedly the continuous study of the drying process graphically for a lengthy period.

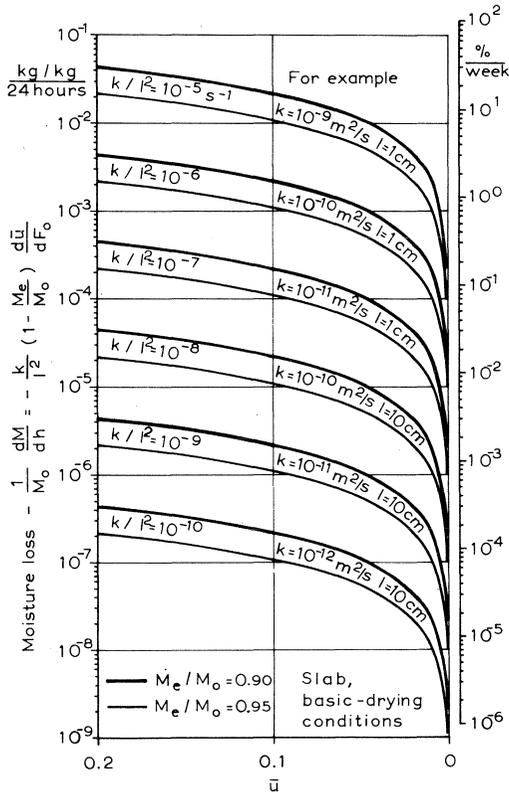


Figure 31. Relative moisture loss of uniaxially drying slabs showing the continuously diminishing drying rate as a function of moisture conductivity  $k$ , characteristic thickness  $l$ , initial mass  $M_0$ , and equilibrium mass  $M_e$ , in basic drying conditions. The selected values of  $k/l^2$  and  $M_0/M_e$  are related to practice. The values of  $d\bar{u}/dFo$  have been taken from Fig. 30.

7.54 Prediction of the equilibrium moisture content of concrete,  $C_e$ , when the equilibrium moisture content of cement paste is known

In studies of the drying of concrete, one of the principal tasks is prediction of the equilibrium moisture content of concrete,  $C_e$ . The desorption isotherms, which usually form the basic data for the prediction of  $C_e$ , depend upon hydration history. The prediction of  $C_e$  has already been treated in some detail in Report [7]. For the sake of completeness, a brief review of this subject is given below.

If the reasonable assumption is accepted that the equilibrium moisture content  $C_e^{cp}$  (Cf. Section 7.3) for cement paste alone is the same as the equilibrium moisture content of the cement paste in concrete (cement paste + aggregate), there is derived for the equilibrium moisture content of concrete

$$C_e = \frac{\text{volume of cement paste}}{\text{volume of concrete}} C_e^{cp} \quad \text{or,} \quad (51)$$

$$C_e = \frac{C_e^{cp}}{1 + \frac{a}{cp}},$$

where  $a/cp$  is the aggregate - cement paste ratio by volume or

$$\frac{a}{cp} \approx \frac{0.37 \cdot Q_{ag}/Q_c}{0.32 + w/c} \left( = \frac{Q_{ag}/\rho_{ag}}{Q_c/\rho_c + Q_w/\rho_w} \right) \quad (52)$$

where  $Q_{ag}$  is the aggregate content ( $\text{kg}/\text{m}^3$ ),  $Q_c$  the cement content ( $\text{kg}/\text{m}^3$ ),  $w/c (= Q_w/Q_c)$  the water-cement ratio; and densities ( $\rho$ ) of water, aggregate, and cement are estimated to be respectively  $1000 \text{ kg}/\text{m}^3$ ,  $2700 \text{ kg}/\text{m}^3$ , and  $3100 \text{ kg}/\text{m}^3$ .

Preliminary investigations of concrete mortar and corresponding cement paste have indicated that the assumption made above is valid. The assumption may need further confirmation.

## 7.6 SURFACE AREAS

### 7.61 General

The surface area of portland cement paste is an important characteristic which plays a decisive role in the moisture transfer, and the strength and dimensional changes of concrete. The method most generally applied for determination of the surface areas of hydrated pastes of portland cements has been of gravimetric water vapour adsorption nature, supported by the well-known BET-theory. The physical adsorption of gases and vapours on solid surfaces has been treated in numerous publications; a short review of the subject, for present needs, has been

presented in internal report [80]. It must be remembered that the hardened cement paste is a colloidal material, and the unique properties of a colloid are attributable to its large specific surface area, and the large amount of energy residing in the surface [80]. Consequently, the most significant basic physical property of hardened paste is probably its surface area, which is of the order of 200 m<sup>2</sup>/g dry paste (water vapour adsorption method).

It is necessary to mention that a gas or vapour adsorption method is based mainly on two postulates, which are not necessarily true, viz. 1) that a definite adsorbed amount covers the whole surface of the adsorbent with a uniform monomolecular film, and 2) that this amount is detectable from the adsorption isotherm. Once these assumptions have been made, the point which corresponds to a monolayer must be selected on the adsorption isotherm, and, unfortunately, this necessitates a somewhat arbitrary choice. All these obstacles lead to experimental surface areas which hardly represent "true" surface areas. [81].

As regards the gas-solid interface sorption phenomena, divergences in opinion still exist [82]. The reasons for the great differences between surface areas of cement pastes obtained by using nitrogen or water vapour are not yet completely solved [42], [43]; the factors involved might include some chemisorption. Consequently, improvement of the technical accuracy in experiment does not of necessity introduce an essential improvement in the value of the surface area so obtained.

#### 7.62 One-point desorption method

The following observations have been applied in selection of the simple surface area measurement method based upon gravimetric desorption in the air at one humidity point ( $p/p_s = 0.2$ ).

1. The desorption and adsorption isotherms almost coincide at small pressures when the isothermal datum point is used. The results of Powers & Brownyard [19] seem to indicate that this is true at pressures below about 0.1.
2. The adsorption of water vapour from humid air is virtually the same as the adsorption from water vapour alone (vacuum). The results of Powers & Brownyard [19] indicate that this is true, except at pressures below about 0.3, where the adsorption in the absence of air is expected somewhat to exceed that in the presence of air. Evidently air cannot compete with water for the surface of cement paste. This is also true for a number of other materials, even at low humidities [81].
3. The adsorption method involves two disturbing effects which may induce changes in the "original" surface area:
  - the drying process prior to the test,
  - the adsorption process itself, e.g. if irrelevant gas is used.

The one-point desorption method is convenient, and in the present stage of knowledge of water vapour sorption isotherms, it seems sufficiently reliable enough for techno-scientific purposes. In application, it calls for no high vacuum and drying treatment before the test. The surface area obtained is probably greater than that obtained by means of adsorption methods, and it is not a "true" surface area; but neither are the surface areas determined by the adsorption method. The nitrogen adsorption surface area does not appear to take into account the smallest pores in cement paste [42]. However, there are supported conceptions that the nitrogen adsorption method, which gives small surface areas, results in the "true" surface area [43]. In addition, the fact that the pore size distribution is more important than the surface area in moisture transfer, limits the significance of knowledge of the surface area in this connection. (Nonetheless, no Cranston - Inkleby analysis of pore size determination has been essayed here [42], [43]). This point of view provides further validity for the adoption of the simple one-point desorption method.

Calculation of the surface area by means of the one-point method is very simple. If the amount of moisture in equilibrium with the air of 20 % RH, after desorption, is denoted by  $v_m$ , and is expressed in grams per gram of dry paste, the surface area  $S$  is

$$S = a v_m, \quad (53)$$

where  $a$  is the surface area covered by a gram of moisture:

$$a = a_1 \frac{N}{M'} \quad (54)$$

$a_1$  = the surface area covered by a single molecule of water, at present  $a_1 = 11.4 \text{ \AA}^2$  [20]

$N$  = Avogadro's number,  $6.02 \cdot 10^{23}$  1/mole

$M'$  = molecular weight of water, 18 g/mole

The formula of the surface area for the one-point method is thus

$$S = 38.1 v_m \text{ m}^2/\text{g}, \quad (55)$$

if  $v_m$  is expressed as a percentage.

### 7.63 BET - method

The BET-method [74], [80] is based upon the BET-equation of sorption isotherms

$$\frac{P}{v(P_s - P)} = a' \frac{P}{P_s} + b', \quad (56)$$



where  $a'$  is the slope,  $b'$  the intercept of the straight line, and  $v$  the amount of equilibrium moisture at relative humidity  $p/p_s$ . Most vapour sorption isotherms plotted according to the above equation give straight lines within the range  $p/p_s = 0.05 \dots 0.35$ . The amount of moisture necessary to cover the entire surface with the monomolecular layer is

$$v_m = \frac{1}{a' + b'} \quad (57)$$

#### 7.64 Experimental results

The surface areas presented in Table 9 are based upon the data to be found in Fig. 23. As was expected, the adsorption surface areas are about one half of the desorption surface areas. The desorption surface areas are somewhat higher than the adsorption surface areas put forward by Powers [20, Table 5], and arrived at by application of the isothermal datum point. The smaller surface areas for 0.3-paste are probably a result the smaller degree of hydration. Evaluation of the  $a'$  and  $b'$  parameters of the BET-theory is illustrated in Fig. 32.

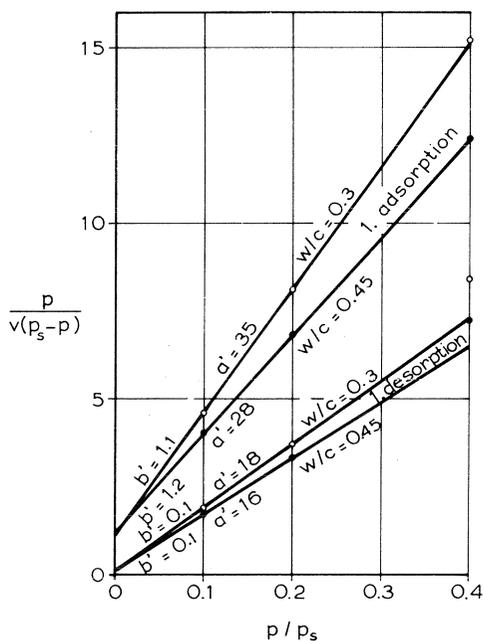


Figure 32. Typical BET-plots used for the evaluation of  $a'$  (slope) and  $b'$  (intercept) in treatment of the experimental results presented in Fig. 23. (Cf. Table 9).

## 8 SOME EXAMINATIONS OF RELATED PHENOMENA

### 8.1 ON THE INTERRELATION OF DRYING AND SHRINKAGE

The relationship between drying and shrinkage is one of the subjects most frequently treated in concrete research. This important subject is also taken into consideration here, since one of the final aims of concrete moisture content studies is clarification of the interplay of deformations and moisture. The treatment is brief, and in this context the subject is a subsidiary one.

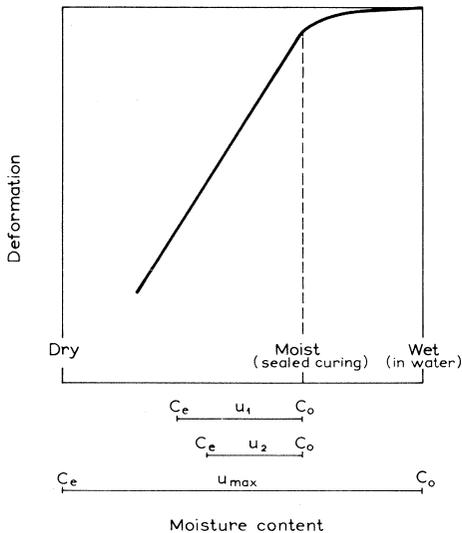


Figure 33. Schematic relationship between moisture content and deformations attributable to change in moisture content.

Fig. 33 illustrates the schematic relationship which exists between deformations (brought about by moisture content changes) and the moisture content of concrete. The figure is based upon numerous experiments, and has been earlier presented also by the author [15], [2]. Several tests have indicated, as is suggested by Fig. 33, that the shrinkage and moisture content are linearly related if concrete is not cured in water. The findings reproduced in Fig. 34, originating in the author's experiment with concrete mortar, closely agree with this conception. The

The guiding idea is that unstrained shrinkage (or swelling) can be expressed by the diffusion equation. If the deformations induced by moisture changes are linearly related to the moisture content, the corresponding mathematical analogy is simple:

$$s = \frac{S'}{S'_\infty} \quad (58)$$

$$\text{value of } s = \text{value of } (1 - u) \quad (59)$$

$$\frac{\partial s}{\partial h} = k \nabla^2 s; \quad \frac{\partial u}{\partial h} = k \nabla^2 u \quad (60)$$

In the equations,  $S'$  is free unrestrained linear shrinkage strain,  $S'_\infty$  final shrinkage strain under fixed ambient conditions, or a value of  $S'$  when  $h = \infty$ . In accordance with this basic idea, shrinkage and shrinkage stresses have been treated by Pickett [83], and later by Rostasy [84] and Wischers [85].

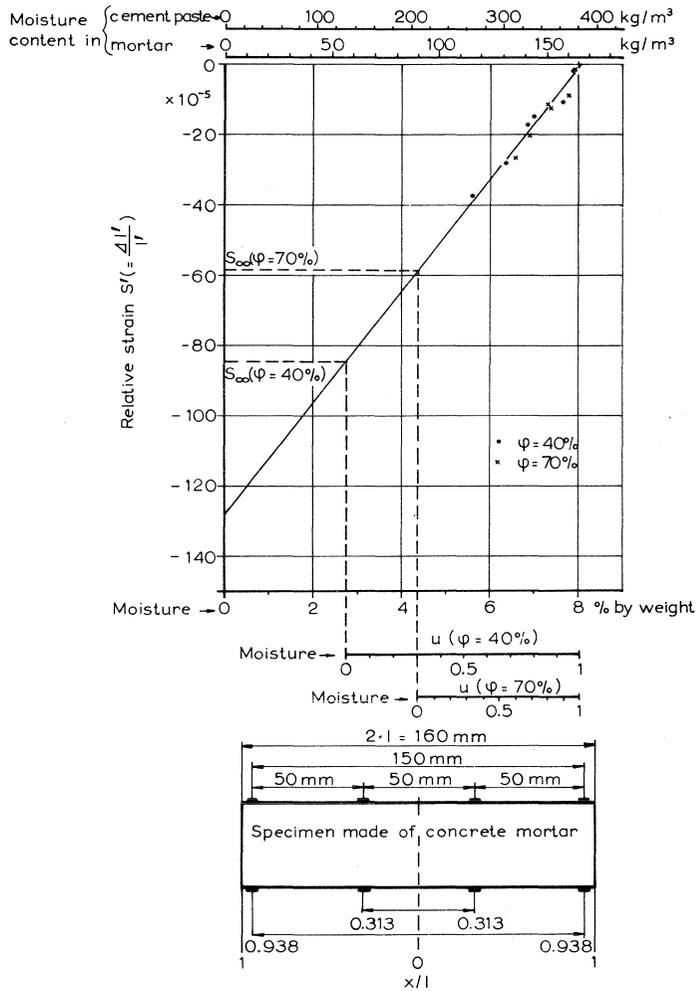


Figure 34. Interrelation of shrinkage and moisture of mature cement prisms (4 cm x 4 cm x 16 cm) dried uniaxially from the end surfaces only in two climate rooms ( $t = 20^\circ\text{C}$ , RH 40 %, 70 %;  $\text{CO}_2$ -content of the air about 500 ppm by vol.). Strain was measured with a mechanical deformer (DEMEC-system) at 50 mm intervals, as observable in the figure. Distribution of the moisture was determined with split parts of the prisms.

specimens (4 cm x 4 cm x 16 cm) made of concrete mortar belong to the same series as that presented in Section 3.3. The specimens were tightly covered with glued metal sheets, apart from the end surfaces, which were exposed to drying in two climate rooms (RH 40 %, 70 %). The shrinkage strains were measured uniaxially with a mechanical deformer from the holes in metal studs (gauge plugs) 50 mm apart, glued on opposing surfaces with Araldite (Photos 14 and 15, Fig. 34).

From the above explanation, it seems evident that the shrinkage and moisture content loss of concrete have a linear relationship, if the concrete has not been stored in water. This implies that the distribution of shrinkage strain and moisture content are similar. These problems need through study in the future (Cf. Pickett [83]).

It is perhaps worthwhile mentioning that investigation is also needed for the establishment of an adequate relationship between the drying shrinkage of small unrestrained concrete specimens, and the corresponding deformations of reinforced concrete members of sections commonly encountered in design. Studies of concrete concerned with long-term deformations and with broad-range stresses are generally of very complicated nature, as concrete under these conditions and in accordance with rheological examinations [11] seems to be an elastic-viscous-plastic material in which as a rule there exists no unambiguous and reversible relationship between stresses and deformations. As a consequence, simple relationships in this respect apply to limited cases only.

## 8.2 ON DRYING-STRENGTHENING AND WETTING-WEAKENING

### 8.21 Introduction

An extremely important and significant phenomenon in concrete, known as drying-strengthening (earlier drying-hardening) and wetting-weakening, has already been treated in the author's reports [2], [6], [8]. Fig. 35 illustrates the phenomenon [Cf. Report 8]. The figure shows, inter alia, that in ordinary concrete structures concrete gains in strength as a result of drying to the extent of about 20 per cent. The strength of completely dry concrete can be even 70 % higher than that of thoroughly wet concrete. This strong effect indicates that physical bonding plays a principal role in the strength formation of concrete.

The change in strength values attributable to the change in moisture content evidently finds its origin in short range forces. Research on porous glass has indicated that the variations observed in its strength apparently result from the changes in free surface energy, which is a good way of expressing the energetic variations of surfaces. Each solid has part of its energy resident in its body, and part of it in its surface. The larger the specific surface area the larger is the fraction of total energy residing in the surface. A large specific surface area is important, since it implies large surface energy [86]. Cement paste has a large

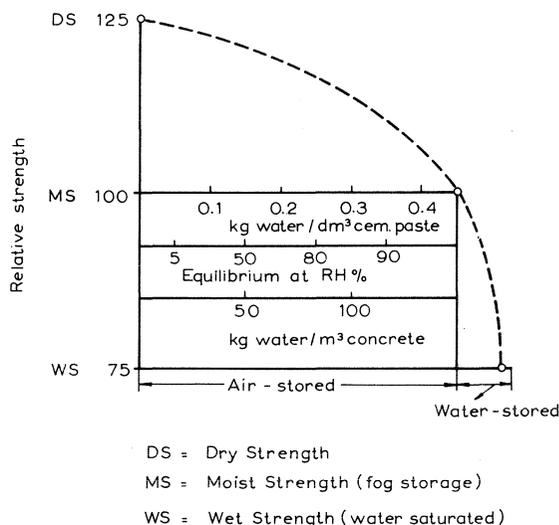


Figure 35. Schematic figure showing the inter-relation of the equilibrium moisture content of cement paste and concrete, air humidity (RH), different storage conditions, and relative strength. The strength obtained after equilibrium in fog-room storage (RH about 100 %) was selected at 100. The figure was drawn on the basis of the information presented in report [2].

specific surface area, and accordingly the adsorbed material on its surfaces induces great changes in surface-free energy, and as a result, great changes in the strength properties of concrete can be anticipated. A good example of the major effect exercised by the adsorbed material on the strength properties is that the free surface energy of mica, when cleaved in vacuum, amounted to 4500 ergs/cm<sup>2</sup>, but when this was done in air, the free surface energy was no more than 375 ergs/cm<sup>2</sup> [74]. It can be stated that the fracture of brittle solids, and the dimensional changes of porous rigid adsorbents, depend upon the changes in free surface energy [87].

On the foundation of the discussion published by Hiller [87], the following equation can be written; this is based on Griffith's theory of brittle solid fracture, and on the dimensional change in porous rigid adsorbents:

$$(\sigma/\sigma_0)^2 = 1 - \kappa \frac{\Delta l'}{l'} \quad (61)$$

$\sigma$  is the stress required for the growth of a crack with an adsorbed film in equilibrium with a vapour, and  $\sigma_0$  is the stress required in vacuum.  $\Delta l'/l'$  is the relative strain due to adsorption, and  $\kappa$  is the parameter dependent on the surface free energy and elastic properties of the material concerned.

By experimental means, Hiller [87] found for cylindrical specimens of porous Vycor glass, which failed in tension, that the compressive strength at RH 100 % was about 0.5 of that at RH 0 %.

The relationship of the moisture change - strength change (drying-strengthening and wetting-weakening) of concrete is part of a general subject, the mechanism of fracture in concrete. A good review, including Griffith's theory, of this subject has lately been presented by Goyal [88].

### 8.22 A tentative theory

The theory proposed below rests essentially on the theory presented by Hiller [87], and outlined briefly in the introduction (Section 8.21). The theory is based on the assumption that the material must be brittle, and that the material fails in tension. It is presumed that concrete fulfills both assumptions satisfactorily in short-term tension, compression, and bending tests [96].

If the equation given in Section 8.21 is generalized, then

$$(K/K_0)^2 = 1 - e \frac{\Delta l'}{l'}, \quad (62)$$

where  $K_0$  is the "basic" strength of concrete in an oven dry state (or in vacuum), and  $K$  is the strength of concrete in a more or less moist state.  $\Delta l'/l'$  is the relative uniaxial deformation owing to wetting from dry state, and  $e$  is an adjustable parameter.

On the foundation of the results of the deformations brought about by drying and wetting of concrete not stored in water (Cf. Fig. 33), the reasonable assumption is made that

$$\Delta l'/l' = (\Delta l'/l')_{\infty} u, \quad (63)$$

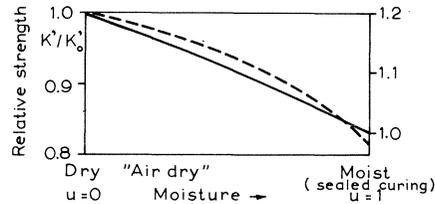
If following denotation is made

$$q = (\Delta l'/l')_{\infty} e, \quad (64)$$

Equation (62) with Equation (63), and (64), inserted gives

$$(K/K_0)^2 = 1 - qu \quad (65)$$

Figure 36. An example of the relative strength change to be expected in ordinary concrete by reason of the change in its moisture content. The solid curve represents theoretical Equation (66). The broken curve is reproduced from Fig. 35.



Deformations and moisture content must be linearly dependent starting from dry state. It is then believed that Equation (65) describes the drying-strengthening and wetting-weakening of concrete. When concrete is dry ( $u = 0$ ), the greatest strength is obtained ( $K = K_0$ ). When concrete is moist ( $u = 1$ ), the strength obtained is lowest.

In what follows, Equation (65) is tested against some of the experimental results presented in Fig. 35. From Fig. 35,  $K/K_0 \approx 0.8$ , if the ends of the moisture content range  $0 \dots 0.4$  kg water/dm<sup>3</sup> cement paste are used as the ultimate points for  $u$  ( $u = 0, u = 1$ ). A moisture content 0.4 kg water/dm<sup>3</sup> paste is approximately the moisture content in concrete cured under sealed conditions. In this case, Equation (65) gives

$$(K/K_0)^2 = 1 - 0.36 u \quad (66)$$

The graphical presentation of Equation (66), and the corresponding broken curve of Fig. 35, are to be seen in Fig. 36.

It is obvious that further empirical examination of the validity of Equation (65), and of the phenomenon in general, is necessary.

### 8.3 ON THE EFFECT OF GRAVITATION ON DRYING

The moisture flow in a porous material, like drying, takes place in a gravitational field. Consequently, the moving fluid is subjected to a directed movement superimposed upon the more or less random diffusive motions. The effect of gravitation has been generally ignored in studies of the drying of microporous solids by virtue of its rather minor role. On the basis of the studies made by a number of researchers and of the preliminary theoretical and experimental studies made by the author [9], it seemed reasonable to conclude that gravitation exercises in practice an almost insignificant effect on the drying of ordinary concrete. However, the results of a preliminary test series are presented below. The principal purpose of the presentation is to show that gravitation effect can be observable, and well merits study.

Fig. 37 shows the experimental drying curves of six water-stored standard cement mortar plates during 8 weeks in the preliminary gravity test made by the author

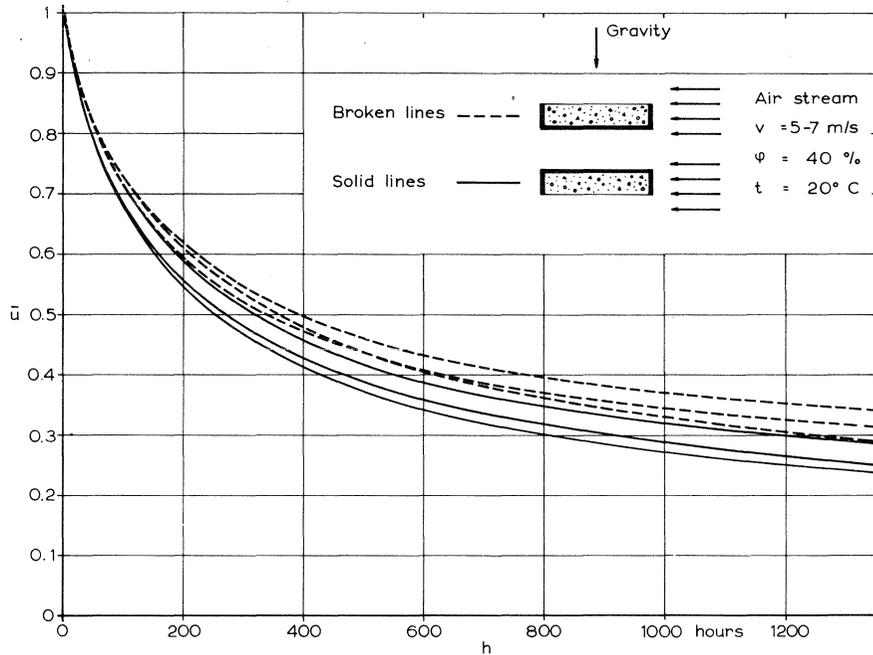


Figure 37. The results of a gravity experiment with three plates or cups, free surface facing upwards, and with three plates or cups, free surface facing downwards. The plates were made of standard cement mortar (Cement: Pa 6500). During the test, the plates were kept in horizontal position in a wind tunnel, to preclude a free convection effect.

(Appendix 7). The test system is discernible in the upper part of the figure. High wind-velocity was used to preclude free convection effects (Photo 18). Basic-drying was applied (See Glossary). The curves were drawn through experimental points, and the small moisture loss through the covering (Araldite) was reduced. Application of the simple statistical Student-t-test indicated that the differences of the average curve of each family of the curves can hardly be accidental. However, the reader should be warned not to take too seriously the results arrived at in this preliminary experiment. By employment of the average curve of the each family of the three curves, an average moisture conductivity  $k$  could be estimated, and furthermore the average differences  $\Delta \bar{u}$  of both curve families. By comparison of the  $\Delta \bar{u}$ -values obtained with the differences of the theoretical curves  $\bar{u} = \bar{i}(\alpha, Fo)$  presented in Publication [9] at the same Fourier-numbers,  $\alpha$  is obtained at various points and moreover, by application of the formula

$$\alpha = k/k_g l, \quad (67)$$

values for  $k_g$ . Table 10 shows the results of the estimation of  $k$ ,  $k_g$ , and  $\alpha$ .

Table 10. Estimation of  $k$ ,  $k_g$ , and  $\alpha$  with the aid of a preliminary experiment on the effect exercised by gravitation on the drying of standard cement mortar plates (Cement: Pa 6500).

$\bar{u} = 0.8 \dots 0.45$		
Quantity	Average	Range
$k \text{ m}^2/\text{s}$	$4.0 \cdot 10^{-11}$	$3.6 \cdot 10^{-11} \dots 4.3 \cdot 10^{-11}$
$k_g \text{ m/s}$	$0.89 \cdot 10^{-9}$	$0.6 \cdot 10^{-9} \dots 1.4 \cdot 10^{-9}$
$\alpha$	3	1.8 $\dots$ 4
$\bar{u} = 0.90$		
$k \text{ m}^2/\text{s}$	$2.5 \cdot 10^{-11}$	-
$k_g \text{ m/s}$	$1.4 \cdot 10^{-9}$ ( $1.2 \cdot 10^{-9}$ )	-
$\alpha$	1.2 (1.4)	-

The results in parenthesis were calculated from the simple equation  $k_g = \frac{1}{2} \frac{\Delta J}{(C_0 - C_e)}$

(See Appendix 7).

#### 8.4 ON THE POROSITY AND PORE SIZE DISTRIBUTION IN CEMENT PASTE. EFFECT OF CARBONATION

When due consideration is given to the importance of the subject it becomes apparent that rather little research has been devoted to clarification of the pore size distribution in cement paste. The latest achievements in this field are to be seen in reports [40], [41], [42], [43].

The main aim of the present study was that of throwing light upon the effect exerted by carbonation on the porosity, including pore size distribution, of cement paste. The methods applied were mercury porosimetry [90], and surface area determination with the aid of water vapour adsorption at RH 20 per cent. Samples of crushed (fraction  $\neq 0.25 \dots 0.5$  mm) mature cement paste, cured sealed for 3 months before "exposure", were utilized. The results, including the legend of the samples, are presented in Fig. 38. It is apparent that the surface area of a carbonated cement paste is about one half of that of a non-carbonated cement paste. The pore size distributions also indicate changes in porosity as a result of carbonation.

These experiments further show clearly that the microstructure changes in cement paste attributable to carbonation are very significant.

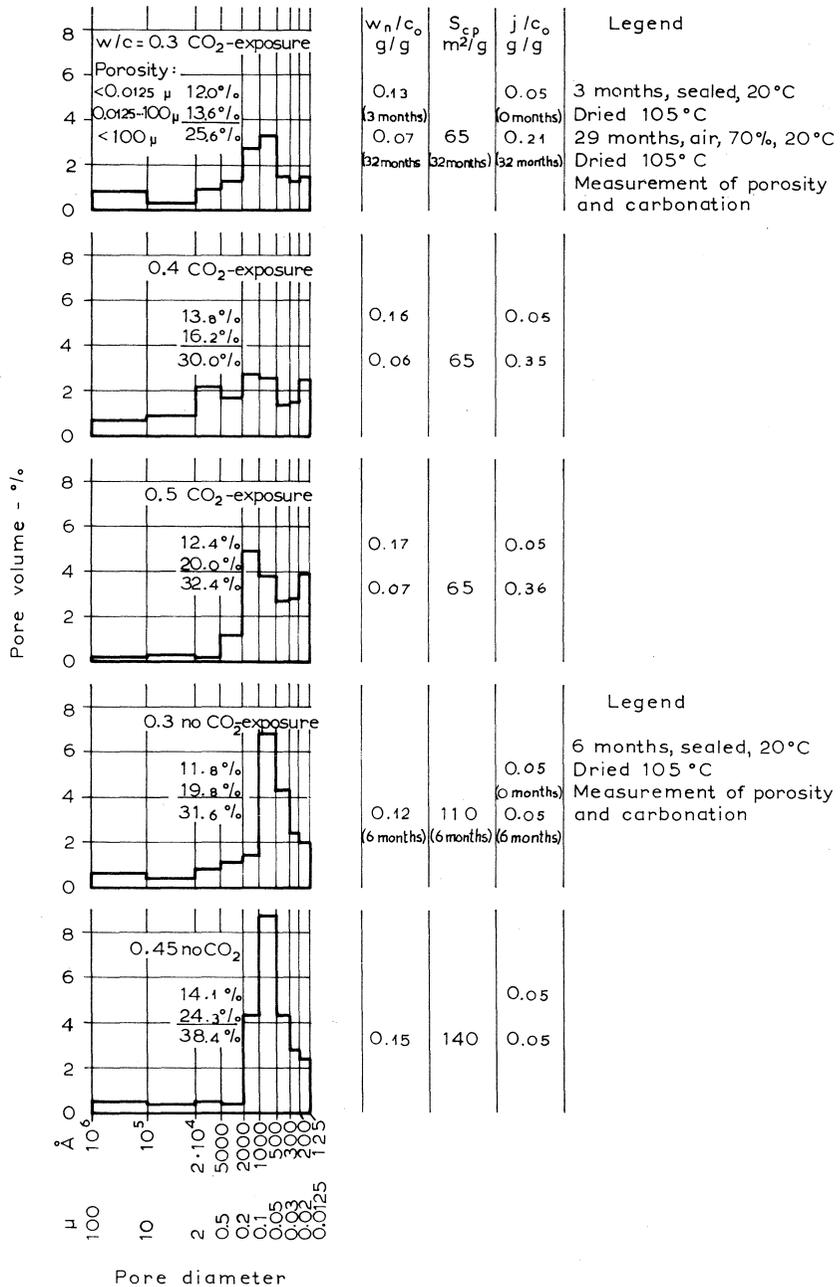


Figure 38. Porosity distributions and specific surface areas ( $S_{cp}$ ) of carbonated (in air of CO<sub>2</sub>-content of about 500 ppm by vol.) and of noncarbonated mature cement pastes (Cement: Pa 6800). The mercury porosimeter employed is depicted in Photo 19.

### 8.5 TRANSFER OF MICROSTRUCTURE CHANGES OWING TO CARBONATION

Practice, and research, have shown that carbonation exerts a great effect on the properties of concrete. Discussions on and experimental evidence of this fact have also been presented in this publication. Estimation of the penetration of the carbonation process into concrete is therefore of practical importance, to say nothing of its major significance in concrete research in general. The carbonated layer of concrete may possess properties which differ completely from those of the parts of concrete not carbonated. In accordance with Section 4.5, the following simple equation provides an estimation of the thickness of the carbonated layer in concrete, or in other words the transfer of microstructure changes attributable to carbonation in ordinary air

$$L = B(h \text{ in years})^{1/2} \text{ cm,} \quad (68)$$

in which coefficient B depends upon the carbonation degree selected and upon carbonation conductivity. For example,  $B = 0.5$  seems to be a reasonable choice for preliminary examinations (Cf. Sections 4.4 and 4.5).

## 9 ON THE ACCURACY OF THE RESULTS OF THE EXPERIMENTAL DETERMINATIONS

### 9.1 GENERAL

Most of the determinations in this research study have been gravimetric, i. e. by weighing, one of the most reliable and accurate physical measurements. The main aim of the weighing procedures has been that of measuring differences in the weight of cement paste or cement mortar specimens induced by the divergence between the humidity of specimens and that of the ambient air. The second entity frequently measured has thus been the humidity of the air, principally the relative humidity. In addition, two other main climatic factors, air temperature and air velocity, have been measured more or less continuously.

The measurements in this study were made by the employment of good, and relatively new laboratory apparatus, and by the application of efficient and careful laboratory technique. As an example, weighings were made with accurate precision balances. Generally speaking, therefore, the accuracy of an individual measurement value obtained from one specimen usually greatly exceeds the accuracy of the mean value for the whole consistent population arrived at with the aid of a group of specimens forming a sample of the population. This entails that the variations in the properties tested are greater than the accuracy of the individual values of the properties derived from one specimen, or in other words that the variations in the properties of materials are greater from specimen to specimen than those attributable to the inaccuracy of a measurement apparatus.

The variations in testing conditions, for instance of climatic conditions, during the long-term tests, were often appreciable, although always under continuous control, but never so large that the main features obtained in studying the properties could be regarded as misleading, or the order of magnitude of the values so obtained as incorrect.

The chief objective of the present publication has been clarification of the main features and methods of investigation of the various aspects of the subject. To arrive at this goal within a reasonable time, it was necessary to limit the number of test specimens in each test. As was noted in Chapter 1, subsequent detailed studies of each individual subject, with a larger number of specimens of each population, will provide a more exact knowledge of the entities examined, including their variations.

Before this paragraph is concluded, it is necessary to make some remarks on the definitions of the words accuracy and precision [92]. Accuracy in measurement is the degree of correctness, or freedom from error, with which a method of meas-

uring yields the "true" value of a measurement. The actual error in measurement can seldom be determined, but its magnitude may usually be estimated. The precision of measurement is the degree of reproducibility among several independent measurement of the same value under specified conditions. Accuracy and reproducibility are usually expressed with the aid of statistical methods and entities, e.g. with standard deviation and range. Scientifically, the problem of accuracy is generally complicated.

In the following paragraphs, the data of "accuracies" are based on the information furnished by the manufacturer of the instruments, and/or on the experience gathered during the experiments, but also on the accuracy tests proper.

## 9.2 WEIGHTS

Weighings were made with two Mettler balances, dependent upon the weight of the specimens and the capacity of the balance:

- a) Mettler H 6  
Capacity 160 g, precision or reproducibility (standard deviation)  $\pm 0.05$  mg.  
Readability 0.1 mg. Accuracy of weight set better than USA class S.
- b) Mettler K 7 T  
Capacity 800 g. Readability 0.01 g. Accuracy (range)  $\pm 0.03$  g.

The effects of buoyancy, temperature and static electricity were always considered. The normal buoyancy effect was so insignificant that it was not taken into account. The effect of temperature has been avoided, and the weighings were made at approximately 20°C. The effect of static electricity was significant in some instances, and thus led to the rejections of some measuring values, and reweighings.

## 9.3 HUMIDITY

Continuous humidity determinations were effected with ordinary round hair-hygrometers and hair-hygrographs. Hygrometers were regenerated with RH 100 ... 95 % treatment, and calibrated with the aid of an Assman psychrometer:

- a) Lambrecht-psychrometer (Aspirations-Psykrometer nach Assman).
- b) Lambrecht-hygrometer (Rund-Hygrometer Nr. 190 ... 195), Fischer-hygrometer (Rund-Hygrometer Nr. 111).  
Accuracy of calibrated and regenerated meter: Range smaller than  $\pm 3$  %.
- c) Lambrecht-thermo-hygrograph recorder. Accuracy of regenerated and calibrated meter: Range less than  $\pm 3$  % (for temperature  $\pm 1^\circ\text{C}$ ).

The accuracy of the humidity above  $H_2SO_4$  solutions [94] used in desiccators was  $\pm 2\%$ .

The humidity variations were most marked in the climate rooms and chamber (Photos 1, 2, 3, 4), and were of the order of  $\pm 5\%$ , although their humidity level was kept at the fixed nominal value by means of continuous control and adjustment.

#### 9.4 AIR TEMPERATURE

- a) Temperature range  $0 \dots 110^\circ C$ : Temperatures in the various test spaces varied generally  $\pm 1^\circ C$  around the fixed nominal value; in the climate rooms, the variation could rise to  $\pm 2^\circ C$ , but in the desiccators kept in the thermostats the variation was  $\pm 0,2^\circ C$ . The accuracy of the thermometers (mercury bulb) used was of the order of  $0,1^\circ C$ .
- b) Temperature exceeding  $110^\circ C$ : The only occurrence of temperature exceeding  $110^\circ C$  and up to  $1000^\circ C$  was when the furnace (Photo 11) was used for ignition. The temperatures indicated by the temperature meter of the furnace were checked with the aid of colour-change indicators (Thermocrom, Faber Castell) and Seger cones up to  $1000^\circ C$ ; the accuracy could be estimated as of the order of  $10^\circ C$ .

#### 9.5 AIR VELOCITY

Air velocity variations in the test spaces were of the order of  $0,3\text{ m/s}$  and the following meters were used in the measurements (Photo 12).

- a) Lambrecht-anemometer (Flügelrad-Anemometer Nr. 1905)  $0,3 \dots 20\text{ m/s}$ . Practical accuracy: Range less than  $10\%$  calculated from the reading obtained.
- b) Wallac-thermo-anemometer  $0,1 \dots 10\text{ m/s}$ . Practical accuracy: Range less than  $10\%$  calculated from the reading obtained.

#### 9.6 AIR PRESSURE

Air pressure measurements were mostly made with respect to the airtightness of desiccators and of climate chamber. In addition, air pressure was measured in the containers in which hardening specimens were cured under sealed conditions; lids were opened when the pressure drop was some tens of mm Hg of normal air pressure. Some checks of air humidities were also made by pressure measurement. The accuracy of these measurements depends upon the device used, but in any case surpasses that required.

## 9.7 CARBON DIOXIDE CONTENT OF THE AIR

The carbon dioxide content of the air varies considerably, dependent upon climatic conditions. The normal values of CO<sub>2</sub>-content are approximately:

Climate	ppm by vol.	ppm by weight
Maritime	300	450
Continental	400	600
Indoor	500	750

(ppm = parts per million)

As regards the indoor climate, the variations in CO<sub>2</sub>-content upwards can be appreciable. A CO<sub>2</sub>-content of 1000 or 2000 ppm by vol. in the air of a room is a sign that ventilation is necessary. In the indoor air there can be a CO<sub>2</sub>-content up to 20000 ppm (2 per cent of air volume) without noticeable consequences, except perhaps as regards the depth of breathing [95].

During the course of this study, 75 CO<sub>2</sub>-determinations of air samples were made in the Institute of Occupational Health. The samples were sent to the Institute in gas sample bottles. CO/CO<sub>2</sub> apparatus was employed: Gasanalysengerät "Ultragas" (Wösthof Apparatenbau, Bochum), accuracy superior to 1 ppm by vol.

The normal value for the climate rooms employed in the experiments could be fixed at 500 ± 50 ppm by vol.

## 10 SUMMARY AND CONCLUSION

### 10.1 INTRODUCTION

The main purpose of this study was that of deepening the general understanding of drying and closely related phenomena in concrete, or in other words presentation of the main ideas and methods of investigation of the subject. The publication is consequently not necessarily an account of final results achieved, or of detailed definite conclusions; it is intended to serve as a basis for subsequent detailed studies.

Although the results of experiment in relation to a specific individual subject have been limited to some extent, the basis of old and new knowledge and comprehension seems to provide justification for the assumption that the general features determined are at least reasonable hypotheses, and the methods of investigation outlined applicable to cement pastes and concretes, in general. Of course, it is evident that the continuous progress in the science of concrete always brings in its train refinements and modifications of conceptions and methods, as well as improvements in them.

The author hopes that the contributions published earlier [1]... [10], with the present publication, are or have been useful in improving knowledge of the drying of concrete, and of moisture flow and related phenomena in concrete, or will on a broader scale benefit the evolution of physics concerned with concrete in general.

### 10.2 MODELS FOR MOISTURE TRANSFER IN CONCRETE

The structure of concrete is very complicated. The dominating constituent of concrete, especially where drying is concerned, is cement paste, principally a colloidal capillary-porous material. The role of aggregate can also play a significant role in the drying process.

Model diagrams and a few micrographs are hardly sufficient to provide a complete picture of cement paste, although they enable elucidation of the principal features of the structure, viz. by demonstrating that the structure consists of particles, pores, voids, and channels of various shape and size.

By reason of the complicated microstructure, practically all types of vapour and liquid flows, as introduced by the general drying theories, are possible in concrete during the course of drying, even simultaneously. This implies that detailed description of the drying process in cement pastes and concretes, as a consequence of its complexity, is hardly feasible. Generally speaking, the drying or moisture

flow in concrete is a very complicated phenomenon of porous-medium non-steady hydro- and thermodynamics. The unstable and irreversible nature of cement paste attributable to the changes and variations in moisture content and temperature, to ageing and carbonation, also creates a serious obstacle to the formation of reliable concepts and theories, especially with respect to long-term processes. It is worthwhile in this connection to point out that the life-time of a concrete structure is so long, and the time-dependent changes in the properties of concrete so great, that special attention is due to the properties of concrete at later ages; values relating to 28 days are inadequate.

Notwithstanding the serious difficulties presented above, isothermal mathematical models have been presented in Chapter 2. The general differential field equation given is too complicated for general solution, at least at the moment, but it is shown that reasonable restrictive assumptions and approximations simplify the equation, so that many valuable solutions can be found, particularly in respect of engineering application. Some of them are currently ready for practical calculation, and it will soon be possible to achieve more numerical solutions with the assistance of electronic computers.

### 10.3 MOISTURE DEPENDENCE OF MOISTURE CONDUCTIVITY

The moisture conductivity in the concrete drying process depends upon the various properties of concrete, and the changes in them. At the moment, rather little is known about the moisture conductivity of concretes; this is especially true of the forecasting of drying. One of the most interesting questions of the moisture conductivity of a certain concrete relates to its dependence on moisture content. The experiments made clearly indicated that the moisture conductivity is mainly moisture-content dependent under wet conditions, i. e., when concrete dries from a wet state to a moisture state which corresponds to equilibrium with air of a relative humidity of about 70 %. Moreover, the results appear to point to the conception that in the middle moisture content, corresponding to approximately RH 70 % to 40 %, the moisture conductivity depends to a rather minor extent upon the moisture content. The results of experiment currently available do not permit of description of the behaviour of the moisture conductivity at lower humidities.

The results of experiment indicate that the mathematical expression of moisture dependence on moisture conductivity can be put in the form

$$k = k_e(1 + bu^n), \quad (69)$$

where the parameters depend on the absolute moisture content range within which drying occurs. For instance, when concrete dries from a wet or moist state to moisture equilibrium which corresponds to about RH 70 % of the air,  $n = 1$  and  $b \approx 5$  may give sufficient accuracy in applications. Consequently, the moisture conductivity is then linearly moisture dependent, and the results published in Report [10] are of utility.

The preliminary concept of the moisture dependence of moisture conductivity formed on the basis of the earlier and present experiments is that  $b$  varies approximately within the range 0 ... 10, and  $n$  within the range 1 ... 5, dependent upon the absolute moisture content and the properties of concrete. The results obtained here indicate that the phenomenon involves several factors not clearly understood at the moment.

#### 10.4 CARBONATION

Very little study has been devoted to the carbonation of cement paste or concrete from the physical point of view, and no earlier theory of the carbonation transfer satisfactory enough in cement paste and concrete structures has been presented as far as the author knows.

The main purpose which prompted the treatment of carbonation in this publication was that of creating a hypothesis or a theory of carbonation transfer. The theory proposed is based on the diffusion theory, which seems to govern the essential features of the carbonation phenomenon. In Chapter 4, there is a presentation of the mathematics of the carbonation process and transfer, including experimentally determined values for parameters. Simple equations are introduced for the preliminary examination, along with estimations of the penetration of carbonation in practice.

Section 8.4 contains an experimental study of the effect of carbonation on the porosity, especially on the pore size distribution. This effect, and the loss of fixed water in concrete as a result of carbonation provide clear evidence that carbonation continuously and significantly transforms the structure, and hence the properties of concrete, apart from the corrosion of steel reinforcement. Although the effect on the massive concrete structure may be slight, the penetration of carbonation may essentially change the properties of modern thin structures during the years, and obey the equation

$$L = (h \text{ in years})^{1/2} \text{ cm}, \quad (70)$$

as put forward in Section 8.5. The equation implies that, in some cases, in 6 years a concrete wall or slab 5 cm in thickness can be considerably transformed as a result of carbonation, and in 25 years a concrete wall 10 cm in thickness will have attained the same state.

#### 10.5 INTERRELATION OF THE EVAPORATION DRYING, FIXATION DRYING AND CARBONATION OF CEMENT PASTE

Moisture, fixed water, and fixed carbon dioxide are generally mutually dependent. No gain in fixed water content can occur when the moisture content is lower than a certain limit. Carbon dioxide take-up depends also on the moisture content, and in turn, the carbon dioxide take-up decomposes fixed water. Consequently, it is evident that the interrelation of the substances mentioned are worthwhile studying

from several points of view. In Chapter 5, the problem has been treated mainly with a view to examination of the validity of the assumptions of the drying theory contained in Section 2.22, and for elucidation of the general features of this interrelation under various conditions. Experimental results and a schematic figure are presented, and demonstrate that cement paste, and hence concrete structures in practice, are usually undergoing continuous transformation.

#### 10.6 FIXATION DRYING. ON THE ESTIMATION OF $C_0$

The most vital process undergone by cement paste is hydration or fixation drying, as it is termed in drying studies. This process transforms a wet plastic mass into an artificial stone, termed hardened cement paste or cement stone, or more generally, if the cement paste contains aggregate, referred to as concrete. This extensive problem is briefly studied here; mainly this is concerned with the possibilities and theory of computative estimation of the important entity in the drying process of concrete, viz. the initial moisture content of concrete,  $C_0$ .

#### 10.7 SORPTION ISOTHERMS OF CEMENT PASTE: MOISTURE EQUILIBRIUM

Moisture equilibrium is one of the parameters of primary importance in the drying process. Knowledge of this basic property alone, with an order-of-magnitude value of drying time, can be of major significance. Furthermore, it gives information on the internal surface area of porous materials, thus elucidating their microstructure.

Chapter 7 deals with sorption isotherms, i.e. moisture equilibrium curves at fixed temperatures, including their temperature dependence and the hysteresis of desorption and adsorption processes. Difficulty inherent in the selection of a datum point is also discussed. Special attention has been paid to the stability and estimation of moisture equilibrium in the drying process. The large surface areas obtained indicate that cement paste is an extremely fine porous material.

The results of experiment indicate that the sorption isotherms of cement pastes made of different kinds of ordinary Finnish portland cement are almost equivalent, pointing to minor divergences in their microstructures. The equilibrium moisture content after desorption was about two times as much as that after adsorption. The temperature-dependence of the desorption isotherms is considerably greater than that of the adsorption isotherms, and the dependence is rather slight within the temperature range of order of  $10^\circ\text{C}$ . The hysteresis curves indicate that the hysteresis is temperature-dependent, and is greater at lower temperatures.

The tests indicate that good moisture equilibrium could be found for small specimens of cement paste made of ordinary Finnish portland cement.

Theoretical examination showed that the criterion for the attainment of moisture equilibrium depends upon moisture conductivity and the dimensions of the specimen.

A fixed value, such as a moisture loss of 0.1 % per week near equilibrium, cannot be generally valid.

Surface areas determined with the aid of desorption isotherms were of the order of 200 m<sup>2</sup>/g. Against this, the adsorption isotherms (water vapour) gave 100 m<sup>2</sup>/g, indicating the irreversibility of the deformation (shrinkage) brought about by drying (105°C).

#### 10.8 SOME EXAMINATIONS OF RELATED PHENOMENA

The moisture variations in concrete have many important, closely related phenomena. Chapter 8 deals with some of them.

The relationship of moisture content (loss) and shrinkage has been presented. It is shown that the relationship can be even approximately linear, although the problems concerning deformations are generally very complicated.

The phenomenon of drying-strengthening and wetting-weakening has been previously treated by the author [2], [6], [8]; this publication contains a modification of a theory on drying-strengthening and wetting-weakening of other porous materials, as formulated and applied to concrete.

An experimentally-obtained effect of gravitation on the drying of standard cement mortar plates is reported; the problem is shown to be an interesting one although the effect on ordinary concrete may be slight. The underlying theory has been put forward in Publication [9].

The results of mercury porosimetry, and application of the one-point water adsorption method, demonstrate the porosity and pore size distribution of cement paste, including the effect of carbonation. The surface area of a carbonated cement paste is about one half of that of non-carbonated cement paste. The pore size distribution also exhibits changes in porosity attributable to carbonation. (Cf. Section 10.4).

A carbonated layer of concrete may have properties which are completely different from parts of concrete not carbonated. A simple equation is given for preliminary estimation of the thickness of the carbonated layer as a function of time in ordinary air (Cf. Section 8.4).

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## PHOTOGRAPHS AND DESCRIPTION OF SOME EQUIPMENT

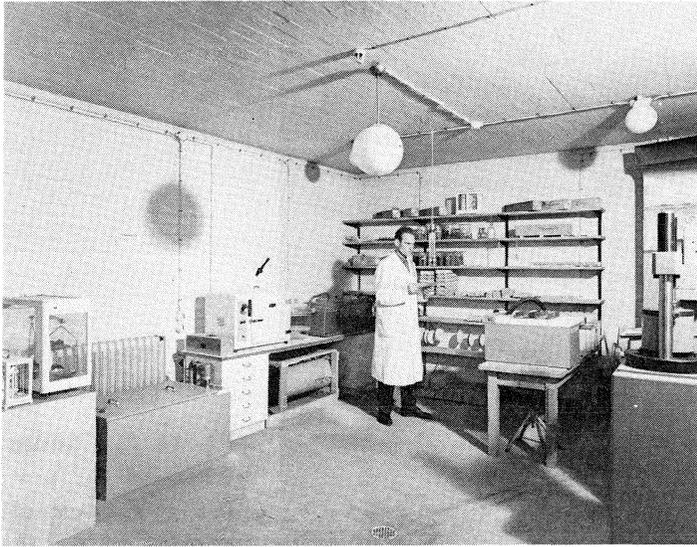


Photo 1. Climate room:  $\varphi = 40\%$ ,  $t = 20^{\circ}\text{C}$ ,  $v < 0.5$  m/s. Apparatus used in the experiments discernible; for example the arrow indicates oven ( $105^{\circ}\text{C}$ ).



Photo 2. Climate room:  $\varphi = 70\%$ ,  $t = 20^{\circ}\text{C}$ ,  $v < 0.5$  m/s. Apparatus used in the experiments discernible.



Photo 3. Climate room:  $\varphi = 95 \dots 100 \%$ ,  $t = 20^\circ\text{C}$ ,  $v < 0.5 \text{ m/s}$ . Demoulding and/or crushing of the specimens was effected here.

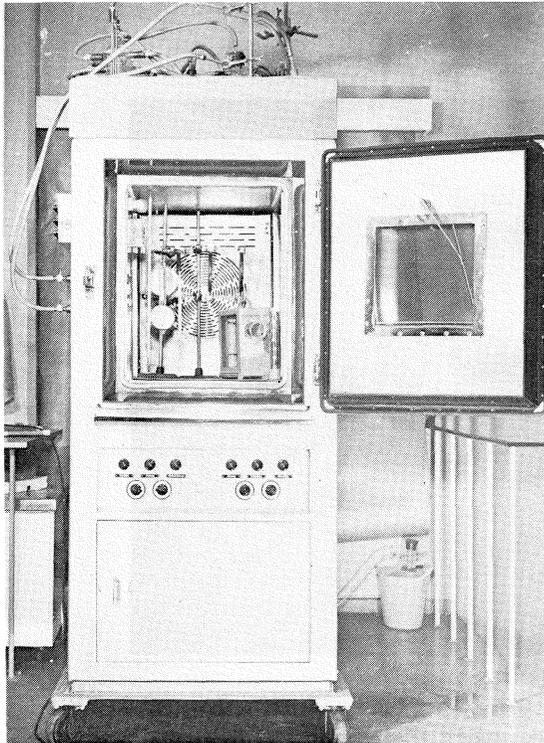


Photo 4. Variable climate chamber, Vötsch-Junior-Klima-prüfschrank, Type VKJA/150:  $\varphi = 20 \dots 95 \%$ ,  $t = 90 \dots -35^\circ\text{C}$ ,  $v \approx 1 \text{ m/s}$ .

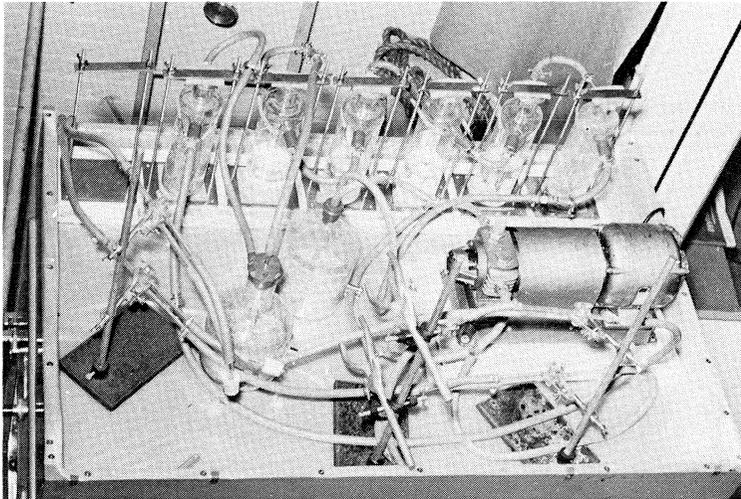


Photo 5. Carbon dioxide removal system of the climate chamber built on its roof (Cf. Photo 4). The system consists of six gas-washing bottles containing KOH-water solution (five bottles) for  $\text{CO}_2$  removal and silica-gel (one bottle) for the filtration of the air passed through. Two larger bottles are for safety. Flow capacity 10 litres/min;  $\text{CO}_2$ -level about 50 ppm by vol. could be attained.

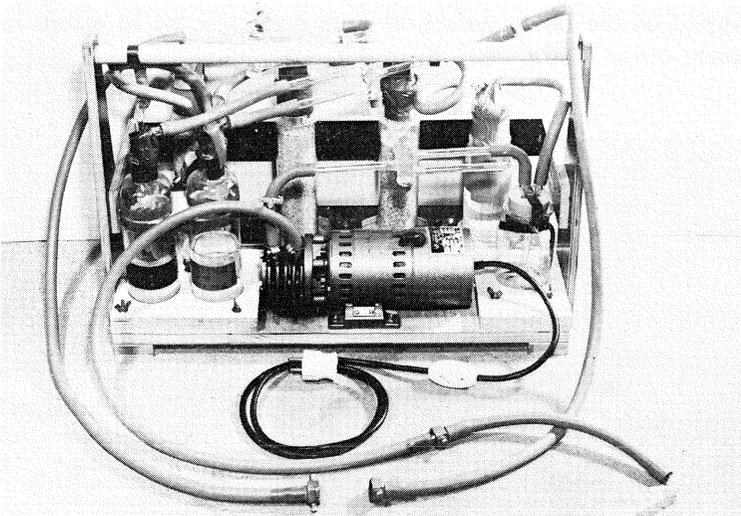


Photo 6. Self-made portable apparatus for carbon dioxide take-up from the air: practical obtainable minimum  $\text{CO}_2$ -content 10 ppm by vol. Consists of gas-washing bottles containing granular Ascarite or KOH-water solution for  $\text{CO}_2$ -removal and salt solutions for moistening of the air passed through.

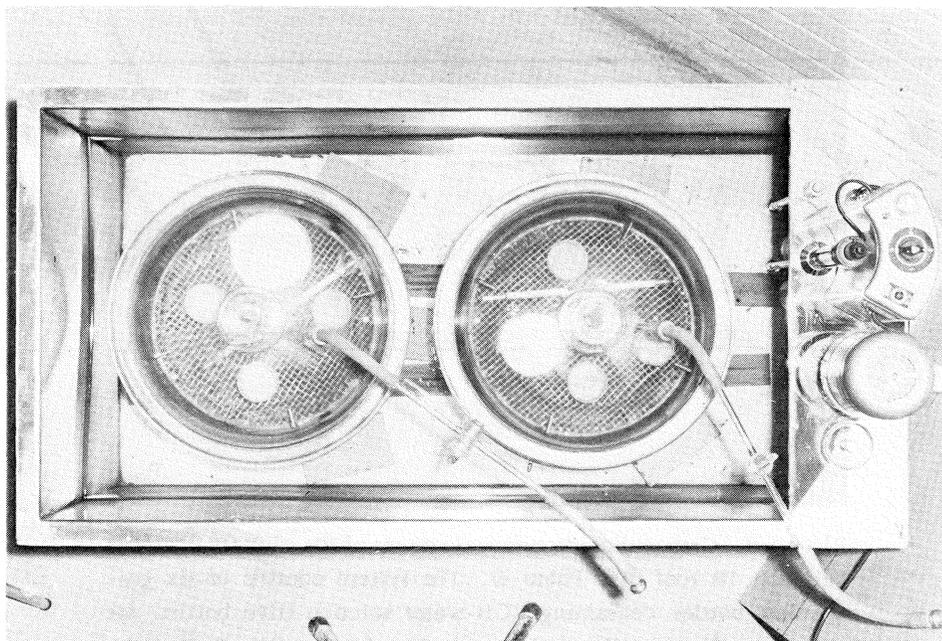


Photo 7. Interior view of the water-thermostat box containing desiccators. Humidity in the desiccators is maintained with suitable  $\text{H}_2\text{SO}_4$ -water solution [94]. Weighing bottles, hair-hygrometers, and thermometers discernible. Later, an electrical fan was fastened on the inside surface of each desiccator lid to ensure forced convection, about 0.5 -- 1 m/s. (Cf. Photo 8.)

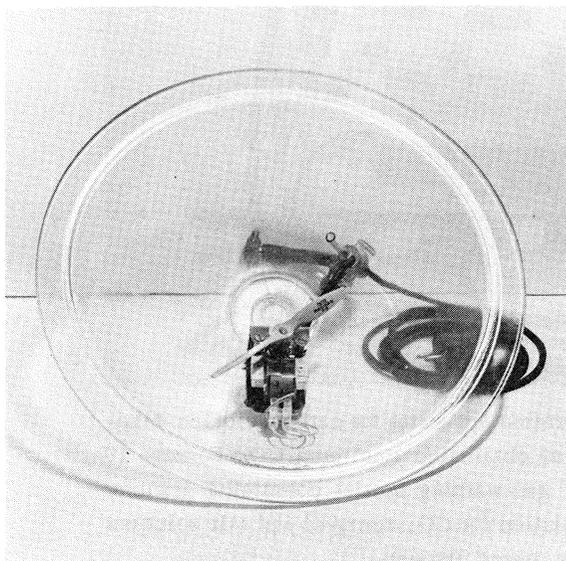


Photo 8. Small electrical fan fastened on the inside surface of desiccator lid to ensure forced convection, and hence correct humidity. (Cf. Photo 9.)

Photo 9. A desiccator as humidity chamber. Circular plates of standard cement mortar, hair-hygrometer, thermometer, and fan discernible.  $H_2SO_4$ -water solution on the bottom of the desiccator. (Cf. Appendix 3.)

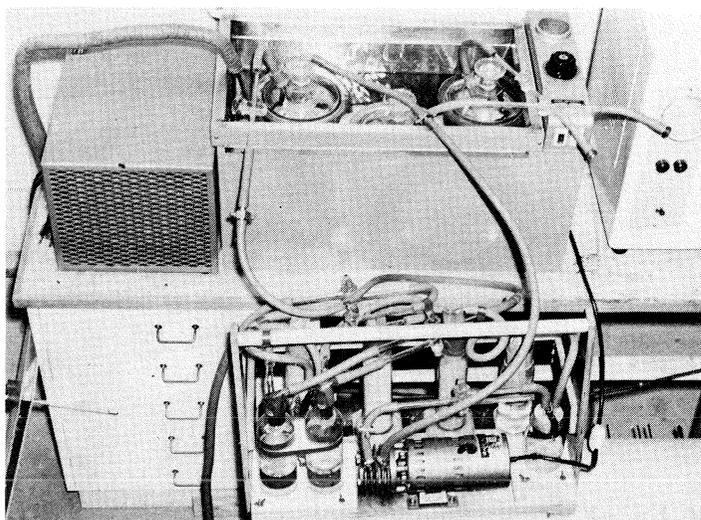
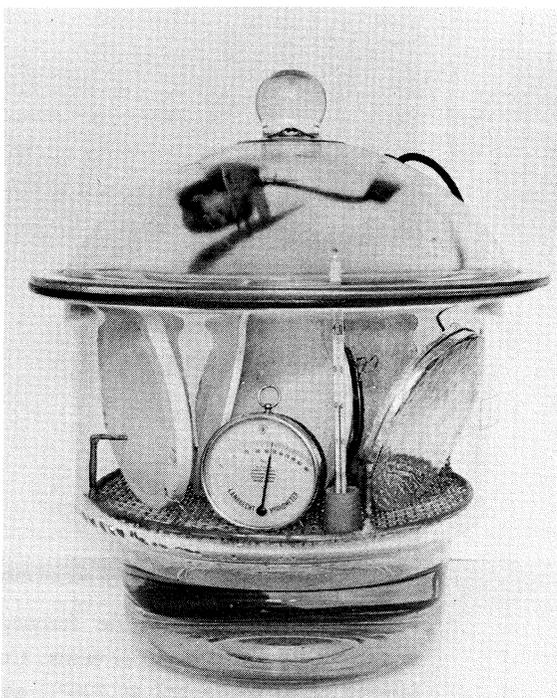


Photo 10. Water-thermostat box equipped with freezer (+0 ... 90°C). The system presented in this photo (during  $CO_2$  removal process) was used in determination of the temperature-dependence of sorption isotherms (Section 7.4 and Appendix 6).

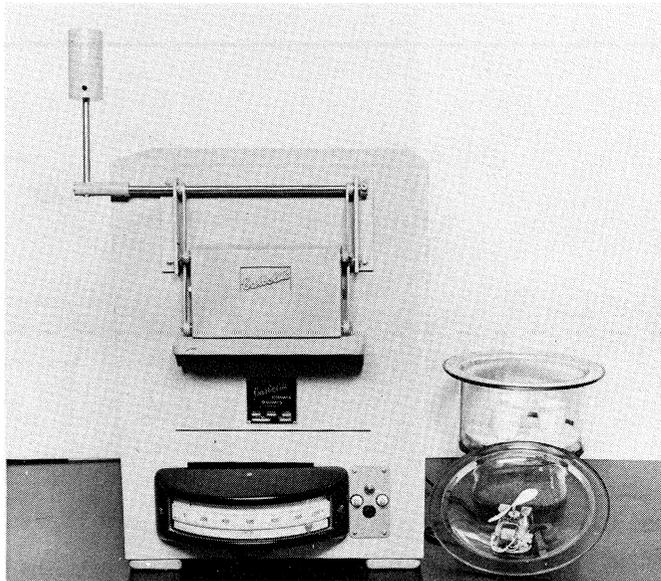


Photo 11. Electric muffle furnace (100 ... 1000°C) used in various temperature treatments. Cooling desiccator containing dried silica-gel at 105°C also discernible.

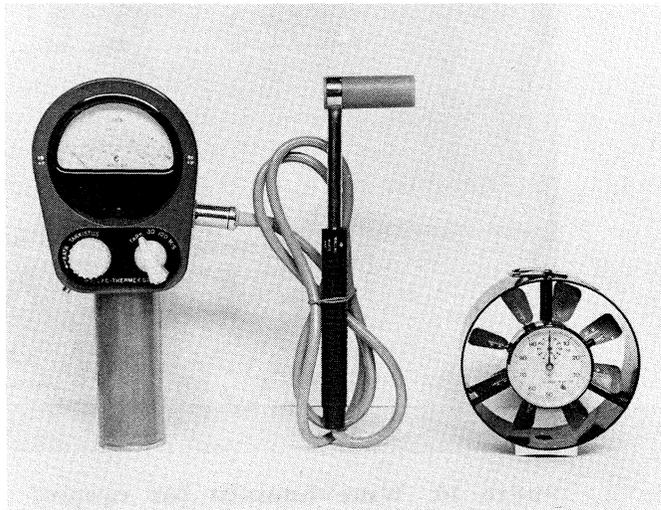


Photo 12. Electric anemometer and mechanical anemometer. (Cf. Section 9.5.)

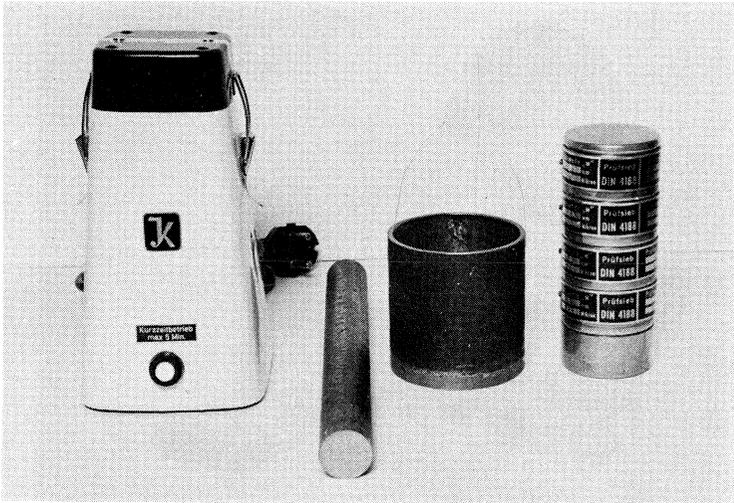


Photo 13. Electrical crusher, and simple steel container in which a material can be crushed with a steel rod. The latter device proved to be more convenient and the process created only insignificant temperature rise. Crushed cement pastes and cement mortars were made with these devices. Sieve series discernible.

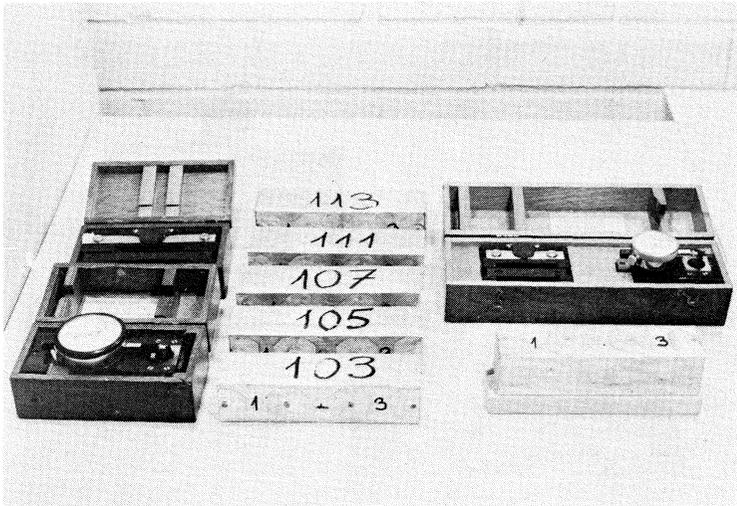


Photo 14. Standard cement mortar prisms used in Egner's method (Section 3.3), in the determination of carbonation (Section 4.44), and in determination of the relation between moisture loss and shrinkage (Section 8.1). Mechanical deformaters and studs (gauge plugs) discernible. The prisms are carefully covered with metal and plastic membranes.

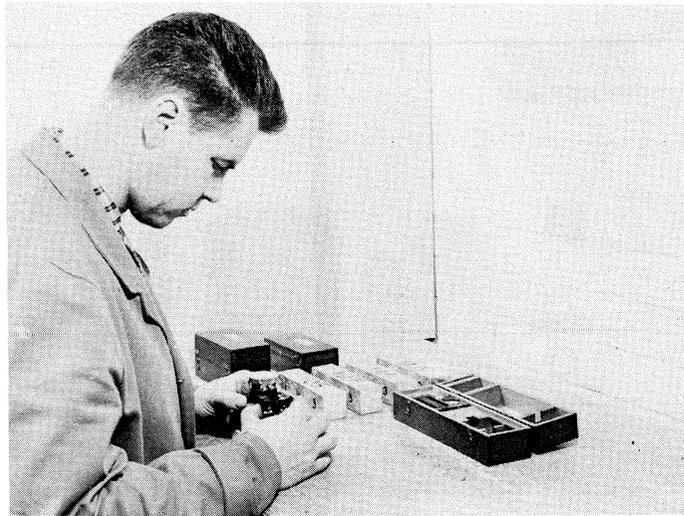


Photo 15. Measurement of shrinkage. (Cf. Photo 14.)

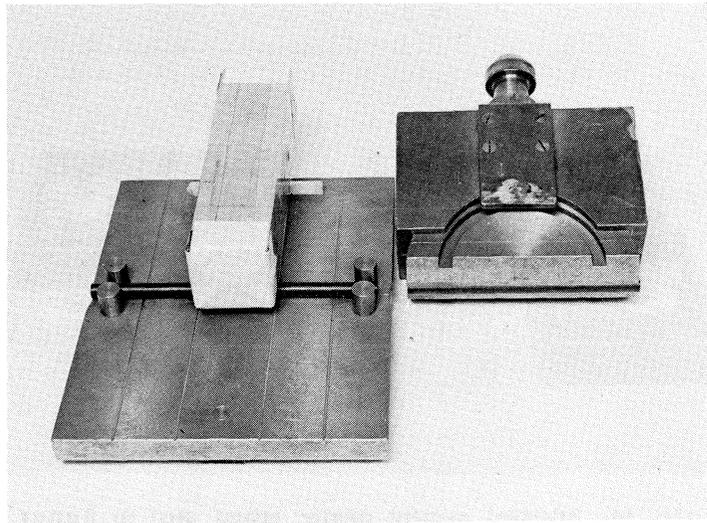


Photo 16. A device specially constructed for the splitting of cement mortar prisms; it was used in determination of the moisture and carbonation distribution in the prisms. (Cf. Sections 3.3 and 4.44. See Photo 17.)

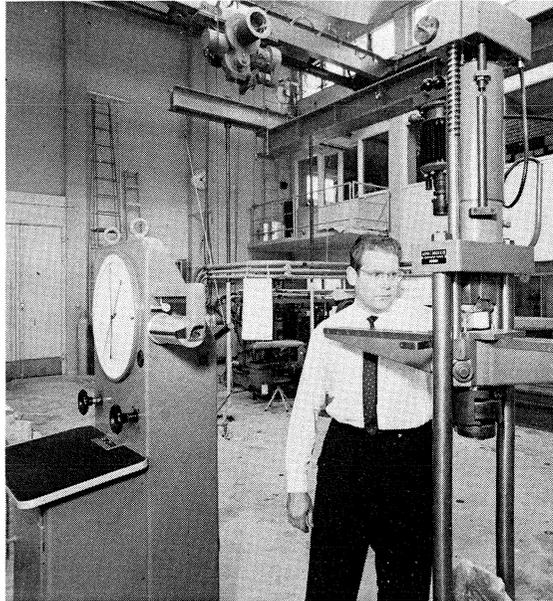


Photo 17. The splitting device (and 10-ton loading machine) cuts a cement mortar prism into pieces.

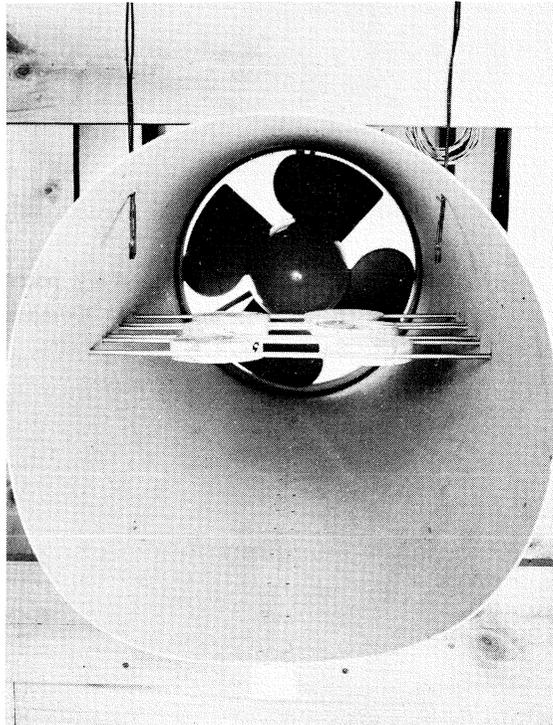


Photo 18. Plates in the wind tunnel ( $v = 5 \dots 7$  m/s) ready for a gravity experiment (Section 8.3).

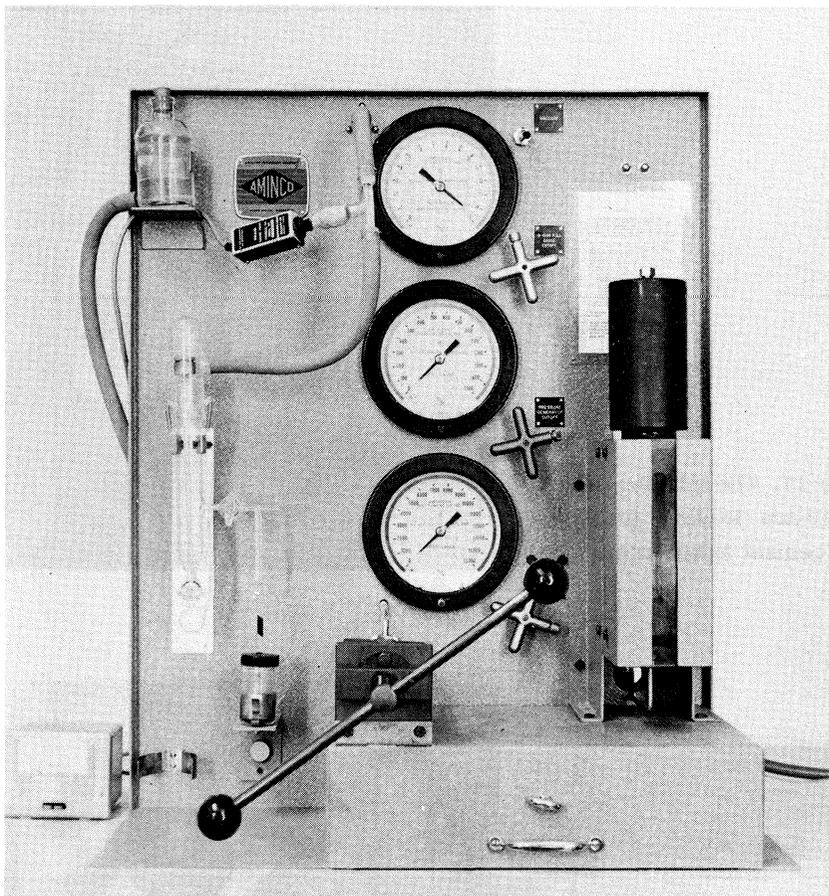


Photo 19. Aminco-Winslow mercury porosimeter, max. 15 000 psi, Cat. No. 5-7109; American Instrument Company, Silver Spring, Maryland, U.S.A. (Cf. Section 8.4.)

## CEMENT USED IN THE EXPERIMENTS

All the cements used in the experiments were ordinary Finnish portland cements made in three Finnish cement factories denoted by Pa, La, Lo.

Cement No.	Factory Pa				Factory Lo	Factory La	
	Pa 6500	Pa 6800	Pa 7100	Pa 7800	Lo 7300	La 7600	
Compressive strength							
age 7 days	kp/cm <sup>2</sup>	322	313	338	338	290	299
28 days	kp/cm <sup>2</sup>	415	409	423	418	400	397
Flexural strength							
age 7 days	kp/cm <sup>2</sup>	64	58	59	66	57	57
28 days	kp/cm <sup>2</sup>	80	76	75	78	71	70
Setting (Vicat, 20°C)							
initial set	h, min	4.35	2.40	3.45	2.20	2.55	2.45
final set	h, min	6.23	4.05	5.00	4.00	4.15	4.15
Autoclave expansion test (ASTM C 151-54)							
expansion	%	-	0.14	0.30	0.21	0.10	0.03
Specific surface area (Blaine) cm <sup>2</sup> /g							
		-	-	3170	3370	3460	3470
Constituents %							
ignition loss	550°C		(0.46)	(0.64)	(-)	(0.65)	(0.13)
	1000°C		4.40	3.71	2.97	2.86	4.47
insoluble (HCl)			5.88	5.20	3.82	1.61	1.32
SiO <sub>2</sub>			18.67	19.12	19.66	22.41	19.58
Al <sub>2</sub> O <sub>3</sub>			5.20	4.68	4.75	4.81	3.61
Fe <sub>2</sub> O <sub>3</sub>			1.49	1.74	1.79	2.10	2.56
CaO			58.11	58.38	60.06	58.04	62.87
MgO			3.13	3.23	3.19	4.39	2.42
SO <sub>3</sub>			2.52	2.47	2.34	1.93	2.33
Total			99.40	98.53	98.58	98.15	99.16

Each strength value is an average obtained from six prisms (4 cm x 4 cm x 16 cm) made of standard cement mortar (See Glossary).

The setting times are the average values of four tests.

The expansion values are the average values obtained from three prisms (2.5 cm x 2.5 cm x 25 cm).

All the determinations the results of which are presented in this appendix have been carried out in the Chemistry Section of this laboratory.

## EXPERIMENTAL PROCEDURES OF THE EXPERIMENTS ON MOISTURE DEPENDENCE OF MOISTURE CONDUCTIVITY

### 1 NARROW HUMIDITY-RANGE METHOD

#### 1.1 Specimens

The specimens were 5 plates (thickness 1.2 cm, diameter 13.5 cm), made of standard cement mortar (Cement: Pa 6500).

The cement mortar was poured into plastic rings resting on glass plates covered with a wetted plastic sheet. Pouring was carried out in a climate room (RH 70 %, 20°C). The mortar was strongly consolidated by means of a mechanical vibration table (Haegerman, 20 strokes per plate). The open surface was carefully smoothed, and covered with plastic sheets. The plates were then kept in a climate chamber (RH 95 ... 100 %, 20°C) for 24 hours. Following this, the plastic sheets on both main surfaces were removed, and the plates stored in water at 20°C for up to 28 days. The plates then underwent a six month drying test not described here; during this period, the plates were kept in a climate room (RH 40 %, 20°C, CO<sub>2</sub>-content about 500 ppm by volume). After the test, the plastic rings were removed, and the edges covered with two layers of rubber paint (NEOPRENE), and an intermediate layer of plastic ribbon. After thorough drying at 105°C at the age of 212 ... 239 days, the plates were put in water (20°C), and stored there for 2 1/2 years.

As regards the test mentioned in the heading, the other surface of two plates, which was free at pouring, was tightly covered with glued metal foil (Rein-Metallband Nr. 1091, Vang, thickness 0.07 mm; the uppermost of two layers also covered the edges of the plates). These two plates could then dry from one surface only. Before covering was applied, the surfaces were allowed to dry until the start of the second falling-rate period [2]. The surface left uncovered was kept continuously wet during the covering.

#### 1.2 Test procedure

The test proper began when the open main surfaces of the five plates had attained, after removal from water, the second falling-rate period of drying. At this moment, the plates were quickly weighed and moved into a climate chamber (Vötsch Junior Klimaprüfschrank) (Photo 4; Appendix 1), in which the climate was: RH 85 %, 25°C, about 1 m/s, CO<sub>2</sub>-content 50 ppm by volume.

Three of the uniaxially-drying plates dried simultaneously on the two main surfaces, and two of them dried on one main surface only. The respective characteristic thicknesses were  $l = 0.6$  cm and  $l = 1.2$  cm.

It was planned that the test would proceed gradually isothermally (25°C) from high to low humidity, after the moisture equilibrium of the plates had been reached at each humidity (water, 85 %, 70 %, 55 %, 40 %, 25 %, 10 %, 0 %, 105°C oven drying). The test was so carried out that the humidity was changed after "sufficient" equilibrium had been attained (Cf. Fig. 5 a). Later, it was observable that it would have been more satisfactory to wait until better moisture equilibrium had been reached. When moisture equilibrium was attained at RH 55 %, the climate chamber ceased to function properly, and the plates were moved into a 20-litre desiccator equipped with a small electric fan (Photo 9). The air humidity was maintained at the desired level by means of a suitable H<sub>2</sub>SO<sub>4</sub>-water solution on the bottom of the desiccator. The air velocity was 0.5 ... 1 m/s in the desiccator, and the temperature 22°C.

The moisture content change was measured by weighing with a METTLER K 7 T balance once a week. The results obtained during 8 months of testing are presented in Fig. 5 a. Cf. Section 3.22.

## 2 EGNER'S METHOD

### 2.1 Specimens

The specimens were 15 prisms (4 cm x 4 cm x 16 cm) made of standard cement mortar (Cement: Pa 7100). The results obtained from 6 prisms only will be presented in this publication, as the experiment will take several years.

The mortar was poured into steel moulds, and strongly consolidated by hand with a tamping rod. Pouring was carried out in a climate room (RH 70 %, 20°C). An open surface was carefully smoothed and covered with a plastic sheet. The prisms were then kept in a climate chamber (RH 95 ... 100 %, 20°C) for 24 hours. The sheets and the moulds were then removed in a climate room (RH 70 %, 20°C) and the prisms wrapped in plastic sheets and put in an airtight desiccator. At mould removal, the weight at the prisms was 579 ± 3 g, and the density of the mortar 2240 ± 10 kg/m<sup>3</sup>.

At the age of 7 1/2 months, the specimens were covered first with a metal foil (two layers) and then with a plastic foil (one layer). The metal foil (Rein-Metallband Nr. 1091, Vang) was 0.07 mm thick, and one surface was furnished with glue beforehand. One surface of the plastic foil was also glued. The foils formed a tight, moistproof covering on the surfaces of the prism. This was effected by careful rubbing of the coverings with a piece of wooden board.

For the deformation measurements, metal studs (gauge plugs) 50 mm apart were fastened on the two opposing side surfaces of the prisms with Araldite-glue

(See Fig. 34). Before the application of glue, circular holes were cut through the coverings. The holes were additionally sealed with pieces of metal foil. One of the prisms was not furnished with studs.

Seven of the prisms were then stored in a climate room (RH 40 %, 20°C,  $v < 0.5$  m/s), and the other seven prisms, plus the studless prism, in another climate room (RH 70 %, 20°C,  $v < 0.5$  m/s). When the prisms had been in these rooms for two months, the test proper was started.

## 2.2 Test procedure

### 2.21 The beginning of drying

When the mortar was about 10 months old, the covering on the end surfaces of the six prisms kept in each climate room (40 % and 70 %) was removed, including the glue fastened on the surfaces. Thus, in each climate room there were six uniaxially drying prisms plus one sealed prism. In addition, one sealed, studless prism was stored in a climate room of RH 70 %.

The sealed prisms were reference prisms for indication of the possible effects attributable to the changes in the structure of the mortar, the moisture loss through the covering, and so on.

The studless prism was reserved for determination of the moisture equilibrium,  $C_e$ .

The weight and the deformation of each prism were determined once a week. The balance used was a METTLER K 7 T. The linear deformation was measured with mechanical DEMEC-deformeters (Photos 14 and 15).

### 2.22 Determination of moisture distribution

The main purpose of the experiment was that of determining the interrelation of moisture conductivity  $k$  and moisture content, with the aid of moisture distribution, by the application of Egner's method.

For determination of the moisture distribution, one prism from each climate room was taken away after 68, 179 and 293 days of drying, and split into ten pieces. Before splitting, the open ends of the prisms were sealed with cloth tape, and slits were cut with a knife through the covering at the splitting lines 16 mm apart. Splitting was effected by a compression machine, and a specially constructed device, so that two opposing steel bars, 8 mm in diameter, broke the prisms into pieces (Photos 16 and 17). After splitting, the broken pieces were still under the coverings, and thus in a practically sealed condition. The coverings, including the glue fastened on the surfaces, were carefully and quickly removed, and the pieces

weighed in a climate room at RH 70 %. The moisture content of each piece was measured by temperature treatment in an oven (105°C).

When the moisture distributions had been determined, the pieces were crushed and ignited at 550°C and 1000°C.

The moisture distribution curves are presented in Fig. 7 a. In the figure, the moisture values have been transformed into relative moisture content  $u$ , using the determined values of  $C_0$  and  $C_e$ .

## 2.23 Determination of the initial moisture content and the equilibrium moisture content of the cement mortar

The values of initial moisture content  $C_0$  and equilibrium moisture content  $C_e$  were needed for calculation of relative moisture content  $u$ .

The value of the moisture content arrived at from the innermost pieces of the split prisms at 68 days, was taken as the initial moisture content. On the basis of earlier experience, it could be assumed that after this short drying time the innermost pieces could not have changed in their moisture content. The results obtained indicated that this value, 8.05 % by weight, the same for the two prisms, had been correctly selected. Thus the initial moisture content  $C_0 = 166 \text{ kg/m}^3$ .

The equilibrium moisture content was determined in air at relative humidities of 40 % and 70 % respectively, and also under conditions of carbonation and non-carbonation. Consequently, the equilibrium moisture content was determined in both climate rooms (RH 40 %, 70 %,  $\text{CO}_2$ -content about 500 ppm by vol.) and in the desiccators ( $\text{CO}_2$ -content smaller than 50 ppm by vol.) above corresponding  $\text{H}_2\text{SO}_4$ -water solutions. The desiccators (20 litres) were in a water-bath thermostat ( $25^\circ\text{C} \pm 0.2^\circ\text{C}$ ) equipped with small electrical fans (forced convection, 0.5 ... 1 m/s).  $\text{CO}_2$  was removed from the desiccator air with the device specially constructed for the purpose (Photo 10).

For determination of the equilibrium moisture content, a part of the studless prism kept in the climate room of RH 70 % was cut into pieces at the age of 10 months (at the start of the drying test) and at the age of 20 months. Only those results of the determination started at the age of 10 months are included in the following table; the second determination gave similar results. The drying time for a sufficient moisture equilibrium was 2 1/2 months. On the basis of the results presented in the following table, the values of the equilibrium moisture content were fixed as follows:

$$C_e = 57 \text{ kg/m}^3 (= 2.76 \%), \text{ when RH } 40 \%$$

$$C_e = 90 \text{ kg/m}^3 (= 4.38 \%), \text{ when RH } 70 \%$$

The weighings were carried out with a METTLER-balance H 6.

Equilibrium moisture content; drying time 2 1/2 months.

Storage	Sample		Eq. moisture	
	No.		%	kg/m <sup>3</sup>
Room 40 %	1	inner piece	2.61	54
	2	powder**)	2.61	54
	3	end piece	2.49	51
Desiccator 40 %	4	inner piece	2.77	57
	5	powder	2.76	57
	6	end piece	2.77	57
Room 70 %	7	inner piece	4.04	83
	8	powder	- *)	-
	9	end piece	4.20	87
Desiccator 70 %	10	inner piece	4.80	99
	11	powder	4.38	90
	12	end piece	4.75	98

\*) broken weighing bottle,

\*\*\*) all the powder samples  $< \neq 4$  mm.

After the equilibrium moisture content had been determined, the samples were ignited at 550°C and 1000°C. The carbon dioxide content in the samples stored in desiccators was approximately 0.10 ( $= j/c_0$ ) and in the samples stored in the climate rooms about 0.20 ( $= j/c_0$ ); for original cement the corresponding value was about 0.06 ( $= j_0/c_0$ ).

#### 2.24 Moisture loss through the coverings of the prisms

The moisture loss through the coverings of the test prisms was examined with the aid of the similar sealed prisms kept under the same conditions. The results obtained with these reference prisms are given in the following table

Drying time days	Moisture loss of reference prisms					
	$\varphi = 40 \%$			$\varphi = 70 \%$		
	g/prism	moisture- %-units	kg/m <sup>3</sup>	g/prism	moisture- %-units	kg/m <sup>3</sup>
68	0.22	0.04	0.8	0.10	0.02	0.4
179	0.53	0.10	2.0	0.28	0.05	1.1
293	0.84	0.16	3.2	0.43	0.08	1.7

Consequently, during one year the moisture loss at RH 40 % is about 1 g/prism or 0.2 moisture-%-units or 4 kg/m<sup>3</sup>, and at RH 70 % about one half of the values obtained at RH 40 %. The effect can thus be considered as insignificant, at least as regards the application of Egner's method presented in this publication.

## EXAMPLES OF THE CALCULATION OF CARBONATION

- Ex. 1 Calculate the carbon dioxide take-up, water released, and mass gain if water released has escaped, of a wide slab of thickness 1 cm in normal air at a relative humidity of 50 ... 70 per cent. Both surfaces of the slab are exposed. The slab made of cement mortar ( $w/c = 0.56$ ,  $Q_c = 500 \text{ kg/m}^3$ ) has been cured under sealed conditions (no water exchange, no  $\text{CO}_2$  exposure) for several months before a carbon dioxide attack. The carbonation period is 2 years, and  ${}^c k = 10^{-13} \text{ m}^2/\text{s}$ . Answer in per kg cement. (See Chapter 4).

Answers: 1)  $\bar{r} = f({}^c Fo)$ ;  ${}^c Fo = \frac{{}^c kh}{l^2}$

$${}^c Fo = \frac{10^{-13} \cdot 2 \cdot 360 \cdot 86400}{0.005^2} = 0.25$$

$$\therefore \bar{r} = 0.56 \quad (\text{Fig. 12})$$

2)  $\bar{r} = \frac{\bar{D} - D_0}{D_e - D_0}$

$$\frac{\bar{D} - D_0}{Q_c} = \bar{r} \frac{D_e - D_0}{Q_c} = 0.56 \cdot 0.39 = 0.22$$

$$\frac{\bar{D} - D_0}{Q_c} = \frac{\bar{j} - j_0}{c} = 0.22 \text{ kg CO}_2/\text{kg cement}$$

3)  $\frac{{}^c \bar{C}}{{}^c C_e} = f({}^c Fo) (= \bar{r})$ ;  $\frac{{}^c \bar{C}}{{}^c C_e} = 0.56$

$$\frac{{}^c \bar{C}}{Q_c} = \delta \bar{r} (D_e - D_0) \frac{1}{Q_c} = 0.38 \cdot 0.56 \cdot 0.39$$

$$\therefore \frac{{}^c \bar{C}}{Q_c} = 0.08 \text{ kg water/kg cement}$$

$$4) \frac{c\bar{M}}{cM_e} = f(cFo) (= \bar{r}); \quad \frac{c\bar{M}}{cM_e} = 0.56$$

$$\frac{c\bar{M}}{Q_c} = (1 - \delta)\bar{r}(D_e - D_0) \frac{1}{Q_c} = 0.62 \cdot 0.56 \cdot 0.39$$

$$\therefore \frac{c\bar{M}}{Q_c} = 0.14 \text{ kg/kg cement}$$

$$5) \text{ Check: } \frac{c\bar{C}}{Q_c} + \frac{c\bar{M}}{Q_c} = \frac{\bar{D} - D_0}{Q_c}; \quad 0.08 + 0.14 = 0.22$$

Ex. 2 The slab introduced in Ex. 2 is cut into pieces of area  $A_1 = 1 \text{ m}^2$  and  $A_2 = 0.01 \text{ m}^2$ . Calculate the carbon dioxide take-up, water release and mass gain for the pieces after two years' carbonation.

$$\text{Answers: 1) } \bar{D} - D_0 = Q_c \frac{\bar{D} - D_0}{Q_c} = 500 \cdot 0.22 = 110 \text{ kg/m}^3$$

$$V_1 = 1 \text{ m}^2 \cdot 0.01 \text{ m} = 0.01 \text{ m}^3$$

$$V_2 = 0.01 \text{ m}^2 \cdot 0.01 \text{ m} = 0.0001 \text{ m}^3$$

$$V_1(\bar{D} - D_0) = 1.1 \text{ kg}$$

$$V_2(\bar{D} - D_0) = 0.011 \text{ kg} = 11 \text{ g}$$

$$2) \delta V_1(\bar{D} - D_0) = 0.38 \cdot 1.1 \text{ kg} = 0.4 \text{ kg} (= V_1 c\bar{C})$$

$$\delta V_2(\bar{D} - D_0) = 0.38 \cdot 11 \text{ g} = 4 \text{ g} (= V_2 c\bar{C})$$

$$3) (1 - \delta) V_1(\bar{D} - D_0) = 0.62 \cdot 1.1 \text{ kg} = 0.7 \text{ kg} (= V_1 c\bar{M})$$

$$(1 - \delta) V_2(\bar{D} - D_0) = 0.62 \cdot 11 \text{ g} = 7 \text{ g} (= V_2 c\bar{M})$$

CALCULATION OF CARBON DIOXIDE CONTENT  $j/c'_0$  OF  
CONCRETE

$$j/c'_0 = \left[ 1 + \left( 1 + \frac{H}{100} \right)^n \right] \frac{1}{1 - \frac{E}{100}} B \Delta CO_2(550 \dots 1000^\circ C) \quad (1)$$

n aggregate to cement (c) ratio by weight

H weight change of cement within temperature range 20 ... 1000°C as percentage by weight at 1000°C

E amount of an insoluble (HCl) material in cement as percentage by weight at 1000°C

$c'_0$  amount of cement proper (see Section 4.44)

B 4/3 (from Fig. 10; straight line)

$\Delta CO_2(550 \dots 1000^\circ C)$  the amount of carbon dioxide liberated from concrete samples between 550 ... 1000°C. Basic weight at 1000°C. (kg CO<sub>2</sub>/kg concrete).

In accordance with the example presented in Section 4.44 (Fig. 17 a), the following values of parameters are valid for that special case (standard cement mortar, w/c = 0.56)

$$n = 3$$

$$H = 5 \%$$

$$E = 5.4 \%$$

Consequently,

$$j/c'_0 = 5.85 \Delta CO_2(550 \dots 1000^\circ C) \quad (2)$$

EXPERIMENTAL PROCEDURE IN THE INVESTIGATION OF  
TEMPERATURE DEPENDENCE OF SORPTION ISOTHERMS

## 1 SPECIMENS

The samples were made from specimens of cement paste (Cement: Pa. 7100). Cement paste (w/c = 0.3 and 0.45) was thoroughly mixed with an electrical mixer, and poured with the aid of a cooky-press in small plastic bags (6 cm x 9 cm), which were kept in glass jars furnished with rubber lids for 87 days at 20°C (sealed curing). The specimens were then crushed in a small electrical laboratory crusher in a climate room ( $t = 20^{\circ}\text{C}$ ,  $\varphi = 95 \dots 100 \%$ ,  $v < 0.5 \text{ m/s}$ ). A sieved fraction  $\#0.25 \dots 0.5 \text{ mm}$  served to provide samples. Six samples of average weight of about 0.5 g were taken, and put in small weighing bottles ( $\text{Ø} = 46 \text{ mm}$ ). The weight was chosen so that the crushed samples formed a thin layer on the bottom surface of the weighing bottles.

## 2 APPARATUS AND ITS APPLICATION

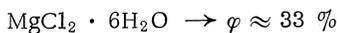
During testing, the samples were kept in the small weighing bottles as described above. The weighing bottles were covered with their lids during weighings. Furthermore, the weighing bottles were put in relatively small desiccators (volume 1.2 dm<sup>3</sup>), in which the humidity of the air was kept constant by means of saturated salt solutions (free convection). The desiccators were put in a water-bath thermostat equipped with heating and cooling units (Photp 10).

To preclude carbonation of the samples, carbon dioxide was removed from the desiccator air by a specially constructed device (Photo 10) consisting of a pump and a train of gas washing bottles containing KOH-solution and Ascarite. After continuous (10 minutes) pumping in the closed circuit of desiccators and carbon dioxide remover, the carbon dioxide content in the desiccators was less than 50 ppm by volume. The carbon dioxide content in desiccators was then less than about 0.1 mg. This small amount was considered insignificant.

The weighings were effected with a precision balance (METTLER H6), with an accuracy of  $\pm 0.05 \text{ mg}$  according to the instruction leaflet. In practice, the accuracy was found to be about  $\pm 0.2 \text{ mg}$ , corresponding to a change of 0.04 % in the weight of the samples.

## 3 EXPERIMENTS

The tests were carried out in three desiccators. On the bottom of each desiccator was a saturated salt solution:



The relative humidities above the saturated salt solutions as a function of temperature are given in detail in the table below, taken from: National Bureau of Standards Handbook 77 - Volume II, 1961: Wexler & Hasegava, Relative humidity - Temperature Relationships of Some Saturated Salt Solutions in the Temperature Range 0° to 50°C.

°C	LiCl · H <sub>2</sub> O	MgCl <sub>2</sub> · 6H <sub>2</sub> O	NaCl
	RH %	RH %	RH %
5	14.0	34.6	75.1
15	12.8	33.9	75.3
25	12.0	33.2	75.8
35	11.7	32.5	75.5

Each desiccator contained 4 samples (2 samples, w/c = 0.3 and 2 samples, w/c = 0.45).

Testing was begun at 5°C. When apparent equilibrium had been reached, the temperature was raised to 15°C, and further to 25°C and 35°C. At 35°C, the temperature was lowered, through the same fixed temperatures, to +5°C.

The samples were weighed once a week. As a criterion of weight equilibrium, there was adopted the maximum change in the weight of an individual sample, which had to be less than 0.1 % of original weight during the course of a week. Equilibrium was usually attained within three or four weeks. The removal of carbon dioxide from the desiccator air was effected after each weighing.

The basic dry weight of the samples was determined by the usual oven-drying procedure at 105°C. To avoid errors resulting from density variations of the air in the weighing bottles, the samples were weighed in smaller weighing bottles (Ø 25 mm). In addition, the weighing bottles were cooled in a desiccator above silica gel, which had been dried at 105°C. The desiccator was equipped with a small electrical fan ( $v = 0.2 \dots 0.7$  m/s) to effect the cooling and moisture take-up of silica gel (Cf. Photo 11).

## 4 RESULTS

The results are presented in Section 7.4.

EXPERIMENTAL PROCEDURE IN THE PRELIMINARY INVESTIGATION OF THE EFFECT OF GRAVITATION ON DRYING AND THE PRESENTATION OF A SIMPLE ESTIMATION OF  $k_g$

1 SPECIMENS AND THEIR TREATMENT

The specimens were 6 circular plates (diameter 7.4 cm; thickness 1.5 cm) made of standard cement mortar. The cement population was Pa 6500. Plates had been stored continuously in water at 20°C for 3 years, excluding some short-time surface drying tests. On the edges of the plates, two grooves were cut so that they could be hung between two metal pins in a wind tunnel. After brief drying, the plates were covered with Araldit glue (3 g Araldit per plate, cover 24 mg/cm<sup>2</sup>) apart from one main surface. After covering, the plates were stored in the water for 18 days to ensure homogeneous wetting. Immediately prior to the test the glued surfaces were dried in a climate room ( $\varphi = 40\%$ ,  $t = 20^\circ\text{C}$ ,  $v < 0.5$  m/s) for 18½ hours, and the whole plates for 2 hours.

2 TESTING

The drying period at which the gravity test proper was begun was the second falling-rate period. The test plates were put in an open-circuit wind tunnel, in which the air velocity was 5 ... 7 m/s. The wind tunnel was in a climate room ( $\varphi = 40\%$ ,  $t = 20^\circ\text{C}$ ). The plates were hung horizontally between metal pins, so that three of them had the uncovered surface upwards and three of them the uncovered surface downwards (Photo 18).

The plates were weighed once a day at the beginning, and once a week at the end of the experiment, using a METTLER K 7 T balance (accuracy  $\pm 30$  mg). The average weight of the specimen was about 140 g. During the weighing procedure, the plates were about 5 minutes in a climate room at RH 70 % and a temperature of 20°C. The plates were continuously kept in the same position in which they had been in the wind tunnel. The initial moisture content of the plates was  $C_0 = 190$  kg/m<sup>3</sup> and estimated equilibrium moisture content  $C_e = 80$  kg/m<sup>3</sup>. The drying time was 16 weeks.

An additional test was made to test leakage through Araldit-coverings. The moisture flow through them amounted to about 10 % of the total moisture loss.

3 A SIMPLE ESTIMATION OF  $k_g$ 

If two watertight boxes without lids are filled with concrete and cured sealed for some months, and exposed to  $\text{CO}_2$  free drying so that the uncovered surface at one cup faces downwards (Case 1) and the uncovered face of the other cup upwards (Case 2), the moisture fluxes can be written in accordance with Publication [9] as follows

$$J_1 = -k_1 \left( \frac{\partial C}{\partial x} \right)_1 + k_g (C_1 - C_e)$$

$$J_2 = -k_2 \left( \frac{\partial C}{\partial x} \right)_2 - k_g (C_2 - C_e)$$

At the start of the drying, and for the same concrete the following assumptions can be made:

$$k_1 \approx k_2 \quad (\text{same concrete, } C_1 \approx C_2),$$

$$\left( \frac{\partial C}{\partial x} \right)_1 \approx \left( \frac{\partial C}{\partial x} \right)_2 \quad (k_g \text{ is small), or}$$

$$k_1 \left( \frac{\partial C}{\partial x} \right)_1 \approx k_2 \left( \frac{\partial C}{\partial x} \right)_2$$

Consequently, and when the moisture content  $C_1 \approx C_2 \approx$  initial moisture content  $C_0$ :

$$J_1 - J_2 = 2k_g (C_0 - C_e), \quad \text{or} \quad k_g = \frac{\Delta J}{2(C_0 - C_e)},$$

if  $J_1 - J_2$  is denoted by  $\Delta J$ . If  $\Delta J$  is expressed in  $\text{kg/m}^2\text{s}$  and  $C$ -values in  $\text{kg/m}^3$ ,  $k_g$  will be expressed in  $\text{m/s}$ .

## 4 RESULTS

The results are presented in Section 8.3.

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ERRATA

Page	Line	In place of	Read
14	25	$M(h)$	$M(h)_t$
18	19	Finish	Finnish
27	Fig. 4	$\varphi \approx 0.7 \dots 0$	$\varphi \approx 0.7 \dots 0.8$
45	Figure text	exponential equation.	power equation.
48	Figure text	temperature, Curve A	temperature. Curve A
72	Fig. 22	$d = 0.65$	$d = 0.65 \text{ day}^1$
92	7	an	and
93	Fig. 34	$S_\infty (\varphi = 70 \%)$	$S'_\infty (\varphi = 70 \%)$
		$S_\infty (\varphi = 40 \%)$	$S'_\infty (\varphi = 40 \%)$
97	Fig. 36	$K'/K'_0$	$K/K_0$
110	bottom line	Section 8.4	Section 8.5

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