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THE STATE INSTITUTE FOR TECHNICAL RESEARCH, FINLAND

TIEDOTUS. SARJA III — RAKENNUS. 74

NOTES ON THE DRYING OF CONCRETE

S. E. PIHLAJAVAARA

HELSINKI 1963

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FOREWORD

This publication is the first written by the author straight into English. The preliminary linguistic checking and corrections were made by Mrs Rakel Toivola M.A. and the final revision by Mr Fred. A. Fewster.

The author wishes to express his gratitude to all those whose efforts have made this report possible. Thanks are especially due to my assistant, Mr Esko Pihlman. The author is also extremely appreciative of the time-consuming work engaged in by Mr Jorma Nyman who carried out the major portion of the numerous experimental procedures. The figures were drawn by Mrs Irja Tennberg.

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June, 1963

State Institute for Technical Research
Laboratory of Concrete Technology

Physics Section

S.E. Pihlajavaara

CONTENTS

NOTATION

a	thermal diffusivity (m^2/s)
A	area (m^2)
B	parameter
b	parameter
C	moisture content (concentration or density of water vapour in the air, concentration of "free" water and water vapour in cement paste and in concrete) (kg/m^3)
C_o	initial moisture content (at the start of drying) (kg/m^3)
C_e	equilibrium moisture content (at the end of drying) (kg/m^3)
c	cement content (kg)
cp/a	cement paste-aggregate ratio (m^3/m^3)
D	diffusion coefficient, in this paper especially as regards water vapour in moist air (m^2/s)
d	parameter
E	parameter
h	time; also as dimension, hour
H	duration of time
J	$= dm/dh \cdot A$, mass flux ($kg/s \cdot m^2$)
k	moisture conductivity (m^2/s)
K	transfer coefficient in general
l	characteristic thickness, e.g. half-thickness of a plate in Fourier and Biot numbers. (m)
L	characteristic length, e.g. length of the surface of a plate in the direction of air flow in Reynolds and Sherwood numbers. (m)
m	mass, mass (moisture) in motion
M	maturity factor ($0 \cdots 1$)
n	parameter
$0(\cdots)$	order of magnitude
p	porosity
P	potential function in general

Q_c	cement content (kg/m^3 concrete)
S	source or sink
s	thickness of water layer
t	temperature (°C)
t_{db}	air temperature, dry bulb temperature
t_{wb}	wet bulb temperature
t_{ob}	air temperature outside of boundary layer (in free flow)
T	temperature °K
u	$= (C - C_e)/(C_o - C_e)$ relative moisture content in a point of a body
$\bar{u}$	$= (\bar{C} - C_e)/(C_o - C_e)$ relative average moisture content of a body
v	air velocity (m/s)
V	volume (m^3)
w	water content used in making cement paste or concrete (kg)
w/c	water-cement ratio (kg/kg) used in making cement paste or concrete
w_n	non-evaporable water, fixed water (kg)
Δw	decrease of moisture content due to hydration or fixation drying (kg)
β	evaporation coefficient or surface conductivity, when driving force is expressed as water vapour difference of the air
β'	evaporation coefficient or surface conductivity, when driving force is expressed as moisture difference of body ($\beta \cdot \Delta C_{vapour} = \beta' \cdot \Delta C_{body}$)
ν	kinematic viscosity (m^2/s)
γ	parameter
ϱ	density (kg/m^3)
φ	relative humidity of the air

Biot number $Bi = \beta' \cdot 1/k$

Fourier number $Fo = k \cdot h/l^2$

Gukhman number $Gu = (t_{db} - t_{wb})/T_{db}$

Lewis number $Le = a/D$

Reynolds number $Re = v \cdot L/\nu$

Schmidt number $Sc = \nu/D$

Sherwood number $Sh = \beta \cdot L/D$

Subscripts:

carb	carbonation
db	dry bulb
e	equilibrium state
o	initial state
ob	outside of boundary layer
s	surface
wb	wet bulb

1. INTRODUCTION

The drying of concrete, or the diminution of its moisture content or its internal water content in the fluid phase, is one of the basic factors in shrinkage, crack formation and the creep phenomenon, very important factors in concrete technique. Although a great deal of research work has been done to clarify these concrete deformations, too few attempts have been concerned with elucidation of the basic factor, the drying phenomenon of concrete. To generalize the information needed, we could say that knowledge of the moisture content of concrete as a function of space and time is of primary importance, as we should not forget the appreciable effect of the moisture content and moisture field on the properties of concrete in general.

The following Notes are based on a study of publications [1], and upon the author's investigations of the drying phenomena of concrete, made over a period of some two years at the State Institute for Technical Research, Laboratory of Concrete Technology, Physics Section (Finland). As planned, this research work will continue for a number of years before "the final stage" is reached. The Notes should be regarded as a progress report, concerned with some of the fundamental work of this research project; they are thus of a tentative nature.

The author is of opinion that comprehension of what occurs in the drying of concrete, with the consequent phenomena, has suffered from the drying process of concrete not being treated as an independent subject, but nearly always connected as a sub-phenomenon with other topics (for instance, shrinkage) which originate in the drying process.

It should be mentioned that 1) the following report does not relate to the drying phenomenon of the systems of different types of concrete, but is confined to the drying of an individual homogeneous concrete in air, and that 2) evaporation drying and fixation drying (for which definitions are given in the text) are treated in the main as mutually independent processes; in general, this is not the case 3) in addition, the moisture transfer brought about by the presence of thermal differences has not been studied, and 4) the examination is limited to the first drying of concrete, which occurs after a curing period performed under sealed conditions or in water. With the results of previous studies, and those of the author taken into consideration, together with the restrictions mentioned above, accordingly, the report will introduce a tentative model for the drying of ordinary concrete, a capillary porous colloid, at about 20 °C.

Advanced mathematical treatment is deemed to be beyond the principal scope of this paper, since research into the drying process of concrete is in the initial stage which needs the clarification of fundamental definitions and ideas. In addition, no special statistical evaluation has been made of the experimental results, i.e. mean values are used without special attention being paid to deviations and their statistical significance.

The cement used in all the author's tests was ordinary Finnish Portland cement, made in the same factory. For the tests presented in Paragraphs 3.2, 4, 5, 6.63, 6.663, and 7, in which were studied the isotherms, the isobars, and fixation drying (hydration process), the cement (No. 6800, Concrete Lab) was taken from the same sack. For the tests presented in Paragraphs 6.2, 6.5, 6.662, the cement was taken from another cement "population" (No. 6500), as was the case for the tests presented in Paragraphs 6.661, and 8.21 (No. S).

The system of units preferred is that of the metre-kilogram-second, in accordance with international recommendations.

The main "items of equipment" used in the tests were:

1) Climate room (t = 20 °C, φ = 40 %)
2) Climate room (t = 20 °C, φ = 70 %)
3) Climate room (t = 20 °C, φ = 100 %)
4) Mettler balance (max 900 g, acc. ± 30 mg)
5) Balance (max 15 kg, acc. ± 100 mg)
6) Balance (max 20 kg, acc. ± 1 g)

7) Water thermostat box ($85 \cdot 50 \cdot 40\ cm^3$)
8) A number of desiccator bowls
9) Open-circuit wind-tunnel (diameter 30 cm, length 100 cm, v = 5 ··· 6 m/s)
10) Two fans (v = 0 ··· 4 m/s)
11) Mechanical anemometer
12) Electrical anemometer
13) Electrical thermometer
14) Oven (25° ··· 150 °C)
15) Oven (25° ··· 200 °C)
16) Furnace (100° ··· 1000 °C)
17) Thermobalance (100° ··· 1000 °C)
18) Assmann hygrometer
19) Hair hygrometers
20) Bimetallic-hair thermo-hygrograph recorders
21) Vacuum oven (25° ··· 150°C)
22) Loading machine (300 tons)
23) Ultrasonic-material tester (sound velocity)

2. ON THE THEORY OF POROUS SOLID DRYING

Many interesting problems are concerned with the interpenetrative motion of a fluid through a porous solid; the drying phenomenon is one of these. Another very important and well-known problem is the calculation of the flow of heat through matter. In this phenomenon, the heat is the internal energy of matter, but its behaviour can be understood as if it were a "fluid". The same fluid concept also applied for instance to neutron "gas", the motion of which is in phenomenological accordance with the process mentioned above.

Although the word "diffusion" is to some extent rather wide in significance, we here restrict its usage to cases in which the moving fluid particles have a random walk character, and when we cannot talk about the over-all "forces" on an element of the fluid: the diffusion flow is not caused by external forces or by pressure gradients due to external forces, but is simply attributed to concentration gradients. It is worthy of note that the evaporation from a water surface into the air is caused by the concentration gradient, although the concentration gradient can also be described with the aid of the pressure gradient of the water vapour, which is in this case an internal "driving force". The drying phenomenon of a porous solid can also involve internal pressure gradients of different kinds, but all of them can be regarded as internal and random-oriented driving forces, caused primarily by the concentration gradient. If we accept the above, the drying phenomenon of a porous solid is a diffusion process.

For diffusion processes there is consequently a generally known rule, a "law": the fluid spontaneously tends to flow from a place of higher concentration to one of lesser concentration, and the flow is proportional to the gradient of the concentration of the fluid. However, this beautiful principle is only valid for homogeneous matter in general. If the medium is not homogeneous, there may be a flow in the opposite direction; viz. from a low concentration or density to a higher one. This leads to a paradox termed "uphill diffusion"; the moisture transfer can take place from a low moisture content to a larger one. This is in fact true in cases where we have a system of separate but touching bodies with different moisture capacities. In such cases, the moisture content gradient cannot be considered as a "driving force" or a potential gradient for moisture transfer, but it is necessary to choose a mass transfer potential based upon a comparison body or a standard body, in accordance with Luikov's idea of using phenomenological thermodynamics analogically in mass transfer [2] [3]. The contradiction mentioned is thus not insurmountable, and the problem can be solved by choice of an applicable driving force or a potential. In examination of the drying of porous bodies, the moisture transfer mostly occurs in one material, and the water finally escapes into the air. In solving this problem we can normally use the moisture gradient as a potential gradient.

Consequently, if we wish to accept the drying phenomenon of a porous solid as diffusion process, the word needs definition: diffusion is the process by which matter is transferred from one part of the system to another as a result of random motions due to a potential gradient. Nevertheless, it is much simpler to say that the drying is a mass transfer process. If the definition of mass transfer is needed, it could be stated simply: mass transfer is the process which takes some entity of physical mass from one point to another. When we identify the drying as a mass transfer process, it is not necessary to ponder whether the drying is a diffusion process or not. The drying phenomenon of a porous solid, e.g. by means of its internal capillary forces, is not generally a true diffusion process, a term which in physical science is applied to random molecular motion, but is a more or less random macroscopic and molecular process of mass transfer.

Following the lengthy and rather tedious introduction presented above, we finally arrive at a simple definition for drying: drying is a mass transfer processes by which the fluid content, strictly speaking the water content, diminishes in the porous matter. It is not reasonable to impose restrictions upon the "driving force" of drying, which can depend on different kinds of forces (i.e. capillary-, osmotic-, frictional-, and gravitational, etc.). However, the external forces can often be neglected in the drying processes of a porous solid, and the driving force described sufficiently with the aid of the concentration.

Research on transfer phenomena has come to the conclusion that all the phenomena which involve the molecular transfer of heat and mass can be analytically described by the following "law": the flux, which describes the rate of the transfer of an examined entity, is directly proportional to the driving force or potential gradient. If we write this in a general analytical form, we get

$$\vec{J} = - K \operatorname{grad} P \qquad (1)$$

where $\vec{J}$ represents the flux, P the potential, and K the corresponding transfer coefficient. On the basis of this "law", the differential transfer equations are derived for the various diffusion processes, and also for the mass transfer and motion of viscous liquids. It should be noted that the formulation of this "law" can be thought wholly empirical, and intuitive or phenomenological.

The various phenomena associated with transfer processes can be described in two distinct ways: a phenomenological description in which transfer is considered without reference to the details of the mechanism involved; a kinetic description, in turn, comprises these details, and endeavours to take them into account. The kinetic approach to the transfer phenomenon is based mainly upon the molecular theories of matter. Although the phenomenological description has been that most used, the kinetic theory has been very successfully applied, and particularly the kinetic theory of a gaseous state. The latter statement originates in the kinetic theories of liquids and a solid state not being at comparable stages of development. The Knudsen flow (effusion) serves as an example of the kinetic theory of gases, which can for instance be applied to the water vapour transfer in porous bodies.

In addition to formulae of type (1), the conservation laws are needed to build the basic equations for transfer phenomena. For the purpose of mass transfer, the following equation of the conservation of mass is used:

$$\frac{\partial P}{\partial h} + \mathrm{div}\,\vec{J} + S = 0, \qquad (2)$$

where $\partial P/\partial h$ represents the change of the potential with time, div $\vec{J}$ the change of the potential in space, and S is source or sink. As regards concrete, the cement paste can have mutually dependent (coupled) and complicated sink and source terms: the sink is due to the chemical and sorptive fixation of water brought about by the hydration process of cement, and the source is due to the water freed by carbonation. If we put the source term $S = 0$, Equation (2), with Equation (1) inserted, is tranformed into the simple and well-known basic equation:

$$\frac{\partial P}{\partial h} = \mathrm{div}\,(K \text{ grad } P). \qquad (3)$$

Unfortunately, in general the different individual transfer phenomena cannot be treated separately. They are coupled processes: transfer processes are said to be coupled when a process proceeding at a particular point in space gives rise to another transfer process at the same or at a neighbouring point. This means, practically speaking, that the drying is influenced simultaneously by heat, mass, and momentum transfer, since the mass transfer will produce heat sources by phase transformation, and the viscous boundary layer on the surface of the body will be affected by aerodynamical conditions. Consequently, the simultaneous system of Equations of type (3) must be used in analytical treatment of a coupled process. When the intensity of the process is sufficiently low, however, the individual transfer processes can be considered mutually independent, which means that one type of transfer is not affected by the other types. For example, we can easily find isothermal drying processes for a material in the air, which are not affected by air velocity. In those cases, the theoretical treatment of drying is considerably simplified.

In addition to the mutual dependence described above, we must bear in mind that transfer coefficient K is generally dependent on potential P, which means in the drying phenomenon that K depends on the moisture content, or on the moisture concentration of the porous material. To simplify calculations, it is often assumed that the transfer coefficient is a constant, at least in some time-ranges and material zones. A considerably simplified equation

$$\frac{\partial P}{\partial h} = K \operatorname{div} \operatorname{grad} P \equiv K \nabla^2 P , \tag{4}$$

or Equation systems of type (4) can thus be employed, and close accord with experimental values is often attainable.

Without undue emphasis, we quite simply assumed in the previous text, more or less, that the porous medium is homogeneous and isotropic. In such substances, transfer coefficient K can be regarded as scalar, presumably some kind of over-all phenomenological parameter, often even a constant with certain restrictions. Porous material tends to be anisotropic, and generally speaking the transfer coefficient is a tensor, which takes into account the directional features of the flow. The concept of anisotropic porous material will be omitted from this discussion and report, and efforts will be concentrated purely on examination of the media to be considered, or simply assumed to be, at least macroscopically homogeneous and isotropic materials. Although one can accept this simplifying assumption for neutron diffusion in mass concrete, it is probable that it will fit only as a crude approximation in the treatment of water transmission through a relatively thin wall made of coarse-aggregate concrete. However, in engineering, there always exists a sound principle: if a phenomenon is complicated, and its behaviour in details unknown, a simple and individual experiment, even without any attempt at generalization of its results, will solve the problem for practical purposes. Although the advancement of technology has often rested on this principle, it will hardly further the development of science, which in technology means real understanding of the phenomenon, success, and economy.

Transfer coefficient K can be divided into different parameters which take into account some properties of the mass in motion, or those of the porous body itself. For example, one can write:

$$K = \frac{p \cdot K_1}{\nu} , \qquad (5)$$

where ν is the viscosity of the fluid, and p the porosity of the matter in which the fluid transfers. In cases where the viscosity of the fluid varies considerably, and the viscosity and the porosity are unambiguous, this can be of advantage. In addition, the transfer coefficient is sometimes divided in the form of a sum, in which different terms elucidate the share of the macroscopic motion (e.g. capillary flow) and the molecular motion (pure diffusion) etc. However, many processes are sufficiently complicated for the detailed mass transfer coefficient to be incapable of giving any real advantage in application.

Mathematical solutions of the Equation of type (4) with various boundary and initial conditions are found in textbooks on heat transfer and diffusion [4] [5]. But when it is a matter of mass transfer and its subdivision "the drying process", we must also take into account the works of Luikov (= Lykow = Lykov) of the Soviet Union, who has in his books and articles [6] [2] [7] [3], published also in German and English, presented the Russian achievements in the field of heat and mass transfer. In the book by Luikov and Mikhaylov [7], there are treated the simultaneous heat and mass transfer with different kinds of boundary conditions, and with constant and parabolic initial conditions. Krischer's book [29] is also a necessity in a "drying" library.

As regards the boundary conditions of a surface covered with water and drying in the air, the boundary layer theory has given the well-known relation for forced convection conditions

$$Sh = 0.66 \cdot Re^{1/2} \cdot Sc^{1/3} \qquad (6)$$

In this case, thus, we are examining the evaporation of water from a flat plate, and the flow in the boundary layer is assumed to be laminar. In addition, it is also presumed that the Lewis number Le = 1, the basis upon which the similarity between the convections of heat and mass transfer rests. The flux from the surface can accordingly be expressed by means of an equation analogous to the well-known Newtonian equation for heat transfer:

$$J = f(Sh, \ldots) \cdot \Delta P, \tag{7}$$

where ΔP is the driving force, or the difference of potential (e.g. pressure difference of water vapour) at the surface and outside the boundary layer. The coefficient in Equation (7) is expressed as a function of the Sherwood number Sh. The relation between the Sherwood number Sh, the Reynolds number Re and the Schmidt number Sc enables calculation of the rate of evaporation of water from a free water surface, that is, when the surface of the body is very wet. The Soviet school (Nesterenko, as presented by Luikov [8]) has presented a relation for the evaporation of a free water surface adding a new term

$$Sh = B \cdot Re^{n} \cdot Sc^{1/3} \cdot Gu^{0.135} \tag{8}$$

The Gukhman number $Gu = (t_{db} - t_{wb})/T_{db}$. In the number, t_{db} is the dry-bulb temperature of the air, and t_{wb} corresponding wet-bulb temperature, both in degrees centigrade, and T_{db} the dry-bulb temperature of the air in degrees Kelvin. The values of B and n are functions of Re. Similar boundary conditions to those presented above, with some modifications, have also been used for moist porous solids with surfaces which are not very wet.

When the surface of a drying porous solid is rather dry, it is often assumed that the surface layer of the body has reached the state equilibrium of determined by ambient conditions. In practice this means that the drying of the body in the air is independent of the air velocity. On application of this simplifying assumption as a boundary condition in solving Equation (4), it means that the thin surface layer of the body has already at the start of the drying reached the final state of equilibrium, or the moisture content is zero with respect to the equilibrium moisture content in that layer. This simple assumption, carefully applied, is often valid, at least for technical purposes. However, when the moisture conductivity of the body is high and/or the air velocity is low, the assumption can be invalid. In the latter cases, there exist possibilities of finding an equation of mass transfer as regards evaporation from the surfaces of a porous solid. However, basic research is necessary in this connection.

The phenomenological theory of drying briefly presented above has advanced to such a degree that with its aid there exists a rather good possibility of solving a technical problem concerned with drying. Three practical obstacles bar the way, however, and must be taken into account on examination of the drying of certain medium. These are:

1) the usage of the theory (or theories) with its large number of concepts seems to need a specialist or scientist

2) the applicable values of the parameters in the theory are scarce, or even non-existent

3) insufficient is known of the particular features of the drying of a certain matter (e.g. the transfer- and fixation-drying of the two-substance system: cement paste-coarse aggregate), not included in the general theory.

The only way to overcome these difficulties for practical application of the drying theory is by continuation of research work and solution of the problems mentioned in points 2) and 3), followed by presentation of the final results in a "popular way" in the form of tables and nomograms. This entails that the scientist will be necessary only for fundamental research; a handbook will take his place. At the moment, we do not possess this easy handbook; even general textbooks on mass transfer or the drying phenomenon were practically non-existent some ten years ago.

Finally, the author wishes to point out that in some instances there is experimental evidence that the "diffusion type" of differential equation presented in the previous test does not describe the drying of a porous solid [9]. Despite solutions of the "diffusion type" equation having in many cases been proved successful in description of the drying of concrete, it should not be taken for granted that this will always hold good.

3. BASIC DEFINITIONS FOR THE DRYING PHENOMENA OF CONCRETE

3.1. INTRODUCTION

In the author's opinion, the basic definitions presented below, are those necessary for practical application of the drying phenomena of concrete. They are thus also basic definitions for technico-scientific research into the phenomenon. I am aware of the detailed classification of the different types of fluids (water) in porous matter in general, for instance the Rebinder system as presented by Luikov [2] [6], and the method of Powers & Brownyard [10], or that of Copeland & Hayes [11] concerning the determination of evaporable water in hardened portland cement paste, not adopted here, as regards the former because the classification is too detailed for the present purpose, and the latter in view of its difficulties in practical application.

In this connection, mention is due of the basic investigations of Powers and his co-workers in general, and especially his series of articles in collaboration with Brownyard [10], which must be regarded as the most fundamental work in concrete physics.

3.2. DEFINITIONS OF THE DRYING PROCESS OF CONCRETE

By the drying of concrete is generally meant the diminution of the "free" water content in a liquid or gaseous phase in concrete. This "free" water content per unit volume, or unit weight, of the "dry" body is termed moisture content (moisture concentration or moisture density) or, in brief, moisture.

The drying phenomenon of concrete can be divided into two main categories:

I **Transfer-drying:** Water transfers as a liquid and/or vapour from the inner parts of a body to the boundary surfaces of a body, from which it escapes in the form of liquid and/or vapour into the ambient space.

II **Fixation-drying:** The drying is here brought about by the fixation of water. In concrete, this is due to the hydration of the cement, with the result that part of the "free" water will be bound chemically, and by sorption or, generally speaking, by "strong" chemical and physical forces.

In transfer-drying, after the water has moved to the boundary surface, water evaporates into the ambient space, usually into the air. It is thus practical to speak of evaporation-drying and not of transfer-drying. When this is taken into account, the drying phenomenon occurs in two main ways:

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

II **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.

The value of the moisture content of porous media, concrete included, depends essentially upon the specified method of measurement, by the aid of which the "dry" basic state of the medium concerned has been arrived at. The method normally applied for determination of the moisture content of porous media is that of measuring by weighing the amount of the water which has escaped into the air under normal pressure conditions at a temperature of 105 °C, after a state of equilibrium has been reached. This procedure is carried out in an oven, through which there circulates the ambient air of an ordinary room, more or less, due to convection. The variations in the vapour pressure of the ambient air at 20 °C and normal total pressure (about 1 atmosphere) exercise an appreciable effect upon the state of equilibrium of the cement paste dried in the oven at 105 °C, as presented in Table 1 and Fig. 1. From a scientific

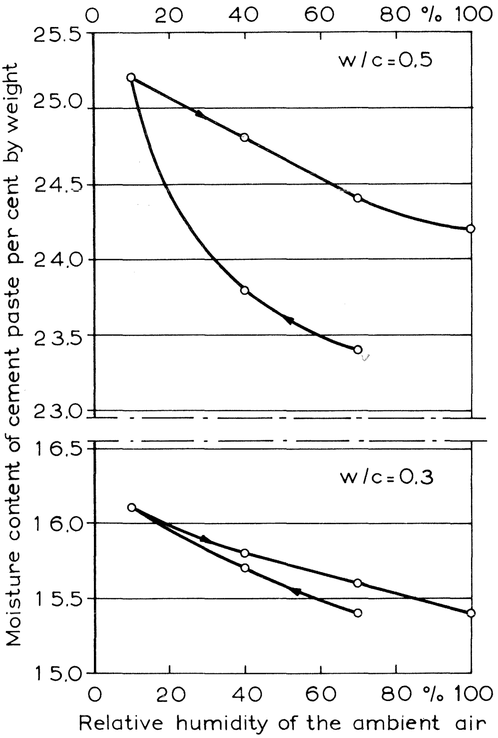

Fig. 1. Hysteresis of the sorption isotherms of cement paste, determined by drying in an oven at 105 °C, with the relative humidity of the ambient room air circulating (free convection) through the oven varied from 70 per cent to 10 per cent and in reverse from 10 per cent to 100 per cent. (Cf. Table 1).

standpoint, accordingly, the method outlined with unspecified vapour pressure is incorrect. As a result, the properties of the ambient air must be standardized, say at temperature 20 °C and relative humidity

40 %. With this restriction imposed, the variations in the properties of the ambient air in the room will introduce relatively minor errors if omitted.

Table 1.

Equilibrium moisture content of the cement paste specimens (pillow-shaped, weight about 40 g), determined by drying in an oven at 105 °C, with the relative humidity of the ambient air circulating (free convection) through the oven being varied from 70 % to 10 %, and in reverse from 10 % to 100 % (about 98 %). The specimens cast in plastic bags had been cured before testing by being hermetically sealed for six months in the mould bags mentioned, and wrapped in plastic sheets. The familiar hysteresis in sorption isoterms is also clearly discernible in this test: the specimens did not reach the same equilibrium at the same elevated water vapour pressure if they had meanwhile been in the lower water vapour pressure (See Fig. 1).

Cement paste		Properties of the ambient room air					
		% °C	% °C	% °C	% °C	% °C	% °C
		70 20	40 21	10 22	40 22	70 20	100 20
		Moisture content per cent by weight					
w/c 0, 3	1	15, 6	15, 9	16, 3	16, 0	15, 8	15, 7
	2	15, 3	15, 6	16, 1	15, 7	15, 5	15, 4
	3	15, 2	15, 5	16, 0	15, 7	15, 5	15, 3
	4	15, 3	15, 6	16, 1	15, 8	15, 5	15, 3
Average		15, 4	15, 7	16, 1	15, 8	15, 6	15, 4
w/c 0, 5	1	23, 1	23, 4	25, 0	24, 6	24, 3	24, 0
	2	23, 4	23, 9	25, 2	24, 8	24, 5	24, 3
	3	23, 6	24, 0	25, 3	25, 0	24, 6	24, 4
	4	23, 3	23, 8	25, 1	24, 6	24, 3	24, 1
Average		23, 4	23, 8	25, 2	24, 8	24, 4	24, 2

The dried body is to be considered absolutely dry or dry when treated by the method described. The moisture content is usually expressed as the ratio of the amount of water which has escaped to the volume (or weight) of a specimen dried in this way. The volume of the dried specimen is in practice usually regarded as being equal to the volume of the wet specimen. The method described above is used in concrete technique principally because of its convenience and purposeful nature.

By the "moisture of concrete", therefore, is meant the amount of water which escapes in the usual oven drying process at 105 °C, when the fixation of water has not been significant during the time of determination. In practice, the above mentioned restriction implies that the sample used for the determination has to be fine-grained to such an extent that the drying will occur rapidly, or that the amount of water bound during the determination can by some means be taken into consideration. In this connection, it should be mentioned that the isothermal method for determination of the moisture content proposed and used by Copeland & Hayes [11] does not need elevated temperature, which can lead to a higher water fixation rate.

The influence of the water content of the aggregate on the water content in concrete, and on its changes, is supposed on the whole to be of relatively minor importance. However, this assumption can be invalid in evaluation of the drying of concrete on the basis of the drying of cement paste. The water absorption of the aggregate of concrete may be relatively small, less than some tenths of per cent by weight of granite aggregate, but the effect may be appreciable, in view of the large aggregate content of concrete. In spite of this, we accept the assumption for the present and as a consequence, cement paste is the primary subject of examination. The water transfer in the system of cement paste-aggregate needs thorough study in future investigations.

An additional remark is necessary on the effect of the carbonation of cement paste: the carbonation of calcium hydroxide induced by the diffusion of carbon dioxide from the air will free water. With respect to relatively large concrete structures, the slow effect of carbonation or "carbonation wetting" on the drying process is fairly small. Nevertheless, the effect on the weight (mass) changes of the small test specimens stored in air is significant (cf. Fig. 2).

3.3. DEFINITIONS OF THE WATER CONTENT OF CONCRETE

Evaporable water, non-fixed water, or free water, is 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.

The state of equilibrium reached by concrete at 105 °C roughly corresponds to the state of equilibrium of concrete at 20 °C when the partial pressure of water vapour is about 10^{-3} mm Hg [10], or the relative humidity of the air about 10^{-4}, or 0.01 per cent.

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 cement gel) by 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. The amount of fixed water is usually expressed as a ratio of the stated weight (mass) loss of a sample between the oven and furnace to the weight of cement, corrected by subtraction of the corresponding weight loss ratio of the cement and the possible loss of carbon dioxide [19]).

Many investigators use a furnace temperature of 1000 °C for determination of the non-evaporable water content. However, the water combined in the hydrated cement compounds, other than $Ca(OH)_2$, is mostly given up at 350 °C, a small additional amount from that source being released between 350 °C and 550 °C; the latter is the temperature at which the dissociation of $Ca(OH)_2$ is complete [12] [13]. It is thus believed that after the ignition at 550 °C all fixed water has been released.

Moisture, moisture content, or moisture concentration, is the amount of evaporable water, generally expressed as its ratio to the volume or weight of concrete dried at 105 °C

(kg/m^3, kg/kg), the latter often being expressed also as a percentage.

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

3.4. THE DEFINITIONS OF POINT OF EQUILIBRIUM AND STATE OF EQUILIBRIUM

If we plot the weight or mass changes of matter against the time, we define the momentary state of equilibrium of matter as a point of equilibrium. The corresponding curve is accordingly horizontal at the point of equilibrium, or the tangent has zero value. If the curve of weight change after a certain time-point is continuously horizontal, we define the corresponding steady state as the state of equilibrium.

The point of equilibrium is thus a momentary dynamic state of equilibrium, and only when the steady state is continuous has the state of equilibrium proper been reached.

For example, when cement paste (concrete) dries in the air, the point of equilibrium can be reached relatively quickly. At the point of equilibrium, the exchange of mass between the body and air, or the changes caused by evaporation and carbonation, are in equilibrium. After that, the weight of the body changes rather slowly, mainly by reason of the slow carbonation. However, it is often possible quite early to fix an assumed asymptote to serve as a state of equilibrium. If the gap between the point and the state of equilibrium is small, there might be ample justification in practical application for assumption that the point and the state coincide.

4. ON THE GENERAL FEATURES OF VARIATION IN WEIGHT (MASS) OF CEMENT PASTE OR CONCRETE DURING THE DRYING

Experimental examination of the drying process is usually effected by means of weighing. There have been numerous investigations of the drying of concrete, in which the assumption are made 1) that the changes in weight are due only to changes in the content of the original moisture in the concrete at the start of drying and 2) that the change in the original moisture in concrete is due only to evaporation. The question arises whether these assumptions are valid or not.

In many cases, fixation drying during evaporation drying can be fairly small especially when the exposed concrete is relatively old and thin, and when the water-cement ratio is small. According to Powers & Copeland [10], hydration virtually ceases when the relative pressure of water vapour in cement paste drops below 0.85. The corresponding limit adopted by Lea & Desch [13] is about 0.80. It is also common knowledge that the smaller is the water-cement ratio in sealed specimens, the smaller is the rate of hydration and the amount of the ultimate fixed water [10] [14] [15]. The lowest water-cement ratio which will permit the maximum ultimate degree of hydration of cement under sealed conditions is of the order 0.45 [10]. If, however the body being dried is massive and/or relatively young, the rate of drying small and the water-cement ratio rather high (as in many large constructions), fixation drying is considerable and cannot be neglected.

There has recently been much interest evinced in the carbonation - as well as in the drying - of hardened portland cement pastes, mortars, and concretes, particularly as regards shrinkage. As Verbeck [16] put it "... an understanding of carbonation may aid the research worker in separating the two causes of shrinkage for more effective study". - Carbonation is mainly caused by the carbon dioxide take-up of the calcium hydroxide liberated during the hydration of the calcium silicates in cement. The amount of the free calcium hydroxide content is approximately 10 per cent after 1 day (24 hours) of the hydration of cement, and 20 per cent after some years of hydration, expressed as the weight of CaO to the ignition weight, according to the investigations of Pressler & Brunauer & Kantro & Weise [17].

Studies have shown that the complete carbonation of Portland cement is possible even at a low concentration (low partial pressure) of carbon dioxide in the normal outdoor atmosphere, about 0.03 per cent, or 0.0003 atmos. pressure [16]. However, it is generally believed, on the basis of various investigations, that the carbonation process in air is very slow, and restricted only in the surface layers of concrete constructions with a maximum thickness of some centimetres after many years of penetration. Therefore, with concrete or cement paste of larger dimensions, the main body of the material remains unaffected [13]. According to Powers [18], it seems reasonable to assume that carbonation process will be limited if the water vapour pressure in cement paste is lowered to 45 per cent of the relative humidity of the air. (However, Fig. 2 shows that carbonation is strong even at 40 per cent). Kroone & Blakey [19] point out that carbon dioxide may be taken up to a limited extent by dry cement materials, and that in the presence of evaporable water the carbon dioxide take-up increases.

In this connection, it is perhaps interesting to estimate the diffusion coefficient (D) of carbonation in concrete. The following approximate formula is used:

$$l^2 = 4 \cdot D \cdot h, \qquad (1)$$

where l is the mean linear displacement of a particle diffusing in a given direction during time h. This may be assumed as approximately being equal to the average penetration depth of the diffusing substance, i.e. to the magnitude often determined with respect to the penetration of carbonation in concrete. In his experiments author obtained a rough estimation of the values: $l = 0.0025$ m, $h = 25$ weeks. This yields $D = 1 \cdot 10^{-13}$ m^2/s. In this laboratory, Aschan [20] has obtained from his thermodifferential gravigrams a value $l = 0.06$ m for a forty-year-old concrete. This gives $D = 5 \cdot 10^{-13}$ m^2/s. The conclusion is that

$$D_{carb} = 0\ (10^{-13}\ m^2/s)$$

The carbonation of 1 mole calcium hydroxide (74 g) releases 1 mole water (18 g) per mole of carbon dioxide (44 g) subjected to reaction. First of all, this means that the water release is 18/74 = 0.24, or 24 per cent of the calcium hydroxide content fully carbonated, and, secondly that the weight will increase (44-18)/74 = 0.35 or 35 per cent of the calcium hydroxide content after the water released has escaped. If we have a cement paste specimen with the fixed water-cement ratio of 0.20:1.0 (the cement paste is dry), and the calcium hydroxide content 0.20 of cement weight, the corresponding water release is $1.0 \cdot 0.2 \cdot 0.24 = 0.048$ or 4.8 per cent of the weight of the cement, and $(1.0/1.20) \cdot 0.2 \cdot 0.24 = 0.040$ or 4.0 per cent of the weight of the cement paste; the corresponding increase in weight is $1.0 \cdot 0.2 \cdot 0.35 = 0.070$, or 7.0 per cent of the weight of the cement and $(1.0/1.20) \cdot 0.2 \cdot 0.35 = 0.058$ or 5.8 per cent of the weight of the cement paste. If the original water-cement ratio of the paste mentioned was 0.40, the corresponding water release is $(1.0/1.40) \cdot 0.2 \cdot 0.24 = 0.034$ or 3.4 per cent of the weight of the original cement paste, and the corresponding increase in weight $(1.0/1.40) \cdot 0.2 \cdot 0.35 = 0.050$ or 5.0 per cent of the weight of the original cement paste.

Let us examine Fig. 2, which shows the changes in the weight of small cement paste specimens when stored 1) in the air of a climate room, and 2) in the air of a desiccator (above H_2SO_4-water solution). In the former case, the specimens were subjected to carbon dioxide exposure, and in the latter practically not at all. In both cases, the conditions of the ambient air were practically identical. H-values are the prehardening times under sealed (hermetic) conditions. The effect of the carbon dioxide exposure was in fact

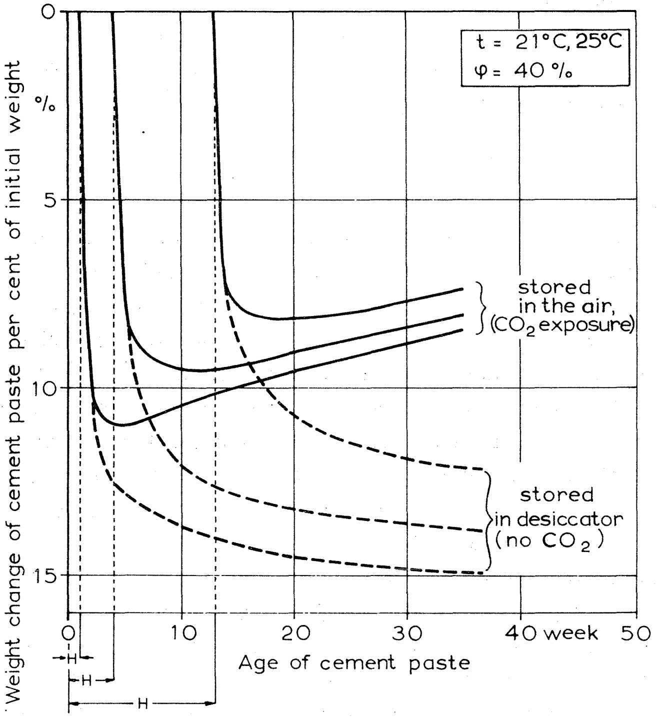

Fig. 2. Change in weight of small cement paste specimens (pillow-shaped, 40 g, water-cement ratio 0.4) under different storage conditions. The specimens were cast in small plastic bags (6 cm by 9 cm) and cured, hermetically sealed in the bags, H weeks (= 1, 4 or 13 weeks) before drying. Some of the specimens were stored in a climate room at an air temperature of 21 °C, relative humidity 40 per cent and velocity below 0.5 m/s, and some of the specimens in a desiccator above a H_2SO_4-solution at 25 °C, RH 40 %, and under free convection conditions.

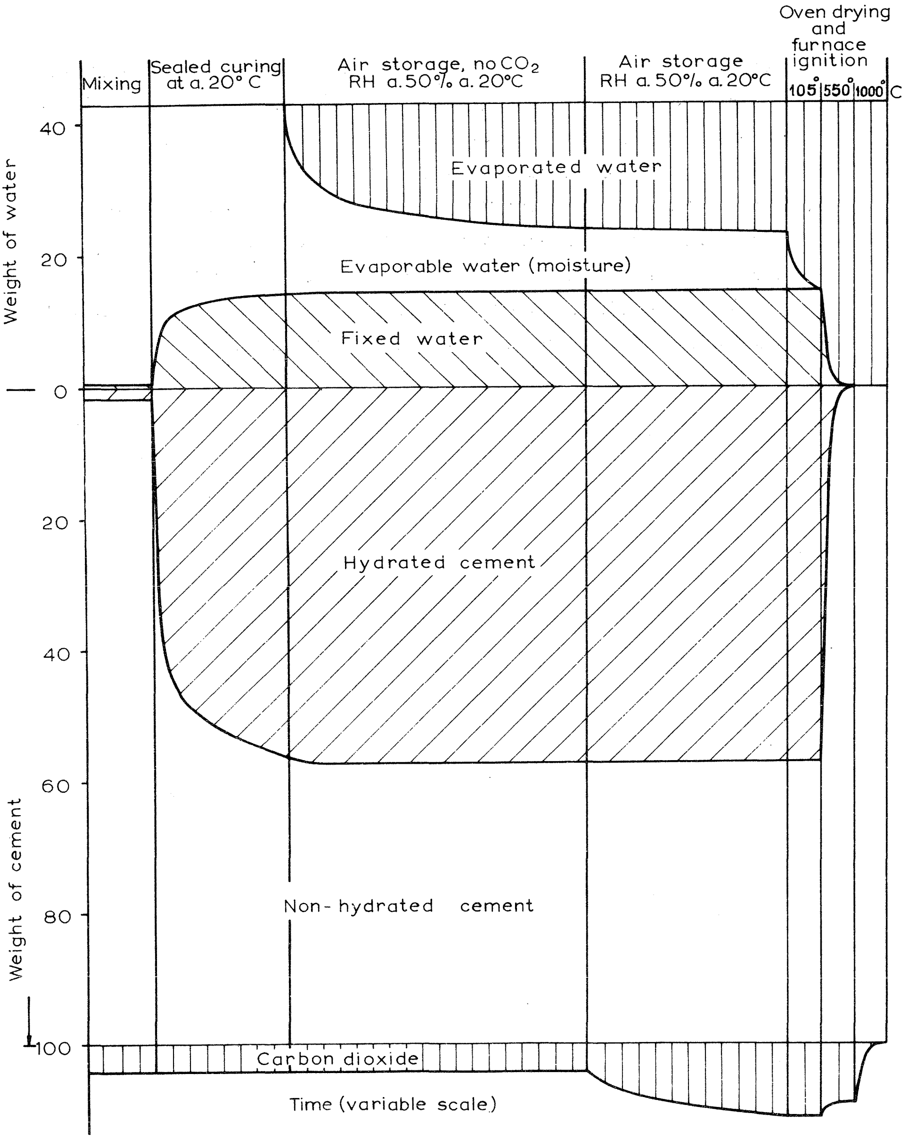

Fig. 3. Schematic figure indicating the mutual relations of the substances in cement paste (water-cement ratio about 0.40) under different conditions. Vertical axis: weight (mass). Horizontal axis: time. The weight of cement ignited at 1000 °C has been taken to be 100.

very significant. In accordance with this, the carbonation process in normal air is slow, and consequently restricted to occurrence only in the thin surface layer of the concrete construction. The desiccator curves thus give a better idea of the drying and of the state of moisture equilibrium of ordinary concrete constructions. Fig. 3 is schematic, and drawn in accordance with some experiments to give a general idea of the changes in cement paste due to fixation drying (hydration), evaporation drying, and the carbonation process, including oven and furnace processes at different temperatures.

5. EFFECT OF TEMPERATURE AND RELATIVE HUMIDITY ON THE WATER OR MASS CONTENT OF CEMENT PASTE. ISOBARS AND ISOTHERMS

5.1. RELATION OF WATER CONTENT (MASS CONTENT) - TEMPERATURE. ISOBARS

A presentation has been made above, in connection with definition of the drying and the water content of concrete, that temperature 105 °C divides the water content (total water content) into two categories: evaporable water and fixed water. The choice of this temperature is based on 1) the sudden vaporization of free water occurring at 100 °C and 1 atmos. pressure, and that 2) the water still left in material after drying at 100 °C being so strongly fixed that it cannot take part in any process of practical significance in which water is needed. An excess of 5 °C (10 °C is also used on occasion) have been adopted for practical reasons, to ensure that 100 °C has been exceeded.

When the drying of a porous solid is carried out at different temperature it is seldom observable that any abrupt change occurs in the relationship between the water content and the temperature, since the water in the porous solid is to some extent fixed by continuously distributed forces. A number of investigations have shown this to be particularly true for concrete [10], a fine particle material (colloid). The author has also made tests to elucidate the relationship of the water content and the temperature in an oven (20 ··· 200 °C), in a furnace (200 ··· 1000 °C), and in a thermobalance (100 ··· 900 °C), to obtain thermogravigrams (isobars). The results are presented in Figs. 4 and 5. The abrupt change after 600 °C is brought about by release of carbon dioxide. This feature is also very appreciable in the curve of cement proper, and by reason of the material (e.g. fine grinded calcium carbonate rock) which may be added to Portland cement clinker in amounts of up to 15 per cent by weight in accordance with Finnish Cement Specifications.

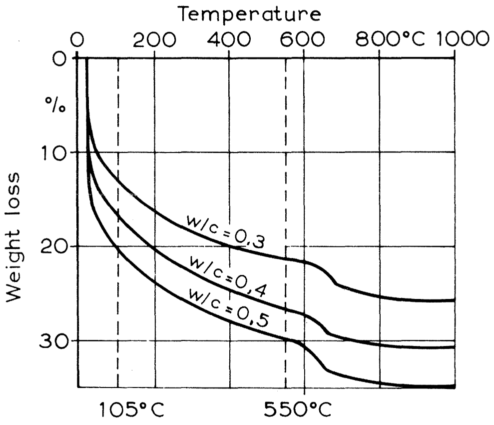

Fig. 4. The weight loss of cement paste in the temperature range 20 ··· 1000 °C per cent of initial weight. The cement paste was cured 170 days under sealed conditions at 20 °C.

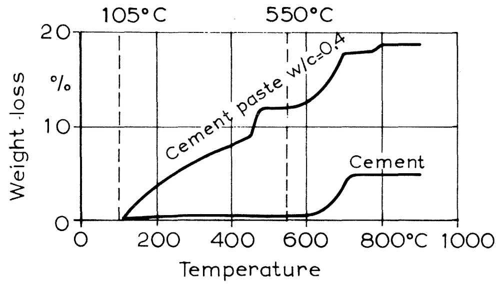

Fig. 5. Results of the thermobalance investigation of cement paste (cured, sealed 100 days) and of the cement used in the making of the cement paste. Weight loss per cent of the weight at 900 °C. Temperature range 105 ··· 900 °C.

5.2. RELATION OF MOISTURE CONTENT - RELATIVE HUMIDITY. ISOTHERMS

Concrete, like any other porous material, has a natural tendency to lose or gain moisture with changes in the moisture concentration or relative humidity of the ambient space.

When exposed to drying, so that the pressure of water vapour is greater in the material than in the ambient air, the material approaches an air-dry condition, which is a state of balance or equilibrium with the water vapour pressure, or with the relative humidity of the ambient air. If the moisture content in the material at the state of equilibrium is substantial, and the material is capable of changing its moisture content by sorption (= adsorption, absorption, capillary condensation) or desorption in the air, the material is called hygroscopic. If we plot the equilibrium moisture content against the relative humidity (or against the relative water vapour pressure, which is the same) of the air at a certain temperature, we obtain a curve known as a sorption isotherm. The moisture content of organic materials can be very sensitive to changes in temperature, i.e. sorption isotherms obtained at different temperatures significantly differ from each other. On the other hand, as regards inorganic materials, if the relative humidity is constant, then the equilibrium moisture content is within certain ranges of temperature practically independent of temperature [21]. If hygroscopic materials, including concrete, are exposed to cycles of decreasing and increasing relative humidities, the sorption curves show that the amount of water held in equilibrium at any given relative humidity may vary substantially, dependent upon whether the material has been losing moisture to ambient space (desorption), or has been taking up moisture from ambient space (sorption). At a certain relative humidity, the equilibrium moisture content acquired during desorption is greater than that obtained during sorption. This is termed a sorption hysteresis.

The first extensive study of the sorption isotherms of cement paste was made by Powers and Brownyard [10]. However, Jesser had presented the first sorption isotherms for cement paste some twenty years earlier [10]. From the data of Powers &

Brownyard [10], Menzel [22] has drawn up the moisture sorption isotherms (i.e. evaporable water sorption isotherms), which are of interest with respect to the drying process. It should be noted that the method for determination of the moisture content (evaporable water content) was not the same as that adopted in the present paper (Chapter 3.3).

Surprisingly little information during the years has been presented on the sorption isotherms of hardened cement paste and concrete. If one wishes to forecast the moisture content of a drying material, it is necessary to know the equilibrium moisture content, i.e. the sorption isotherms. Also, in estimation of the thermal conductivity of a porous material, a knowledge of sorption isotherms is of importance, since the quantity depends on the moisture content. The equilibrium moisture content is needed on a number of other occasions.

Menzel [22] has studied the factors which exert an influence on the equilibrium moisture content of cement paste and concrete. His findings show clearly that the equilibrium moisture content under stated conditions of the ambient air depends to a large extent on the history of the paste or concrete. The sorption properties of cement paste and concrete are dependent, not only upon their original composition but on the curing conditions and their variations. It seems, at the present stage, that reliable prediction of the equilibrium moisture content of concrete is difficult. Consequently, computational forecasting of the drying process of concrete will also be difficult.

By means of tests, a typical one of which was presented in. Fig. 2, there was determined the equilibrium moisture content of cement paste specimens in two relative humidities 40 per cent and 70 per cent. Additional variables were: climate-room drying (carbon dioxide exposure), desiccator-drying above H_2SO_4 - water solution (no carbon dioxide exposure), water-cement ratios 0.3, 0.4, 0.5 (not corrected for bleeding, which was appreciable in w/c = 0.5), and pre-curing times 7, 28, 90 days under sealed conditions. The cement pastes (mixed for 3 minutes with a small efficient electrical mixer) were poured into small plastic bags (6 cm by 9 cm), which were sealed with strong adhesive tape immediately after the pouring. Additionally,

Photo 1. Some cement paste specimens for determination of equilibrium moisture content (sorption isotherms). Water cement ratios 0.3, 0.4, 0.5 are shown. The specimens were poured into plastic bags 6 cm by 9 cm.

the bags were wrapped in plastic sheets to prevent evaporation during the pre-curing times. The average net weight of the pillow-shaped specimens was about 40 g (Photographs 1 and 2). The number of the specimens was 135. The drying time to achieve sufficient equilibrium was 40 weeks. The results (sorption isotherms) are presented in Figs. 6 and 7. The equilibrium moisture content is higher in the pastes stored in the desiccators than in the corresponding pastes kept in climate rooms. This may be in part a result of the higher degree of hydration, since there are peaks in relative humidity (nearly 100 per cent) at 7, 29 and 91 days, when the series were put in the desiccators. Comparison of the results presented in Figs. 6 and 7 with similar curves obtained by Powers & Brownyard, as presented by Menzel [22], and

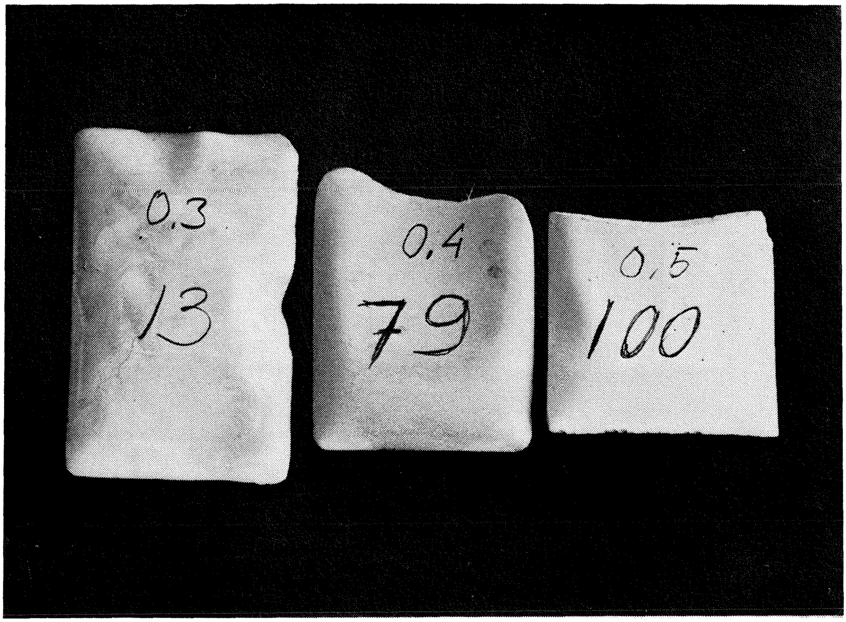

Photo 2. Some average cement paste specimens used in determination of equilibrium moisture content (sorption isotherms). (Cf. Photo 1).

by Johansson & Person [21], demonstrates that the increase in equilibrium moisture content with relative humidity is much greater here than in former instances.

Figs. 6 and 7 also show, if extrapolated, the order of magnitude of the moisture content at which hydration of the hardened cement paste studied virtually ceases: with respect to hydration (fixation drying) we established in Chapter 4 that the critical relative humidity in pastes and concretes is approximately 80 per cent. This value thus corresponds to the critical point as regards moisture content of the paste and of the concrete constructions made with the pastes subjected to examination.

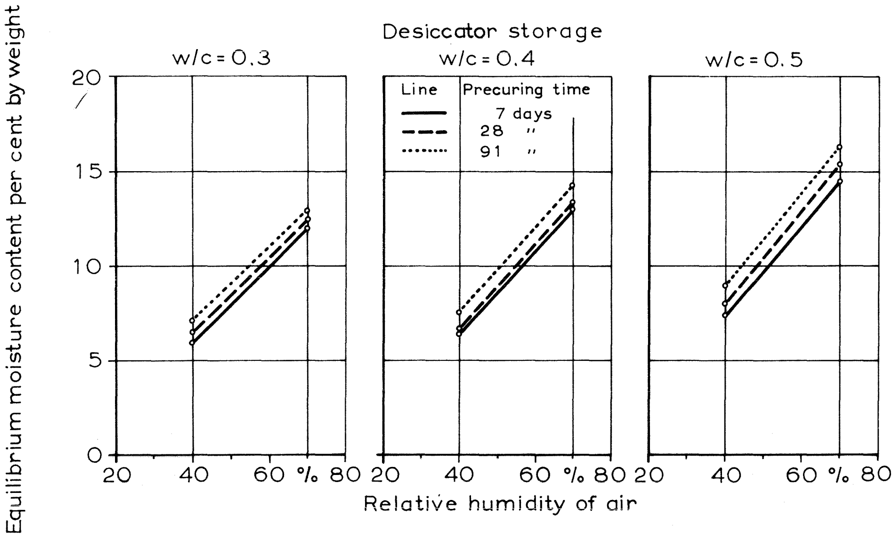

Fig. 6. Equilibrium moisture content (sorption isotherms) of cement paste (obtained at an age of 40 weeks) expressed as a percentage of dry weight (105 °C). Desiccator storage (no CO_2 exposure). Pre-curing temperature 21 °C, storage temperature 25 °C. (Cf. Fig. 7).

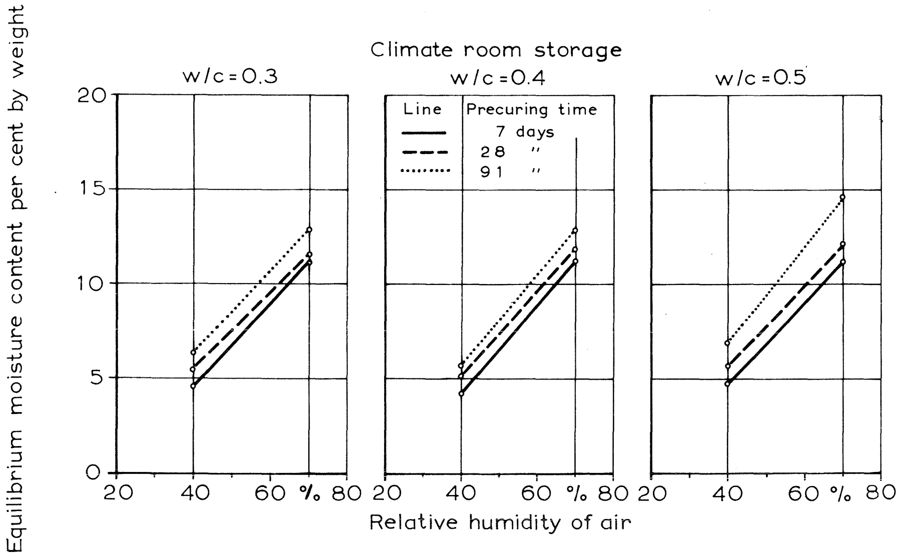

Fig. 7. Equilibrium moisture content (sorption isotherms) of cement paste (obtained at an age of 40 weeks) expressed as a percentage of dry weight (105 °C). Climate room storage. Pre-curing temperature 21 °C, storage temperature 21 °C. The results given in Figs. 6 and 7 were obtained from test specimens taken from the same batches.

6. EVAPORATION DRYING

6.1. DRYING RATE PERIODS OF POROUS SOLIDS

The pioneer paper on drying rate periods is the series "Drying of Solids" by Sherwood [23], presented in 1928 ··· 1930. The paper on "The Drying of Porous Solids: Diffusion Calculations" by Newman [24] published in 1931, falls in a similar category. The system of drying rate periods given in these papers has been in general use, since 1930 [9] [55].

The evaporation drying of practically all moist materials under conditions of constant air temperature, humidity, and velocity, can be divided into three distinct periods. By evaporation drying, there is understood the drying of porous solids by the evaporation of the liquid (water) from the surface of the solids into the air.

1. The constant-rate period, during which the surface remains completely wet, and with the rate of evaporation the same as that from a liquid surface of constant area. The rate of drying is thus independent of moisture content.

2. The first falling-rate period, during which there is a falling off from the wetted surface, the rate being directly proportional to the fraction of the surface which is wet. The rate of drying is an approximately linear function of moisture content.

3. The second falling-rate period, during which the liquid evaporates from a relatively dry surface. The evaporation rate depends on liquid transfer from the interior of the solid, and the liquid transfer from the surface into the air.

The two points between rate periods 1 - 2 and 2 - 3 are termed critical points (the first critical point and the second critical point). At the end of the second falling-rate period, the liquid content (moisture content) will reach equilibrium, termed the state of equilibrium of the material under the particular drying conditions employed.

6.2. THE DRYING RATE PERIODS OF CONCRETE

In a preliminary study of the rate periods of concrete, the drying of small circular plates (diameter 7.4 cm, thickness 1.5 cm) made of concrete mortar (cement/sand ratio 1:3 and water/cement ratio 0.56) were examined by eye, and by weighing, under different conditions of the ambient air: temperature 22 °C, relative humidity 40 per cent, 70 per cent, and velocity about 0.1, 1, 2, 4 m/s in the direction of the horizontal plate surface. The surfaces were smooth and horizontal. Two types of surface were examined: a surface free at pouring, and a ground surface. Prior to testing, the plates were cured in water at 20 °C for four and a half months. Immediately before the tests, the specimens were taken from water and dripped for 10 seconds. At the start of testing, the concrete surface was shining wet and the thickness of the water cover was approximately 0.034 mm, according to tests made with blotting-paper. The test results are presented in Tables 2 and 3, and Fig. 8. Both surface types gave similar results.

The test results obtained, supported by some other findings from our laboratory investigations (cf. Chapter 6.5), lead to the following tentative conclusion concerning the drying rate periods of ordinary concrete taken from water, provided that the surface is smooth and horizontal. It is also assumed that the water and the concrete are not far from thermal equilibrium with the ambient air.

0. The equalizing period, during which the surface is completely shining wet, and during which the concrete and especially its wet surface reaches an equilibrium temperature determined mainly by ambient air conditions. During this period the evaporation is similar to that in the next period, but the rate varies by reason of the change in temperature.

Table 2.

Results of concrete surface drying experiments. Relative humidity of the air 40 %. The test serves only to give a general idea of the rate periods of drying. The values presented in the table are accordingly only for obtaining the order of magnitude.

Air velocity m/s	a. 0.1	1	2	4
Air humidity %	40	37	40	40
Air temperature	21	21	23	22
Period of time in minutes from the start of drying to the time, at which				
a) loose water has been evaporated	5	1.5	1.5	2
b) first "dry" spot observed	14	3	2	1.5
c) half of surface "dry"	16	4	2	2
d) whole surface "dry"	36	5	4	3
Water evaporated 10^{-2} kg/m^2				
e) from start of drying to "dry" surface	5	3	2	3
f) during 2 hours; immediately after the "dry" surface had been attained	5	11	12	11
Avergage drying rate 10^{-6} kg/m^2				
g) from start of drying to "dry" surface	16	79	70	180
h) during 2 hours; immediately after the "dry" surface had been attained	7	15	17	15

1. The constant-rate period, during which the surface is completely shining wet. During this period, it can be assumed that water evaporates in the same way as from the free water surface (or from the free surface of water solution). The drying rate is influenced by air velocity. The drying process is isothermal. It is probable that the drying process exerts no influence on the properties of drying concrete.

Table 3.

Results of concrete surface drying experiments. Relative humidity of the air 70 %. The test serves only to give a general idea of the rate periods of drying. The values presented in the table are accordingly only for obtaining the order of magnitude.

Air velocity m/s	a. 0.1	1	2	4
Air humidity %	68	66	65	68
Air temperature	21	21	21	21
Period of time in minutes from the start of drying to the time at which				
a) loose water has been evaporated	6	3	2	2
b) first "dry" spot observed	30	5	3	3
c) half of surface "dry"	45	7	5	5
d) whole surface "dry"	93	12	7	6
Water evaporated (10^{-2} kg/m^2):				
e) from start of drying to "dry" surface	6	3	2	3
f) during 2 hours; immediately after the "dry" surface had been attained	5	7	8	7
Average drying rate 10^{-6} kg/m^2 · s				
g) from start of drying to "dry" surface	9	41	50	90
h) during 2 hours; immediately after the "dry" surface had been attained	7	10	12	10

2. The first falling-rate period, during which the surface is partially wet. At the start of the period, the surface is only partially shining wet. "Dry" spots appear. At the end of the period, the "wet" spots disappear and the surface seems to be "dry". The intensity of evaporation is less than that from the free water surface. The drying rate is influenced by air velocity. The drying process is not isothermal. The influence

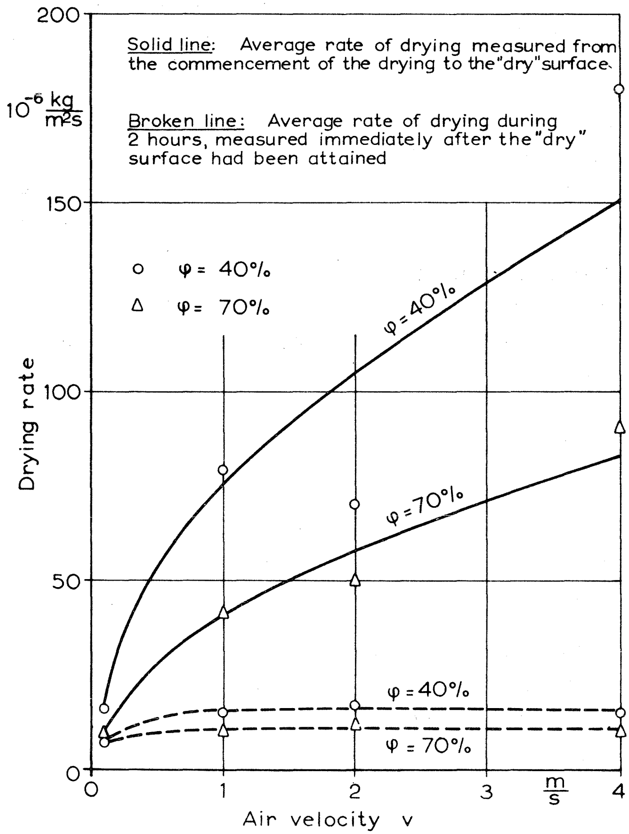

Fig. 8. Drying rate of a concrete surface at an early stage of drying, as a function of velocity v and relative humidity φ of the air. Air temperature, 22 ± 1 °C. Cf. Tables 2, 3.

of the process on the properties of concrete is probably small, although a certain amount of water will be transferred from the layer near the surface to the surface.

3. The second falling-rate period, during which the surface seems to be "dry", and water evaporates from the surface as fast as it can reach the surface from the interior of the concrete. The duration of this period is relatively long, and depends mainly on the dimensions and the moisture conductivity properties of concrete. As regards ordinary concretes, the moisture conductivity and thus the evaporation rate is so small that air velocity, under conditions of forced convection, has no significant effect upon the rate. This means that the moisture content in the thin surface layer of concrete does not differ significantly from the equilibrium moisture content. Consequently, the slow drying process can be assumed to be isothermal, the temperature of concrete being the same as that of the flowing air. The effect of the process is significant on the properties of concrete.

The drying periods of the concrete can be divided into two periods simply, adding the three first periods (0, 1, 2) together. This may be purposeful, because the three periods are short and they depend on air velocity. In addition, the concrete surfaces are often, in practice, so rough that the three periods are probably not separable. In accordance with this we obtain for concrete (stored in water) two drying periods.

I The first drying period, the duration of which is relatively short and depends on air velocity; surface is more or less wet and moist. The drying process is not isothermal, and its influence on concrete properties probably small.

II The second drying period, the duration of which is relatively long and depends on the properties and dimensions of concrete but not under forced convection conditions on air velocity; surface seems to be dry. The drying process can be assumed to be isothermal, the temperature of concrete being the same as that of the flowing air. The effect of the process is significant on the concrete properties.

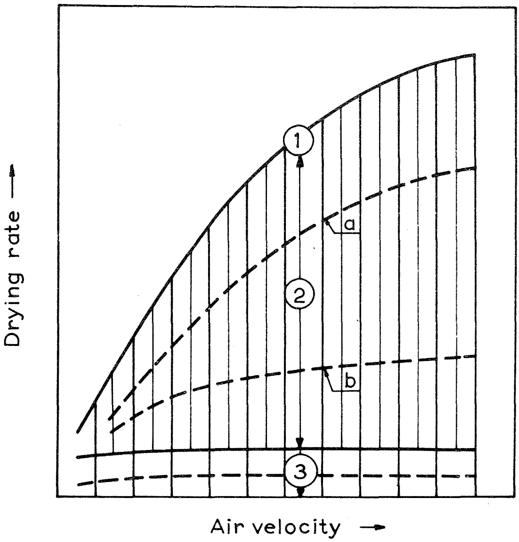

Fig. 9. Schematic figure of the drying periods of concrete, as a function of the drying rate and air velocity.

(1)-curve:	Constant-rate period. Surface shining wet.
(2)-area:	First falling-rate period. Surface only partially shining wet, "dry" spots appear, "wet" spots disappear. Curve a indicates the drying rate in the early part and curve b the drying rate in the later part of the period.
(3)-area:	Second falling-rate period. Surface "dry".
	Cf. Fig. 8.

The storage of concrete construction in water takes place rather rarely. The drying of concrete usually begins after the removal of molds. At this time the concrete surface has a "dry" appearance. This means that the I drying period or the drying rate periods 0, 1, and 2 are of minor significance.

The drying rate periods 1, 2, and 3 of concrete can be presented with the aid of two figures of principle (Fig. 9 and Fig. 10).

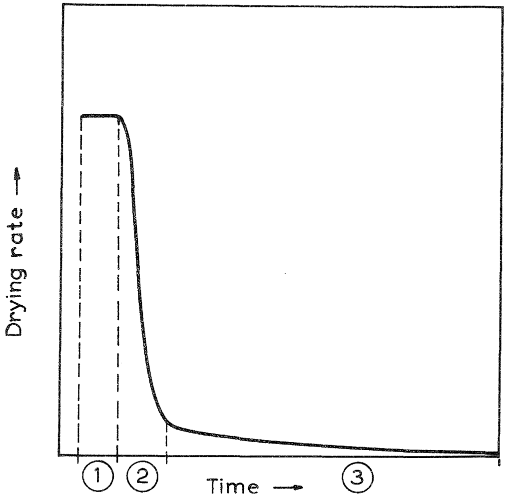

Fig. 10. Schematic figure of the drying periods of concrete as a function of the drying rate and time.

(1) Constant-rate period
(2) First falling-rate period
(3) Second falling-rate period.
Cf. Figs. 9 and 12.

6.3. CONSTANT-RATE PERIOD OF CONCRETE UNDER CONDITIONS OF FORCED CONVECTION

6.31. Introduction

Examination of the constant-rate period of the drying of concrete will be based upon the following assumption: the water on the concrete surface will evaporate like free water from the water surface. Thus the influence of solutes in water is ignored. However, it is well-known that the surface tension of the solution is higher and, consequently, the vapour pressure is lower than that of the pure solvent (Raoult's law). This means that the evaporation rate of water solution is lower than that of pure water.

6.32. Computational treatment

The computational treatment at the constant-rate period of the drying of concrete is intended for calculation of the duration of the constant-rate period when there are known the thickness of the water layer on flat concrete and the properties of the ambient air. This follows from the belief that the main interest is that of determining how long a time it takes to dry out the loose water from a concrete surface.

The equations needed are:

$$J = dm_1/dh \cdot A = \beta \cdot (C_s - C_{ob}) \qquad (1)$$

$$\varrho = \frac{dm_1}{dV} = \frac{dm_1}{ds \cdot A} \qquad (2)$$

$$\left\{\begin{array}{ll} \text{laminar flow:} & Sh = 0.66 \cdot Re^{1/2} \cdot Sc^{1/3} \\ \text{turbulent flow:} & Sh = 0.037 \cdot Re^{0.8} \cdot Sc^{1/3}, \end{array}\right. \qquad (3a) \quad \text{or}$$

$$\left\{\begin{array}{ll} \text{laminar flow:} & \beta = 0.66 \cdot \frac{D}{L} \cdot Re^{1/2} \cdot Sc^{1/3} \\ \text{turbulent flow:} & \beta = 0.037 \cdot \frac{D}{L} \cdot Re^{0.8} \cdot Sc^{1/3} \end{array}\right. \qquad (3b)$$

Equations (1) and (3) are familiar transfer equations (Ref. [25] [26]) and Equation (2) is the definition of density. Equations (3) are valid, at least under conditions in which Le and Sc approximate to 1. This obtains with sufficient accuracy for a system in which the carrier gas is moist air and the evaporating substance is water vapour. For more advanced treatment of steady convective mass transfer, see Spalding [27] and Luikov [28].

Simple integration of Equation (1) with the aid of Equation (2) yields

$$H_1 = \frac{\varrho \cdot s_1}{\beta \cdot (C_s - C_{ob})}, \tag{4}$$

where H_1 is the duration of the constant-rate period when s_1 is the thickness of the water layer on concrete, and β the surface evaporation coefficient which depends on Equation (3 b); ϱ is the density of water (= 1000 kg/m^3), C_s the concentration or density of water vapour at the surface, and C_{ob} that outside the boundary region. The flow on the flat plate can be assumed to be laminar when $Re < 2 \cdot 10^5$. Within the range of $Re = 2 \cdot 10^5$ to $6 \cdot 10^5$, both laminar and turbulent flows are possible [54]. When we fix $\nu = 1.6 \cdot 10^{-5}$ m^2/s, for the kinematic viscosity of the moist air, we get

$$v \cdot L = \nu \cdot Re \approx 5 \text{ m}^2/\text{s} \tag{5}$$

where Re is the critical Reynolds number $3 \cdot 10^5$.

The evaporation process is generally non-isothermal, and the evaporation rate is highly dependent upon the liquid surface temperature, since this determines the concentration C_s of the water vapour at the surface (or vapour pressure of the liquid on the surface), and hence the driving force $C_s - C_{ob}$ for evaporation. In turn, the surface temperature depends on the evaporation rate and on the heat transfer conditions. The values, of the quantities which depend on temperature should be selected in accordance with temperature

$$t = \frac{t_s + t_{ob}}{2} \tag{6a}$$

If at the start of the evaporation process the concrete and the water on its surface were at thermal equilibrium with ambient conditions, the minimum temperature of the surface t_s would be the wet-bulb temperature of the ambient air t_{wb}. However, temperature t_s will be higher, since heat will be transferred to the surface from the concrete itself and by radiation from ambient space. As a zero approximation, there will serve

$$t_s = \frac{t_{wb} + t_{ob}}{2}, \qquad (7)$$

or

$$t = \frac{t_{wb} + 3\,t_{ob}}{4} \qquad (6b)$$

6.4. FIRST FALLING-RATE PERIOD OF CONCRETE UNDER FORCED CONVECTION CONDITIONS

6.41. Introduction

The first pure falling-rate period can be observed only when the examined concrete surface is rather smooth and horizontal, i.e. the different parts of the surface should enter on the second falling-rate period at almost the same time.

6.42. Computational treatment

The basic idea used here for calculation of the duration of the first falling-rate period is based on the following equation, which is analogous with Equation (4) in Chapter 6.32;

$$H_2 = \frac{\varrho \cdot s_2}{\beta \cdot (C_s - C_{ob})}, \qquad (1)$$

where s_2 is an "effective" thickness of the water layer in the first falling-rate period corresponding to the free water layer on concrete in the constant-rate period. If these two equations are divided by each other, the result is

$$\frac{H_2}{H_1} = \frac{s_2}{s_1} \tag{2}$$

or

$$s_2 = s_1 \cdot \frac{H_2}{H_1} \tag{3}$$

The present experiments have shown that the order of magnitude of the s_2-value (cf. Chapter 6.5) is

$$s_2 = 0\,(10^{-4}\text{ m}) \tag{4}$$

Further investigations will elucidate whether the hypothesis of the "effective" water layer thickness presented here, failing something better, is sufficient for calculation of the duration of the first falling-rate period of concrete. It is probable that the s_2-value depends upon the moisture conductivity of concrete.

As regards the temperatures involved in the first falling-rate period, the assumptions made for the constant-rate period are also accepted here.

6.5. SOME EXPERIMENTAL RESULTS OBTAINED IN THE EARLY STAGE OF THE DRYING PROCESS OF CONCRETE

To arrive at a more detailed knowledge of the drying of concrete which has been stored in water, in the early stage of the drying process some plates (diameter 13.5 cm) made of concrete mortar (cement-sand ratio 1:3 and water-cement ratio 0.56) were taken from the water (temperature 17 °C), and kept horizontally in the laminar air flow (velocity 1 and 2 m/s, relative humidity 40 % and 70 %, temperature 21 °C) on a sensitive balance. The evaporation took place from the horizontal top surface only. Some excess of water was dropped on the surface before the test to increase the thickness of the water layer. Analysis of the results showed that there was no

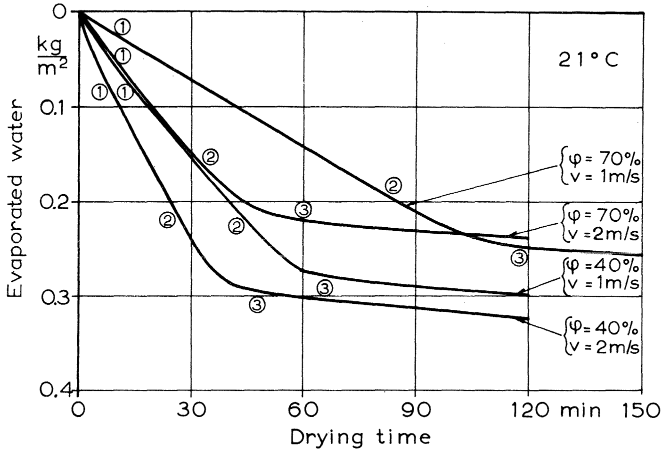

Fig. 11. Water (moisture) evaporated from the surface of a concrete plate (No. 9) as a function of drying time, relative humidity φ, and velocity v of the air. The thickness of the water layer on the surface at the start of the drying was 0.1 … 0.2 millimetres.

(1) Start of the constant-rate period

(2) Start of the first falling-rate period

(3) Start of the second falling-rate period

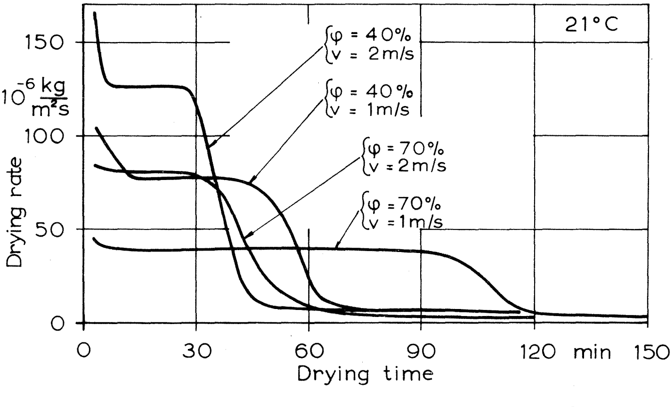

Fig. 12. Drying rate of a concrete plate (No. 9, cf. Fig. 11) as a function of drying time, relative humidity φ and velocity v of the air. The thickness of the water layer on the surface at the beginning of the drying was 0.1 … 0.2 millimetres.

significant difference in the results when 1) the exposed surface was the one against the bottom of the plastic mould on pouring, or when 2) the exposed surface was the free top surface on pouring. However, this "skin effect" question needs further general study.

For reasons of space, only one typical series of results is given in Figs. 11, 12 and Table 4. The surface temperature reached approximately the temperature of the ambient air in the middle of the initial part of the second falling-rate period which is discernible in the figures.

Table 4 also illustrates the respective theoretical evaporation rates during the constant-rate period, calculated in accordance with the theory presented in Chapter 6.3. The accord between the experimental and the theoretical values is fair, despite the zero approximation of surface temperature, and consequently that of vapour concentration C_s on the surface.

Table 4.

Evaporation rates and s_2-values according to the tests presented in Chapter 6.5. The values in parenthesis are theoretical ones obtained on application of the theory outlined in Chapter 6.3. The numerical values of parameters for this theory have been taken from Krischer [29].

Air conditions	$\varphi = 40\%$, $t_{ob} = 20°C$, $t_{wb} = 12.5°C$		$\varphi = 70\%$, $t_{ob} = 22°C$, $t_{wb} = 18.5°C$	
	v = 1 m/s	v = 2 m/s	v = 1 m/s	v = 2 m/s
Constant-rate period	Evaporation rate $kg/m^2 \cdot s$		Evaporation rate $kg/m^2 \cdot s$	
	$0.8 \cdot 10^{-4}$ $(0.9 \cdot 10^{-4})$	$1.3 \cdot 10^{-4}$ $(1.1 \cdot 10^{-4})$	$0.4 \cdot 10^{-4}$ $(0.4 \cdot 10^{-4})$	$0.8 \cdot 10^{-4}$ $(0.6 \cdot 10^{-4})$
First falling-rate period	s_2-value m		s_2-value m	
	$1.1 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	$0.8 \cdot 10^{-4}$	$1.3 \cdot 10^{-4}$

6.6. SECOND FALLING-RATE PERIOD OF CONCRETE

6.61. Introduction

With respect to evaporation drying times, the most important one in concrete technique is the second falling-rate period, as during this period the properties of concrete change significantly. If concrete is not stored in water before drying is started, as a rule the previous drying periods have no practical significance. Even when the concrete is stored in water, the significance of the previous periods to the whole process of drying can be of minor nature. According to the previous discussion (cf. Chapter 6.2) the second falling-rate period of ordinary concrete is practically isothermal.

6.62. On boundary conditions

The first known paper on the drying of concrete, in which mathematical treatment was based upon the analogy between heat and moisture diffusion, was that by R.W. Carlson, the M.I.T. professor, and published in 1937 [30]. The calculations of moisture transfer given in his paper were based strictly on the theory of drying presented by A.B. Newman in 1931 [24]. The boundary condition employed by Carlson was Newman's boundary condition in the second falling-rate period, i.e. with the moisture concentration on the surface falling to equilibrium value immediately at the start of the drying. In 1946, G. Pickett published an extensive study of moisture-loss shrinkage, applying diffusion principles [31]. He pointed out that Carlson could have obtained a "slightly" better agreement with the theory and measurements if he had taken surface conditions into account. In fact, however, the surface or boundary condition utilized by Pickett served as an additional unknown parameter, since he did not specify it in terms of moisture transfer entities with respect to the evaporation from the surface into ambient air. The theoretical and experimental studies of F.S. Rostasy [32] [33] seem to confirm that the drying of ordinary concrete with low moisture conductivities is in accord with the assumption of surface equilibrium.

All the investigations made by the present author with ordinary hardened cement pastes and concrete mortars have shown that under forced convection conditions the drying of concrete in the second falling-rate period is almost 1) independent of air velocity, and 2) isothermal, i.e. the assumption of surface equilibrium is valid. Fig. 13.

The magnitude of the moisture conductivities in the test mentioned above made by Carlson, Rostasy and the author was within the range $10^{-9} \cdots 10^{-11}$ m^2/s.

If the moisture conductivity of concrete is high (very porous concrete), and the concrete is drying under low air velocity, especially under free convection conditions, the simple assumption of equilibrium presented above is invalid. Consequently, it might then be probable that the first and the second falling-rate period for concretes taken from water are not easily separable. According to the suggestion made by P. S. Sergowski, as presented by Lykow [2], the evaporation coefficient could be calculated from an equation of type:

$$Sh = Sh_1 \left(\frac{C_s}{C_e}\right)^n \qquad (1)$$

In Equation (1), Sh_1 is the Sherwood number obtained during the constant-rate period, C_s and C_e are the moisture content of the surface of the porous solid and the equilibrium moisture content of the porous solid under examination respectively. To the best of my knowledge, no experiments concerning the boundary conditions of concrete of this kind have been made.

The general mathematical expression of the boundary condition is taken to be

$$k_s \cdot \left(\frac{\partial C}{\partial N}\right) = \beta' \cdot (C_s - C_e), \text{ or} \qquad (2\,a)$$

$$\left(\frac{\partial u}{\partial \sigma}\right) = \frac{\beta' \cdot 1}{k_s} \cdot u_s \, ; \quad u = \frac{C - C_e}{C_o - C_e} \, ; \quad \sigma = \frac{N}{1}, \qquad (2\,b)$$

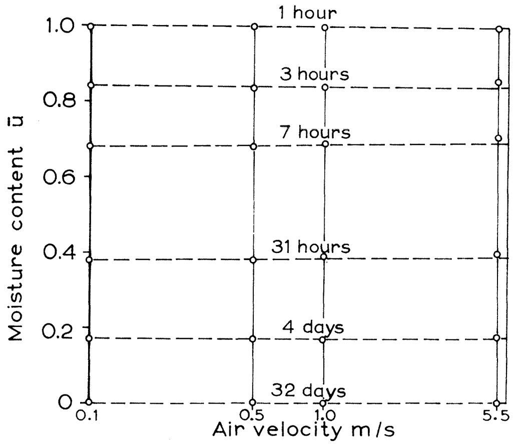

Fig. 13. The independence of the drying rate of a concrete mortar on the air velocity within the second falling-rate period, roughly estimated to begin about 1 hour after removal of the test plates (3 + 3 + 3 + 3) (diameter 13.5 cm, thickness 1.2 cm) from water. The two main surfaces of the plates were exposed. The plates were made of concrete mortar (water cement ratio 0.56 by weight, cement paste-aggregate ratio 1:1.2 by volume). For detailed description, see Paragraph 6.662. The tests were made under forced convection conditions: laminar flow, air velocity about 0.1, 0.5, 1, 5.5 m/s, t = 21 °C, φ = 40 %. The condition marked 0.1 m/s was near to natural convection. (Moisture conductivity k is presented in Fig. 23).

where C_s is the actual moisture concentration of the body just at the surface of the body at any time, and C_e the concentration of the body which would be in equilibrium with the vapour pressure remote from the surface (outside the boundary layer). Moisture conductivity k_s and evaporation coefficient β' are the values which correspond to concentration C_s. $\partial C/\partial N$ is the concentration gradient at the surface, measured in the outward direction along the normal of the surface. u and σ are dimensionless variables, and l the characteristic thickness of the body under examination.

In the following, a theoretical examination is made of the ratio of evaporation coefficient β' to moisture conductivity k. With the aid of Equation (1) in this chapter, and Equation (3) in Chapter 6.3, we can first make an estimation of evaporation coefficient β, which refers to the concentration of water vapour. If there are used the following estimates [29] in the calculation of β: t = 20 °C, L = 0.1 m, $\nu = 1.6 \cdot 10^{-5}$ m²/s, D (water vapour in moist air) = $2.6 \cdot 10^{-5}$ m²/s, v = 0.5 m/s and $C_s/C_e \approx 1$, we obtain $\beta \approx 10^{-2}$ m/s. Since the evaporation refers to the concentration of the moisture in the solid (cement paste or concrete), we have

$$\beta' = \frac{\Delta C_{air}}{\Delta C_{paste}} \cdot \beta \tag{3}$$

The coefficient ratio in Equation (3) can be arrived at with the aid of Fig. 14, and a suitable table for conversion of the relative humidities into water vapour concentrations [29]: for example,

$$\Delta C_{air} = (0.7 - 0.4) \cdot 0.017 = 5 \cdot 10^{-3} \text{ kg/m}^3,$$

$$\Delta C_{paste} = (230 - 120) = 110 \text{ kg/m}^3, \text{ or}$$

$$\Delta C_{air} / \Delta C_{paste} = 0\,(10^{-4}) \tag{4}$$

Thus,

$$\beta' = 0\,(10^{-6} \text{ m/s}) \tag{5}$$

If we fix $k = 10^{-9}$ m²/s, we obtain

$$\beta'/k = 0\ (10^3\ m^{-1}) \tag{6}$$

and

$$Bi = \frac{\beta' \cdot l}{k} = 0\ (10^2) \tag{7}$$

if $l = 0.1$ m. If the diffusion theory is used for prediction of the behaviour of a substance in the drying process, Biot's number Bi > 100 means that surface concentration C_s is very near equilibrium concentration C_e, and hence this assumption is sufficiently valid for calculation. It should further be noted that Biot's number depends on the characteristic thickness of the body under examination, l. If a body is thin (l small) and the moisture conductivity is relatively high, the assumption that the surface falls to the equilibrium value immediately after the start of the drying process will not be valid. The results presented in Fig. 13 show that the Biot number must have been greater than about 100 in that experiment.

In his experiments, Campbell-Allen obtained [34] with $l =$ 0.025, 0.05, 0.075 m, using successive approximations to Bi and to moisture conductivity k with the aid of the diffusion theory, that $Bi = 10^3$ (and $k \approx 2 \cdot 10^{-9}\ m^2/s$). Unfortunately, he did not report on the air velocity in his experiments, but as the specimens were dried in an electric oven (78 °C), it was probably small. It is to be noted that at the start of the drying the specimens were very wet, as they had been cured in water (two weeks at 21 °C, 2 days at 78 °C) before the test. It is encouraging that Campbell-Allen will probably continue his valuable work, because, as he says, "the paper is a progress report indicating that a start has been made in investigating this field and it is proposed to pursue further both the mechanisms of moisture transfer and the relations between shrinkage and moisture conditions".

6.63. On initial conditions

In addition to the boundary condition, there are also needed the initial conditions in mathematical treatment of moisture transfer.

Information on the initial conditions is divided into two parts:

1) knowledge of the moisture content field at the start of the drying, i.e. when $h = 0$
2) knowledge of the moisture content field at the end of the drying, i.e. when $h = \infty$

In correspondence with the situation which often applies in practice, the following simple initial conditions, which simplify the mathematical treatment, are fixed.

1) Uniform moisture concentration C_o at $h = 0$
2) Uniform moisture concentration (equilibrium moisture concentration) C_e at $h = \infty$

It is reasonable to use dimensionless moisture concentration variables

$$u = \frac{C - C_e}{C_o - C_e} \tag{1}$$

$$\bar{u} = \frac{\bar{C} - C_e}{C_o - C_e} \tag{2}$$

in which C is the variable moisture concentration in the moisture field, and $\bar{C}$ the variable average moisture concentration of the whole body under examination. When using the u-values, the initial conditions of the drying process for computational treatment are

$$\begin{cases} h = 0 & C = C_o & u = 1 \\ h = \infty & C = C_e & u = 0 \end{cases}$$

If one wishes to forecast the moisture concentration of the drying concrete, it is necessary to fix beforehand the numerical values for C_o and C_e. The initial moisture concentration C_o, as well as the equilibrium moisture concentration C_e, depends upon the history of the concrete in question, which can be described at least partially in terms of the maturity or of the degree of hydration of the concrete (cement paste). This means that both C_o and C_e depend upon the

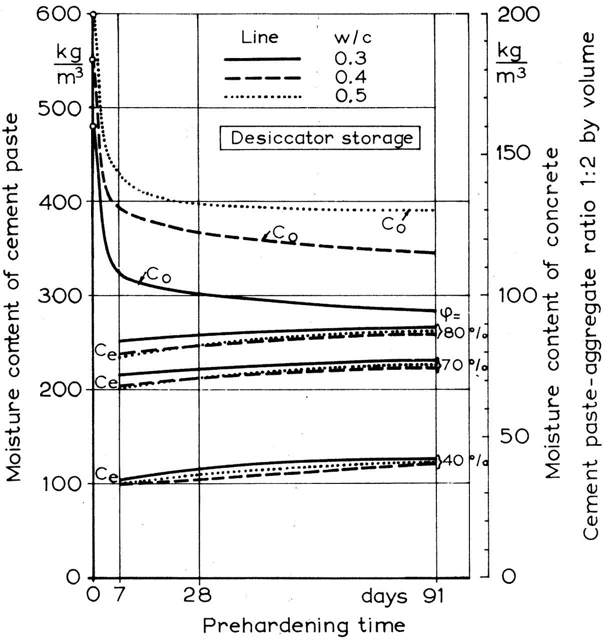

Fig. 14. Dependence of the moisture content of some cement pastes and corresponding concretes on the prehardening time under sealed conditions (21 °C), the cement pastes and concretes being exposed to drying in desiccators at 25 °C (no CO_2 exposure). C_o - curves show the moisture content obtained by drying at 105 °C at the end of the prehardening time. C_e -curves (sorption isotherms) indicate equilibrium moisture content (obtained after 40 weeks). Cf. Fig. 15.

fixation drying and on the degree and type of the formation of hydration products, or, on other words, on the amounts and types of evaporable water and of hygroscopic material in concrete. With the aid of the results of experiment such as those presented in Paragraph 5.2, the curves for C_o and C_e can be drawn with a view to application (Figs. 14

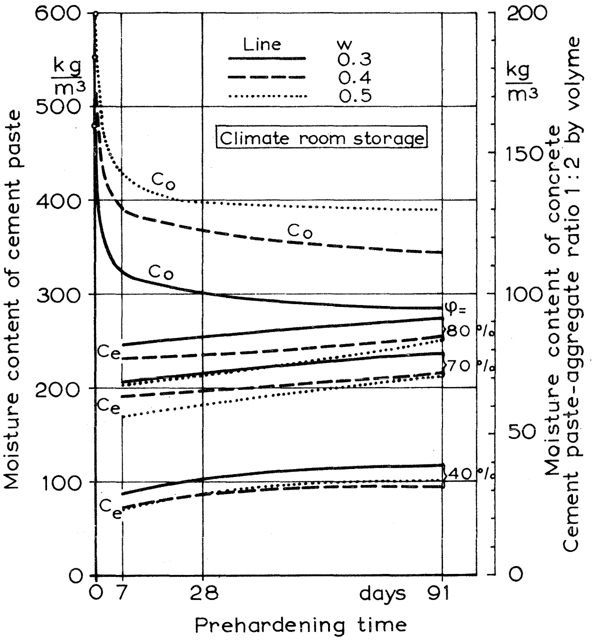

Fig. 15. Dependence of the moisture content of some cement pastes and the corresponding concretes on the prehardening time under sealed conditions (21 °C), the cement pastes and concretes being exposed to drying in climate rooms at 20 °C (CO_2 exposure). C_o-curves show the moisture content obtained by drying at 105 °C at the end of the prehardening time. C_e-curves (sorption isotherms) indicate equilibrium moisture content (obtained after 40 weeks). Cf. Fig. 14.

and 15). It is then presumed that the concrete will be allowed to harden under "normal" prehardening conditions in the following way:

1) sealed, i.e. no moisture exchange between concrete and ambient space during the first 7, 28 or 90 days
2) temperature approximately 20 °C

In some cases it may be reasonable further to assume that

3) the fixation drying (hydration) is insignificant in the course of drying: Thus it is assumed that the degree of hydration at the start of drying is rather high (after which hydration is generally slow) and/or that the concrete relatively soon attains the critical moisture content at which the hydration process ceases. (Cf. Paragraph 7.3).

If the three assumptions presented above are accepted, it is possible to choose suitable C_o- and C_e-values from curves such as those presented in Figures 14 and 15, where C_e-curves are drawn on the foundation of the experimental results presented in Figures 6 and 7, and C_o-curves by means of experimental results obtained in the same tests by drying 27 of the 135 specimens at 105 °C after prehardening times of 7, 28 and 90 days. (Cf. Paragraph 5.2). The 80 %-curves are extrapolated. In Figs. 14 and 15, there is also presented a scale which is valid for concretes with an original cement paste-aggregate ratio of 1:2, following the assumption that the aggregate exercises no influence on the equilibrium moisture, principally retained by the minor pores of hydrated cement paste (cement gel).

The estimation of C_o has also been treated in Paragraph 7.3.

6.64. On basic equations

Most earlier works on the drying of concrete have shown that the diffusion type equation "sufficiently" depicts the drying of concrete. Although there is no reason to believe that the moisture conductivity (moisture diffusivity) is constant, even the usage of constant moisture conductivity, carefully chosen and used, has given "sufficient" solutions for application. However, we have experimental studies on concrete [35] which clearly indicate that the assumption of a constant k, when using the diffusion theory, will lead to results which are completely erroneous. Further experimental work is thus required to obtain more detailed understanding of the drying of concrete [34] [56] [59].

The general basic equation, "diffusion equation", is analogous with Equations (2) and (3) presented in Chapter 2:

$$\begin{cases} \partial u/\partial h = \mathrm{div}(k\ \mathrm{grad}\ u) + S \\ u = \dfrac{C - C_e}{C_o - C_e} \end{cases} \qquad (1)$$

In respect to the concrete, the sink and source term S generally comprises a sink (fixation drying) and a source (carbonation wetting), both moisture-concentration-dependent. It must be borne in mind that the concentration-dependence is more than the dependence of u, since as a rule $u = 1 \cdots 0$ is but a part of the range $C = C_{max} \cdots 0$. The general idea of the solutions of partial differential Equation (1) with different boundary and initial conditions, etc., can be obtained from the textbooks of Carslaw & Jaeger [4] and Crank [5].

In those cases of common occurrence in which the effect on the drying of the moisture source incurred by carbonation and the moisture sink of the fixation drying incurred by hydration are of minor practical significance, we can put $S = 0$. If, in addition, we use the "average" moisture conductivity $\bar{k}$ (= constant) as a moisture conductivity, we acquire a rather simple equation, which can in all probability be adequate in cases where $C_o - C_e$ is relatively small with respect to the whole C-range:

$$\partial u/\partial h = \bar{k}\nabla^2 u \qquad (2)$$

Some previous studies of the drying of concrete, together with the author's preliminary tests, seem to prove that Equation (2) does not sufficiently describe the behaviour of the drying of concrete in cases where $C_o - C_e$ are large. This hypothesis seems to be especially true for concretes stored in water before drying, i.e. when the macroscopic transfer of water is probably significant (Cf. Paragraph 6.66).

In the second falling-rate period of concrete drying, we can further fix rather simple boundary and initial conditions in accordance with the discussions in the previous paragraphs of Chapter 6.6. The solution of Equation (2) is then subject to the conditions:

Fig 98

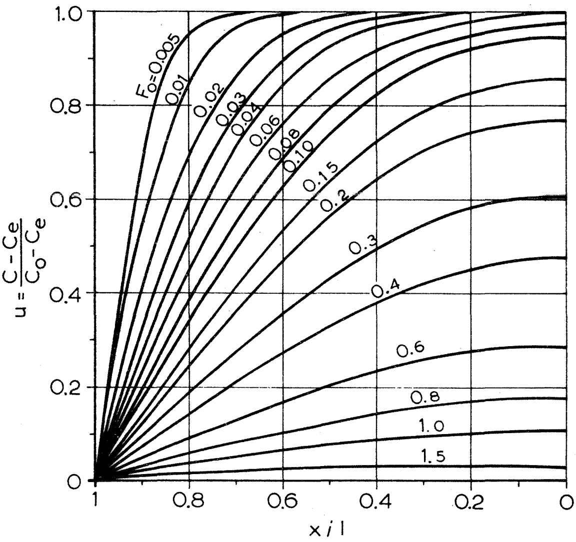

Fig. 16. Moisture distributions at various times in the plate $-1 \leq x \leq 1$ with initial uniform moisture content C_o, and surface moisture content C_e. Numbers on curves are the values of Fourier number $Fo = kh/l^2$. (Reproduced from similar figures presented in a number of publications).

$$\begin{cases} \text{Boundary condition: } u_s = 0;\ h \geq 0\ (\text{Bi} > 100) \\ \text{Initial condition: } u = 1;\ h = 0\ (u = 0;\ h = \infty) \end{cases} \tag{3}$$

The solution of Equation (2), subjected to the simple boundary and initial conditions presented by Equations (3), has been presented in numerous textbooks, for example [4] [5] [26], and also in a condensed form in the pioneer paper by Newman [24]. The solutions for bodies of ordinary geometrical forms can be written in analogous form with relatively simple f-functions:

$$u = f\left(Fo, \frac{x}{l}\right) \tag{4}$$

Fig 20

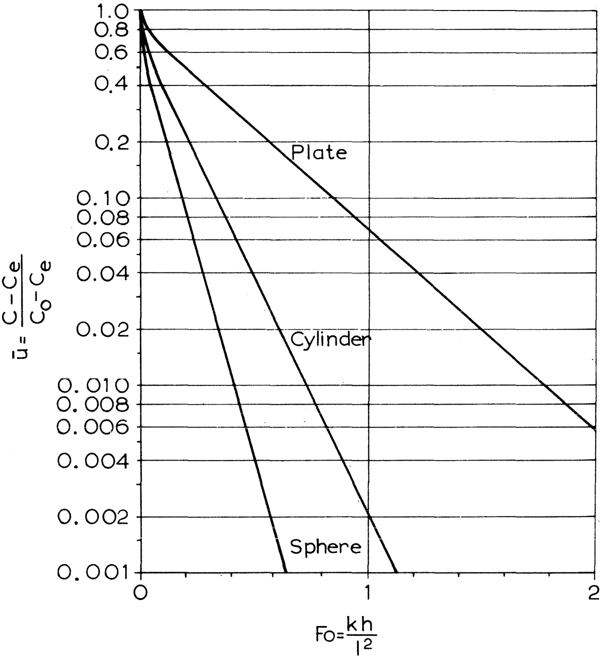

Fig. 17. Drying of an infinitely broad plate or slab, infinitely long cylinder, and sphere as a function of the Fourier number. Initial uniform moisture content C_o, and surface moisture content C_e. (Reproduced from similar figures presented in a number of publications).

$$\bar{u} = f\,(Fo) \tag{5}$$

In Equations (4) and (5) the Fourier number Fo = $\bar{k}h/l^2$, l being the characteristic thickness of the body (= half-thickness of plate, radius of cylinder or sphere), and x the characteristic dimensional variable of the body (Figs. 16 and 17). It can therefore be seen that no difficulty exists in computational treatment, but that the

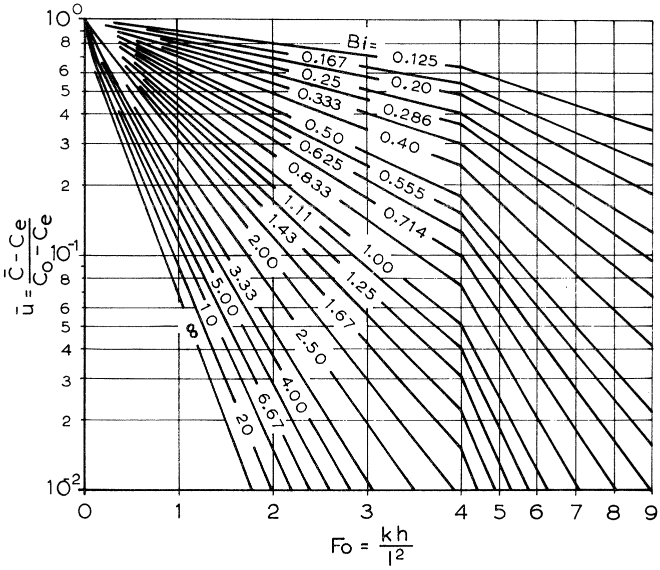

Fig. 18. Drying of an infinitely broad plate or slab as a function of Fourier number Fo and Biot number $Bi = \beta' \cdot 1/k$. Initial uniform moisture content C_0. Curve $Bi = \infty$ corresponds to the plate curve in Fig. 17. (Reproduced from similar figures presented in a number of publications).

serious obstacle lies making a reasonable choice of parameters $\bar{k}$, C_0, and C_e. This choice for the purpose of forecasting the moisture content of a certain concrete body under drying cannot in general be effected reliably if the results of large scale experiments are not available.

The solutions of Equation (2) subjected to the boundary condition presented by Equation (2) in Paragraph 6.62 and uniform initial condition $u = 1$ are simply

$$u = f\left(Fo,\ Bi,\ \frac{x}{l}\right) \tag{6}$$

$$\bar{u} = f\,(Fo,\ Bi) \tag{7}$$

Relation (7) is presented in Fig. 18.

The solutions of Equation (1) in one dimension

$$\partial u/\partial h = \frac{\partial}{\partial x}\left(k\,\frac{\partial u}{\partial x}\right), \tag{8}$$

subjected to the boundary conditions presented by Equations (3), when k depends linearly on u

$$k = k_e\,(1 + bu) \tag{9}$$

gives

$$\bar{u} = f\,[\mathrm{Fo}\,(k_e),\ b] \tag{10}$$

a relation presented in Fig. 19 (5). An approximate solution of Equation (8) under similar conditions has been put forward by Tsang [36].

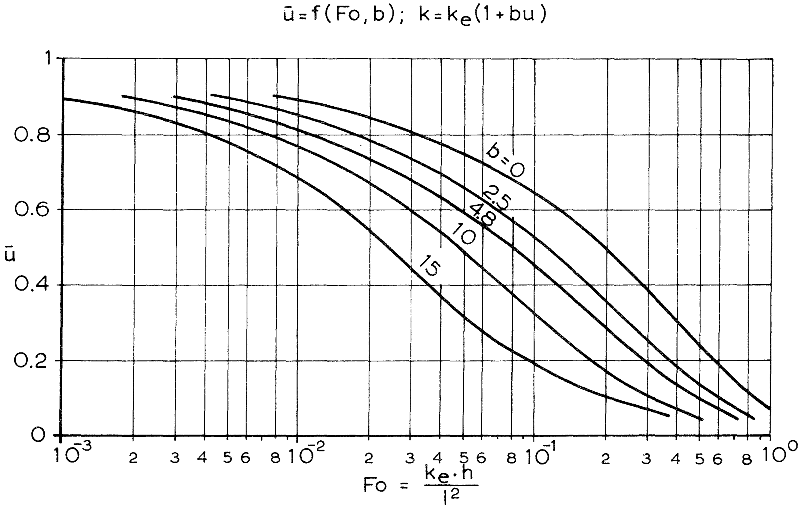

Fig. 19. Drying curves of an infinite slab for the variable $k = k_e\ (1 + b \cdot u)$. Curve $b = 0$ corresponds to curve $Bi = \infty$ in Fig. 18. (Reproduced from Crank [5] Fig. 12. 16; curve $b = 15$ extrapolated).

By means of the mathematical results presented above, it is possible, at least in a preliminary way, to test whether the diffusion theory in its simple form is sufficiently valid to describe the drying process of concrete.

In this connection, a very interesting paper by Ilantzis [35] is worthy of mention; in this, the concentration-dependent k has been calculated for certain concrete mortar prisms by application of the diffusion theory. From the experimental results obtained, he also deduced exponential formulae for k and $\bar{u}$. Unfortunately, it is no easy matter to generalize his results, in view of the unknown air velocity (small?), and the high probability of fixation drying (one-day-old mortar at the start of the drying) and carbonation during the tests. The paper contains no treatment of these three factors. It seems possible that the dependence of k on the dimensions of the specimens obtained, and dealt with in the paper, could be ascribed, in part, to the invalid boundary condition $Bi = \infty$ employed [38] (Cf. Paragraph 6.65).

6.65. On moisture conductivity

The moisture conductivity k of concrete is obviously a rather complicated quantity. Concrete is a capillary porous colloid, in which are possible many kinds of fluid motions. When concrete is wet, moisture will flow in the form of a liquid (macroscopic transfer) and vapour (molecular transfer). In rather dry concrete, moisture can be expected to transfer mainly in the form of water vapour.

A brief examination is due of the basic factors upon which k probably depends. Attention is first drawn to the changes in k from one concrete to another, and then within the same concrete.

Different types of concrete have different moisture conductivity, and the basic factors which exert an influence are:

I Cement paste
    Brand of cement
    Water-cement ratio
    Air content

Hydration conditions
Degree of hydration

II Aggregate (dense)
Grading

III Cement paste-aggregate ratio

IV Moisture concentration

V Temperature

Moisture conductivity also varies in the same concrete, and the basic factors here are:

1. Hydration conditions
2. Degree of hydration
3. Moisture concentration
4. Temperature

It is quite obvious that not even experiments made on a large scale could produce values of moisture conductivities which would be universally applicable. Consequently, great value would be attached to a simple test for determination of the moisture conductivity of an individual cases. Furthermore, information on average values of moisture conductivity, dependent on the properties of concrete, to enable one to obtain a tentative idea of the drying process, is important. If our knowledge is confined to the fact that the range of the average k-values for ordinary concretes is within the range, say, of $10^{-9} \cdots 10^{-11}$ m^2/s, it is of no help in forecasting the behaviour of a certain concrete during the drying process. Should, for example, the estimate be based on the diffusion relation $Fo = 0.05$, then determination of the time at which the centre of a concrete slab of half-thickness 25 cm will begin to dry, will give the answer 1 month, 1 year or 10 years, corresponding to k-values 10^{-9}, 10^{-10} or 10^{-11} m^2/s.

As regards the test for determination of the moisture conductivity k of concrete for the drying process, it is evident that this must be done in an actual non-steady state, since the drying of concrete is fundamentally an irreversible, non-steady process. In addition, the process involves both macroscopic (capillary) and a molecular (water vapour) flow of moisture, which can hardly be simulated. It is thus reasonable to use test specimens, with dimensions of the same order as the actual body or construction to be simulated. The simplest method is founded upon utilization of the weight loss curves of plate specimens exposed to drying, and the simple diffusion relation $\bar{u} = f(Fo)$ presented in Fig. 17. An advanced method frequently applied for determination of k and its moisture dependence, with experimental moisture distribution curves, has been presented by Egner in his thesis for a doctorate [37] [38]. It is evident that only experimental determinations of the moisture distribution curves will provide a really satisfactory conception of the drying process. Egner's method is also easily applicable to concrete when using the splitting test technique, well-known to concrete technologists.

The use of the $Bi > 100$ curve or $Bi \approx \infty$ curve of diffusion theory, when Bi has a low value, gives too low values for k. If k is calculated for a series of specimens of the same material of varying thicknesses, dried under conditions of low Bi, using curve $Bi = \infty$, it is to be expected that the values of k thus obtained will rise with increasing thickness [38].

The magnitude of the moisture conductivities of the concretes used in the tests made by Carlson [30], Rostasy [32], Creutz & Downes [39], Campbell-Allen [34], Ilantzis [35], Waters [56] and the author has been within the range $10^{-9} \cdots 10^{-11}$ m^2/s. Within this range are probably most concretes that are used in making ordinary concrete structures.

6.66. Results of some preliminary tests

6.661. Spheres in desiccators

These tests were made in 1959, mainly on the basis of the method described by Creutz & Downes [39]. The test specimens were spheres (diameter 8.1 cm) made of ordinary concrete (two spheres, T_1 and T_2) and magnetite concrete (two spheres, M_1 and M_2). The

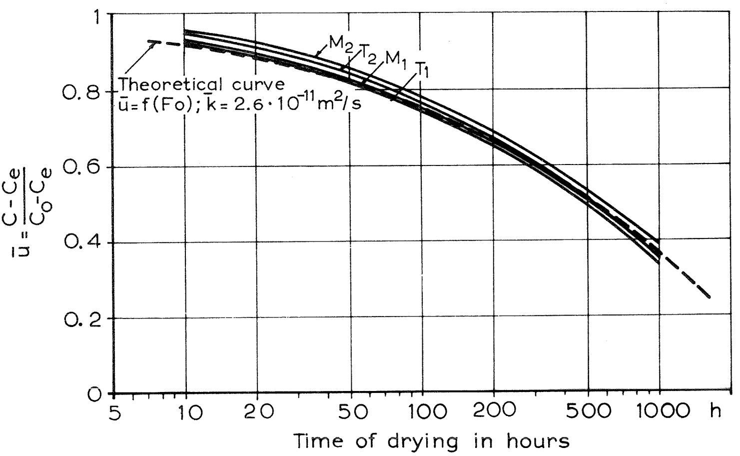

Fig. 20. Drying of spheres (diameter = 8.1 cm) made of ordinary concrete (spheres T_1, T_2) and magnetite concrete (M_1, M_2) in desiccators above P_2O_5 ($\varphi = 0$). The experimental curve is sufficiently fitted by the equation $\bar{u} = f(Fo)$ with $\bar{k} = 2.6 \cdot 10^{-11}$ m^2/s, in $\bar{u}$-range shown. (Cf. Fig. 21).

maximum particle size of the aggregate was about 16 mm, and the grading was continuous, corresponding to "a good grading" for such concretes. In both concretes, the water-cement ratio was 0.67 (by weight, as usual) and the cement paste-aggregate ratio of the ordinary concrete was 1 : 2.4, and that of the magnetite concrete 1 : 1.9 by volume. The cement was ordinary Finnish Portland cement. The concrete mass was cast in sphere-shaped bottles (250 ml). After 1 1/2 months of sealed curing at 20 °C, the spheres were stripped by breaking the bottles. The cement paste film and the angles on the surface of the spheres were removed by means of a steel brush before the drying test, which was performed in desiccators above P_2O_5 ($\varphi = 0$, $t = 20$ °C, free convection). Fixation drying and carbonation exposure during the drying process can thus be neglected; the drying began approximately at the start of the second falling-rate period.

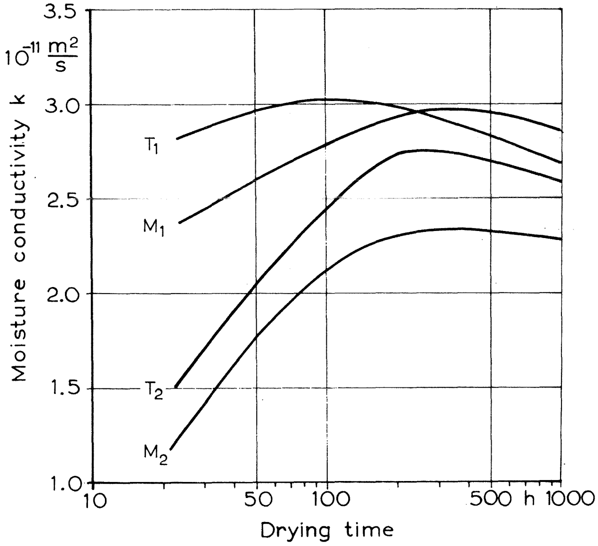

Fig. 21. Moisture conductivity k-drying time relation drawn, using the information given in Fig. 20, and the diffusion theory for spheres presented in Fig. 17.

The results are presented in Figs. 20 and 21. Within the range $\bar{u} = 0.9 \cdots 0.4$, usage of a constant mean value of k, denoted by $\bar{k}$ in the diffusion theory (Fig. 17, sphere), is quite successful as is shown by the theoretical curve in Fig. 20. This theoretical curve appears to confirm that, in spite of the low air velocity (free convection), the Bi-value was comparatively large, owing to the small k-value. Fig. 21 was drawn on the foundation of the information given in Fig. 20 and Fig. 17.

The moisture range $\bar{u} = 1 \cdots 0$ of the ordinary concrete studied corresponds, on an average, to the moisture content range $C_o \cdots C_e = 135 \cdots 0$ kg/m^3. The respective moisture content range of the magnetite concrete was $170 \cdots 0$ kg/m^3.

6.662. Plates in climate rooms, different air velocities

Some of the results of the tests to be presented in this section have already been given in Fig. 13. The tests were carried out during the winter 1961/1962. The test specimens (3 + 3 + 3 + 3, three specimens for each air velocity) were plates (diameter 13.5 cm, thickness 1.2 cm) made of concrete mortar (water-cement ratio 0.56 by weight, cement paste-aggregate ratio 1 : 1.2 by volume). The cement used was ordinary Finnish Portland cement, with a maximum particle size of aggregate of 1.4 mm. The concrete mortar was "normal" or "standard" mortar, generally used for cement-testing purposes in Finland. This mortar was cast in plastic rings (the bottom plate was also of plastic), kept in position during the tests. Thus the two main surfaces of the plates were exposed to drying during the drying tests. During the curing period, the plates were kept for the first day in air (20 °C, 100 %), the second day in water (30 °C), and for the next six days also in water (40 °C), before the tests. Consequently the curing corresponded approximately to one month's curing in water of temperature 20 °C.

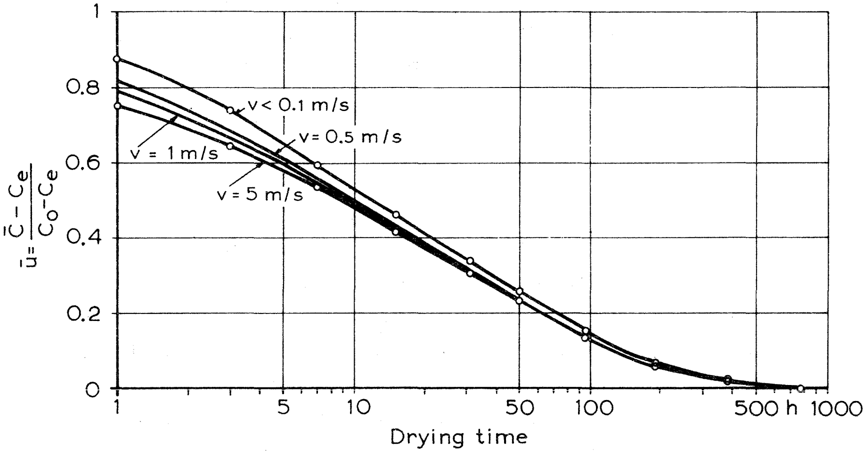

Fig. 22. Drying of plates (diameter 13.5 cm, thickness 1.2 cm) made of concrete mortar in different air velocities. $\varphi = 40$ %.

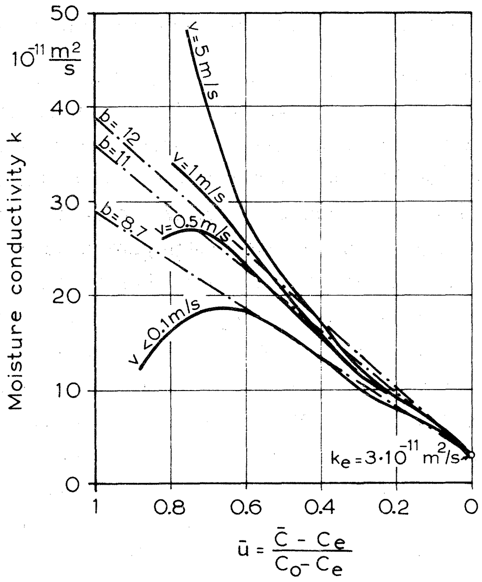

Fig. 23. Moisture conductivity k-moisture content ū relation drawn by means of the information given in Fig. 22, and the diffusion theory for plates presented in Fig. 17. Lines $k = k_e \cdot (1 + b \cdot \bar{u})$; $k_e = 3 \cdot 10^{-11}$ m^2/s, b = 8.7, 11, and 12 are also presented.

The drying tests were made in the climate room, the air conditions being $\varphi = 40\%$, $t = 21\,°C$. The air velocities were: less than 0.1 m/s, and about 0.5, 1, 5.5 m/s. The plates were placed vertically in the air stream; the flow on them can be considered to be laminar. Immediately after the specimens had been taken from the water, the surfaces were carefully dried with a dry sponge, and therefore the effect of the constant-rate period on the drying is small. However, it should be noted that the drying process in the tests theoretically involves all the rate periods. By virtue of the relatively minor effect exerted in these tests by the earlier rate periods on $\bar{u}$, the test results are treated here simply as if the drying periods concerned were related to the second falling-rate period alone. Fixation drying during the test was probably insignificant, but the carbonation effect was clearly evident after the plates had attained the point of equilibrium. Both of these effects were left out of consideration in these preliminary tests.

The average values obtained are presented in Figs. 22, 23 and 24. The moisture range $\bar{u} = 1 \cdots 0$ corresponds, on an average, to the moisture content range $C_0 \cdots C_e = 215 \cdots 55$ kg/m^3. Fig. 22 indicates that the air velocity exercised a minor effect on the drying process, although this effect can be better seen in Fig. 13. By application of the diffusion theory (Fig. 17) Fig. 23 could be drawn. Fig. 24 clearly shows that the diffusion theory, with a constant average of $k = \bar{k}$ is but little in agreement with the experimental curve ($v = 1$ m/s). A closer accord with the theory (Fig. 19) could be obtained if there were applied, as an approximation, the variable $k = k_e \cdot (1 + b\bar{u})$ selected with the assistance of Fig. 23.

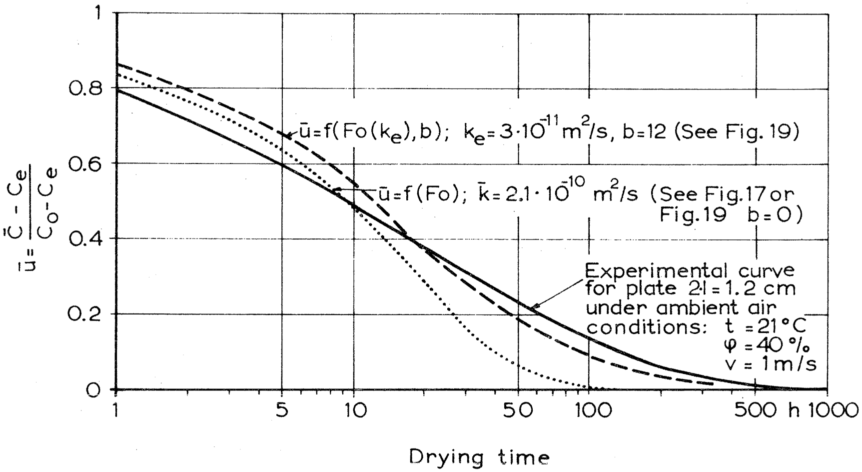

Fig. 24. Some curve fitting. Experimental curve v = 1 m/s taken as an example. Data from Figs. 22 and 23.

6.663. Plates in climate room, different plate thickness

These tests were carried out during the years 1962/1963. Test specimens of different thicknesses (2 + 2 + 2 + (2) $^{x)}$), i.e. two specimens for each plate thickness 0.5, 1, 2, (4) $^{x)}$ cm) were made of the same type of concrete mortar as that used in the tests presented in Paragraph 6.662, but the Finnish Portland cement used was taken from a different cement population (Cf. Chapter 1). The mortar was cast in plastic rings, kept in position during the drying tests. Thus the two main surface of the plates were exposed to drying during the tests. After the pouring, the plates were cured for 28 days in water (20 °C). When the curing had been completed, the plates were taken from the water, and wet circular blotting-paper of the same size as the concrete surface was put on the surfaces. The edges of the plates were dried with the sheets of blotting-paper, and by hanging the plates vertically for about 10 minutes wet circular blotting-papers on the mortar surfaces, in the air stream. After this preliminary treatment, the sheets of circular blotting-paper were removed and the specimens exposed in a vertical position to drying, which was effected in two climate rooms ($\varphi \doteq 40$ %, $t = 20$ °C, $v < 0.5$ m/s and $\varphi = 70$ %, $t = 20$ °C, $v < 0.5$ m/s). The air velocity varied somewhat from plate to plate; unfortunately, this may lead to a confusing effect in the test results.

At the start of the drying tests, the surfaces of the specimens were wet, which means that the drying process comprises all the drying periods 0, 1, 2 and 3 presented in Chapter 6.2. Only the drying during the second falling-rate period will be considered, if choosing $h_{-1} = h - 1$ hours as the drying time for the plates dried in RH 40 %, and $h_{-2} = h - 2$ hours for the plates dried in RH 70 %, where h denotes the whole time of drying without corrections.

The results are presented in Figs. 25 ··· 30. The moisture range $\bar{u} = 1 \cdots 0$ corresponds, on an average, to the moisture content range $C_0 \cdots C_e = 190 \cdots 50$ kg/m^3, when $\varphi = 40$ %. The respective range was 190 ··· 95 kg/m^3, when $\varphi = 70$ %. Fixation drying during the

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$^{x)}$ not dealt with, in view of continuation of the drying test.

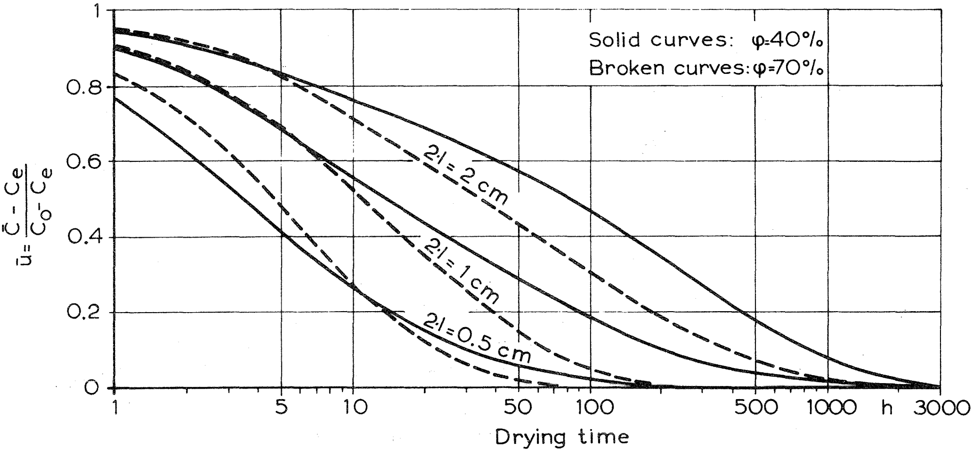


Fig. 25. Drying of concrete mortar plates (diameter 13.5 cm) of various thicknesses (0.5, 1, 2 cm), all drying periods included. φ = 40 %, 70 %.

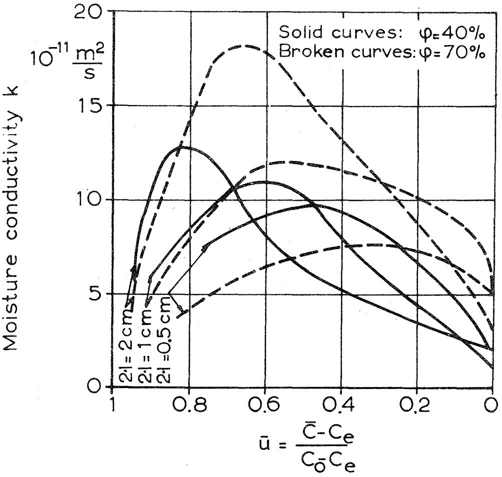


Fig. 26. Moisture conductivity k-moisture content ū relation, drawn by means of the information in Fig. 25, and the diffusion theory for plates presented in Fig. 17.

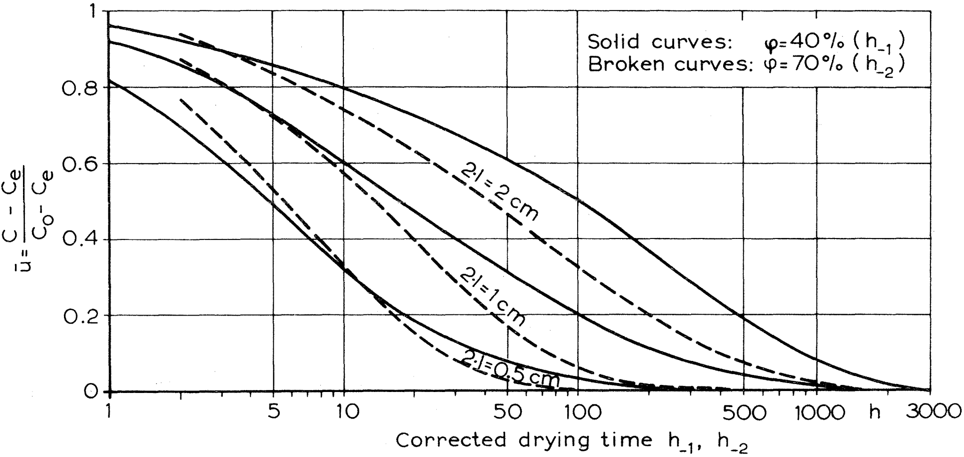


Fig. 27. Drying of concrete mortar plates (diameter 13.5 cm) of various thicknesses 0.5, 1, 2 cm, in the second falling-rate period (corrected drying times h_{-1} = h - 1 hours, h_{-2} = h - 2 hours, cf. Fig. 25). φ = 40 %, 70 %.

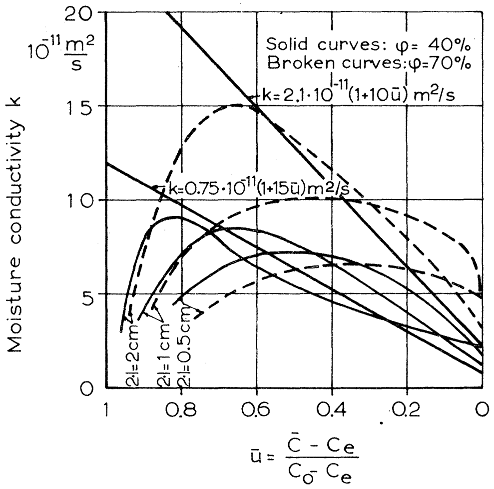


Fig. 28. Moisture conductivity k-moisture content $\bar{u}$ relation, drawn by means of the information in Fig. 27, and the diffusion theory for plates in Fig. 17. k-lines are the lines which give the best linear k-$\bar{u}$ relationship in accordance with the diffusion theory presented in the Fig. 19, and the experimental curves (cf. Figs. 29, 30).

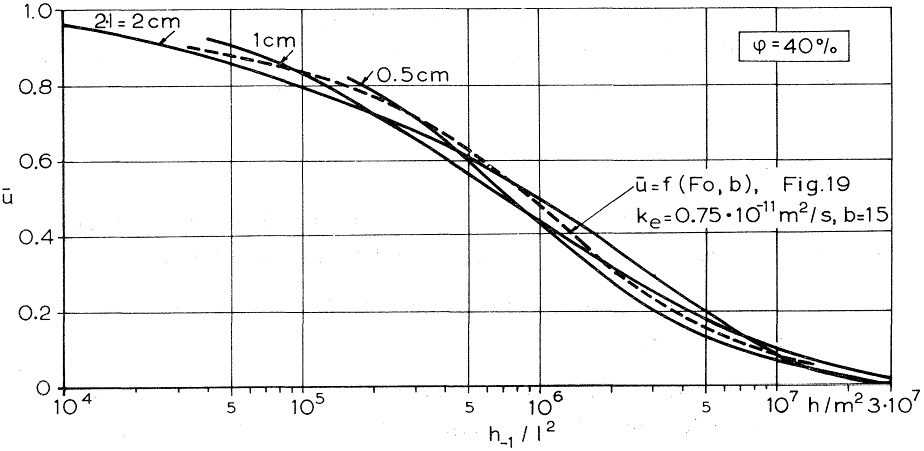


Fig. 29. Moisture content ū plotted against corrected time h_{-1} divided by the square of halfthickness of plates l^2. The experimental curves are fairly well fitted by the equation $\bar{u} = f(\mathrm{Fo}, b) = f\left(k_e \cdot \frac{h}{l^2}, b\right)$ with $k_e = 0.75 \cdot 10^{-11}$ m²/s and b = 15 (cf. Fig. 28).

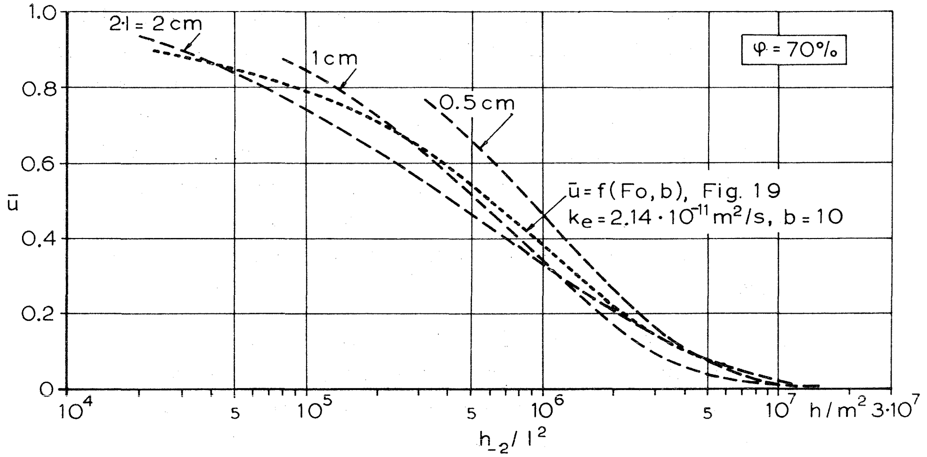


Fig. 30. Moisture content ū plotted against corrected time h_{-2} divided by the square of halfthickness of the plates l^2. It can been seen that the drying process is dependent on the thickness of the plates.

drying test was probably insignificant, but the carbonation effect was clearly evident after the plates had reached the point of equilibrium. Both effects were ignored in these preliminary tests.

6.664. Conclusions

On the basis of the preliminary tests presented in Paragraphs 6.661, 6.662, and 6.663, the following conclusions can be drawn:

1) The moisture conductivity of concrete is dependent on the moisture content.

2) The moisture conductivity of concrete can have a maximum value (Cf. Figs. 21, 23, 28). Within the moisture content range $C_o \cdots C_e = \max \cdots 0$, moisture conductivity possibly depends on moisture content as follows: when moisture content is high, the moisture transfer in the concrete is probably mostly macroscopic (i.e. water transfer in liquid form) and the moisture conductivity is smaller than when the moisture content is somewhat less, and both macroscopic and molecular moisture transfer dominate simultaneously. When the molecular transfer (i.e. water transfer in vapour form) alone begins to dominate, i.e. when the moisture content has decreased below a certain limit, moisture conductivity decreases continuously as moisture content drops. The decrease in moisture conductivity is probably due to the retained water being more fixed than the water which has already escaped, because of adsorptive forces (viscosity increases), shrinkage (pore size decreases), and an increase in concentration of the water solution (viscosity increases) (Cf. Chapter 9).

3) The simple theory of diffusion type with constant moisture conductivity does not describe the decrease in the average moisture content $\bar{u}$ of a concrete body in the whole moisture content range $C_o \cdots C_e = \max \cdots 0$.

4) The simple theory of diffusion type with a constant average moisture conductivity $\bar{k}$ seems adequately to describe the

decrease in average moisture content $\bar{u}$ of a concrete body only if a) the body is rather dry at the beginning of the drying process, i. e. if the concrete body has not been stored in water, and fixation drying has decreased its moisture content, or b) if the wet concrete loses only a relatively small part of its initial moisture content during the drying process, for example when the relative humidity of the ambient air is high (drying potential small = saturation deficit small)

5) It seems possible that the diffusion type theory with concentration - dependent moisture conductivity, can describe the drying process of concrete.

6) Moisture conductivity k, calculated by means of the diffusion theory, varies during drying of the same concrete and concrete mortar. (Cf. Figs. 21, 23, 28).

   a) An ordinary concrete w/c = 0.67, cp/a = 1:2.4
      $k = 1.5 \cdots 3.0 \cdot 10^{-11}\ \mathrm{m^2/s}$
      $C = 135 \cdots 50\ \mathrm{kg/m^3}$

   b) A magnetite concrete, w/c = 0.67, cp/a = 1:1.9
      $k = 1.3 \cdots 3.0 \cdot 10^{-11}\ \mathrm{m^2/s}$
      $C = 170 \cdots 65\ \mathrm{kg/m^3}$

   c) A concrete mortar, w/c = 0.56, cp/a = 1:1.2
      $k = 3 \cdots 50 \cdot 10^{-11}\ \mathrm{m^2/s}$
      $C = 215 \cdots 55\ \mathrm{kg/m^3}$

   d) A concrete mortar, w/c = 0.56, cp/a = 1:1.2
      $k = 1 \cdots 9 \cdot 10^{-11}\ \mathrm{m^2/s}$
      $C = 190 \cdots 50\ \mathrm{kg/m^3}$
      $k = 2 \cdots 15 \cdot 10^{-11}\ \mathrm{m^2/s}$
      $C = 190 \cdots 95\ \mathrm{kg/m^3}$

7) Much work is necessary before a reliable quantitative prediction can be made of the drying process of a certain concrete under certain conditions.

7. FIXATION DRYING

7.1. INTRODUCTION

Fixation drying, which means the diminution of the evaporable water content or moisture in concrete by reason of the hydration of cement, is a well-known phenomenon, normally termed "autogenous desiccation" [40], and at one time also "self-desiccation" [10] [41]. In studying the drying of concrete, it seems preferable to refer to the phenomenon as "fixation drying"; this accordingly means a decrease in the evaporable water, or an increase in the non-evaporable water in cement paste following hydration. Consequently, fixation drying is related to one of the main problems of cement chemistry [15]. However, no adequate quantitative theory of hydration kinetics as a function of time, temperature and moisture conditions has been put forward from the viewpoint of fixation drying. Nevertheless, the suggestions made by Powers [40] and Mills [42] offer a good possibility of finding a theory suitable for the computational treatment of fixation drying. A tentative theory of this kind is presented in Paragraph 7.3.

Curing under sealed conditions has been selected as the standard hydration condition of reference, since it can be assumed that the major part of the hydration process of concrete structures occurs under conditions which are approximately sealed, at least before the forms are removed.

7.2. FIXATION DRYING OF A FINNISH PORTLAND CEMENT

Determination of the amount of fixed water was effected by measurement of the moisture content on drying specimens of cement paste at 105 °C after stated intervals of curing time under sealed conditions at 20 °C. Curing under sealed conditions was accordingly chosen as a standard condition of reference.

Cement pastes with water-cement ratios of 0.3, 0.4, 0.5 (not corrected for bleeding) were poured into small plastic bags (6 cm by 9 cm), which were sealed with strong adhesive tape immediately after the pouring. The bags were further wrapped in plastic sheets to prevent evaporation. As bleeding was substantial in the paste w/c = 0.5, the water-cement ratio after correction for bleeding will be somewhat smaller. The average net weight of the pillow-shaped specimens was about 15 g, and the average size about 5 cm x

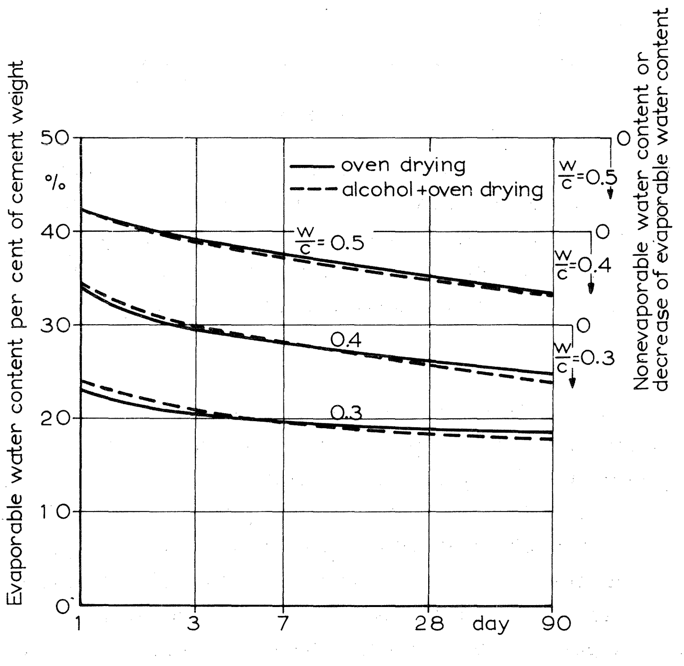


Fig. 31. Mutual relationship between the evaporable water and non-evaporable water in some cement pastes determined at 105 °C after curing times 1, 3, 7, 28, and 90 days under sealed conditions at 20 °C.

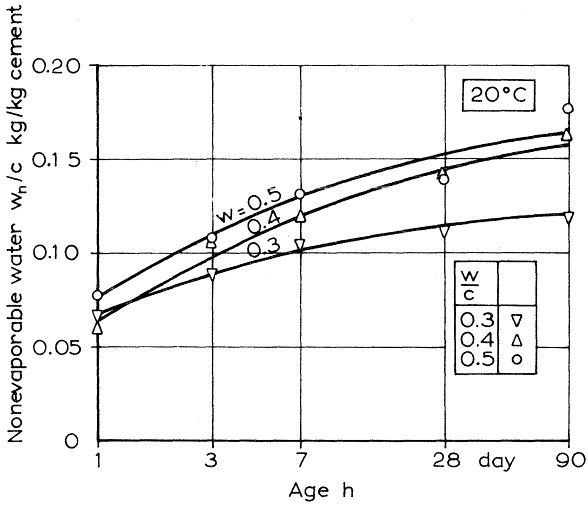


Fig. 32 a. Mean values of the non-evaporable water content determined in the tests, the results of which are presented in another form in Fig. 31. The curves are the M-function curves in best accordance with the experimental points (Cf. Fig. 32 b).

5 cm x 0.5 cm. Some of the specimens were put in the oven immediately after the completion of pre-curing and stripping. Another portion was first ground and desiccated with absolute alcohol to stop hydration before the oven-drying process. Figure 31 shows the mean values obtained with 90 specimens of cement paste. The average variation range of the concents of evaporable water and non-evaporable water, presented in Fig. 31, was 2.6 per cent units at the different stages of determination. The same results are shown in another form in Fig. 32 a.

7.3. TENTATIVE THEORY OF FIXATION DRYING, BASED ON KNOWLEDGE OF THE HYDRATION PROCESS.

The decrease in evaporable water (moisture), or the increase in non-evaporable water Δw due to hydration can be written in the simple form

$$\begin{cases} \Delta w/c = M \cdot \gamma \cdot w_n^{max}/c \text{ (water kg/cement kg)} \\ \gamma = f \text{ (cement, w/c, moisture)} \end{cases} \quad (1)$$

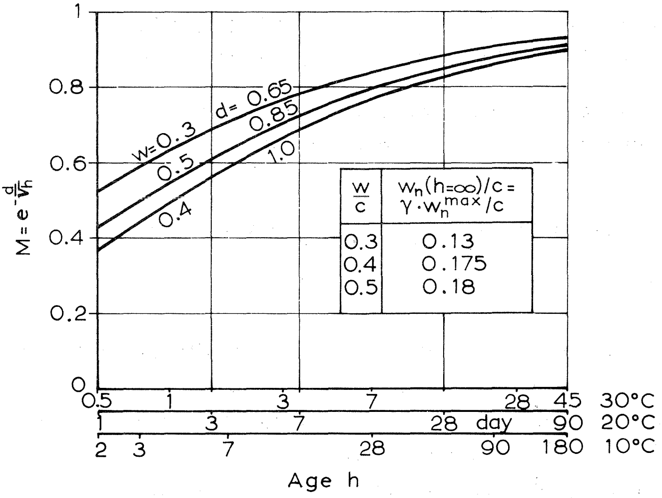
where c is the cement content, M the maturity factor for fixation drying, γ a parameter (≤ 1) dependent, at a given temperature, on the cement, water-cement ratio, and moisture conditions during hydration. w_n^{max}/c is the maximum non-evaporable water content in a cement paste after the total hydration of pure and fresh Portland cement.

According to Rastrup [43], the maturity factor M for a given temperature can be written as follows:

$$M = e^{-d/h^{\frac{1}{2}}} = \exp(-d/h^{\frac{1}{2}}) \quad (2)$$

where h is the time of hydration, and d the parameter depending on cement, water-cement ratio, and moisture conditions during hydration. From the experimental results presented in Paragraph 7.2, the w_n/c-age curves and M-age curves as well as the corresponding $w_n\ (h = \infty)/c = \gamma\ w_n^{max}/c$ and d-values, for a Finnish Portland cement hardened under sealed conditions at 20 °C are shown in Figs. 32. It can be seen, with the aid of the information presented in Fig. 32 b, that the decrease in the evaporable water content $\Delta w/c$ can be calculated from Equation (1). The effect of temperature is also given in Fig. 32 b (horizontal scales), in accordance with the theory stated below.

The effect of temperatures within the range 4.4 to 100 °C on the rate of hydration of cement can be expressed by means of the Arrhenius equation, giving the dependence of kinetic reaction rate K upon reaction temperature T:



$\frac{w}{c}$	$w_n(h=\infty)/c = \gamma \cdot w_n^{max}/c$
0.3	0.13
0.4	0.175
0.5	0.18

Fig. 32 b. M-factor as the function of curing time (age) and temperature (10, 20, 30 °C) under sealed conditions.

$$K = \text{const} \cdot \exp(-E/T), \tag{3}$$

in which E represents the "activation energy" divided by the gas constant, and T is the absolute temperature [15]. The rate of hydration at a given temperature may, for practical purposes, be stated in terms of the maturity factor as [40]:

$$dM/dh = K \cdot f(M, w/c), \tag{4}$$

where h is time and K is the Arrhenius specific reaction rate. The function f (M, w/c) is unknown, but is undoubtedly a complex one. For a cement paste of given w/c, time h required to reach a given degree of hydration, M, is inversely proportional to K. Consequently,

$$\frac{h}{h_{ref}} = \frac{K_{ref}}{K} = \exp(E/T - E/T_{ref}) \tag{5}$$

The reference conditions employed here are sealed curing at 20 °C = 293 °K. According to the old Van't Hoff rule of reaction kinetics (1884), a rise of 10 °C, near ordinary room temperatures, will increase the reaction rate by two or three times. Rastrup [43] has shown that in cement hydration (heat evolution), the increase in the reaction rate is doubled for a temperature rise of 10 °C, at least at temperatures below 40 °C. On this basis, E in Equation [5] can be evaluated as follows:

For $T = 283\,^\circ K$, $T_{ref} = 293\,^\circ K$

$$2 = \exp(E/283 - E/293); \quad 1.21 \cdot 10^{-4} \cdot E = 0.693$$

$$E = 5730\ (^\circ K)$$

For $T = 303\,^\circ K$, $T_{ref} = 293\,^\circ K$

$$\tfrac{1}{2} = \exp(E/303 - E/293); \quad -1.13 \cdot 10^{-4} \cdot E = -0.693$$

$$E = 6130\ (^\circ K)$$

Consequently, for the range 10 ··· 30 °C, a value of 5900 would be adequate for practical purposes. We finally obtain a group of equations

$$\left\{\begin{array}{l} M = \exp(-d/h^{\frac{1}{2}}_{293}) \\ h_{293} = h_T \cdot \exp(5900/T - 5900/293) \\ T = 283^\circ \cdots 303\,^\circ K\ (10\,^\circ C \cdots 30\,^\circ C) \end{array}\right. \qquad (6)$$

For a Finnish Portland cement, we have, as presented in Fig. 32 b

w/c	d
0.3	0.65
0.4	1.0
0.5	0.85

If one wishes to calculate the moisture content of concrete at a stated curing time, under sealed conditions and at a stated temperature, C_0, this is easily accomplished by use of the following simple equation

$$C_o = Q_c \cdot (w/c - \Delta w/c) \text{ kg/m}^3, \qquad (7)$$

in which Q_c is the cement content of concrete kg cement/m^3 concrete, w/c the water cement ratio kg water/kg cement, and (Equation (1))

$$\Delta w/c = M \cdot w_n (h = \infty)/c \qquad (8)$$

For instance, as regards Finnish concrete, $w/c = 0.5$, $Q_c = 350$ kg/m^3, the approximate moisture content C_o after 7 days of sealed curing at 20 °C (293 °K) is

$$C_o = 350(0.5 - 0.73 \cdot 0.18) = 130 \text{ kg/m}^3,$$

after application of the information given in Fig. 32 b for determination of $\Delta w/c$.

To the best of the author's knowledge, the effects of moisture (evaporable water content) on the hydration of cement, i.e. on the fixation drying, are

1) The hydration process virtually ceases when the moisture content of cement paste is in equilibrium with a relative humidity of the air of 80 %. (Cf. Chapter 4).

2) The hydration process has sufficient water to reach the maximum ultimate degree of hydration under sealed conditions when the water-cement ratio is greater than about 0.45. (Cf. Chapter 4). If the water cement ratio is less, the rate of hydration and the ultimate degree of hydration will be lowered. (Cf. table in Fig. 32 b).

3) The rate of hydration is highest when concrete is water-saturated (stored in water) [15].

4) Under sealed conditions, the rate of hydration is highest during the first two-three days at ordinary temperatures [15]; the main part of the hydration process is completed during the first week.

On these grounds, we can conclude that as soon as concrete is exposed to dry air, hydration or fixation drying ceases very quickly, and thus the increase in the amount of fixed water is relatively small when the concrete structure under examination is cured for some days under sealed conditions (i.e. before form removal) and is comparatively thin. Consequently, on the basis of present day knowledge it is reasonable to apply an approximation for such concrete structures: practically no fixation drying occurs during the drying (Cf. Paragraph 6.63). If, on the other hand, the concrete structure exposed to drying is massive, it is reasonable to assume that on an average the fixation drying takes place under what are approximately sealed conditions. The theory of and the information concerning the drying process presented in Chapters 6 and 7 give some idea of which assumption seems more reasonable, and which C_0-value will be the most suitable. Basic research should be carried out to clarify the hydration process as a function of moisture content field in cement paste and concrete.

8. ON THE INFLUENCE OF MOISTURE CONTENT ON CONCRETE PROPERTIES

8.1. INTRODUCTION

It can generally be stated that a moist material has properties which differ from those of the corresponding dry material. This statement contains nothing new, but the influence of moisture is often neglected cases where such influence is very significant. The important effect of moisture on the strength of concrete has surprisingly enough too often been assumed as of minor significance, although the strength is considered to be the main criterion of concrete quality.

The first article known to the author on the differences in the characteristics of wet and dry concrete was that published by Fitzpatrick [44] in 1946. It is worth-while to quote the first part of this article: "Reinforced concrete design is based upon a number of assumptions that do not hold, in many cases, during the working life of concrete. There seems to be need for an exhaustive experimental investigation over a range of concrete mixes, as to the physical characteristics when tested in various conditions from perfectly dry to fully saturated. It is broadly known that: 1) concrete expands substantially (and reversibly) by moisture absorption; 2) the strength (in tension and compression, and shear) falls off as the amount of absorbed moisture increases; 3) the modulus of elasticity becomes lower as the amount of absorbed moisture increases; 4) at the same time, bond resistance tends to increase, in saturated as compared with dry concrete; 5) the elastic behaviour, and the creep (or plastic flow) are different in the case of saturated or partly saturated concrete". Fitzpatrick put forward that the saturation of dry concrete decreases the tensile strength and the modulus of elasticity by approximately 20 per cent. The "dry concrete" was probably "air dry". Terzaghi [45] made some comments on the

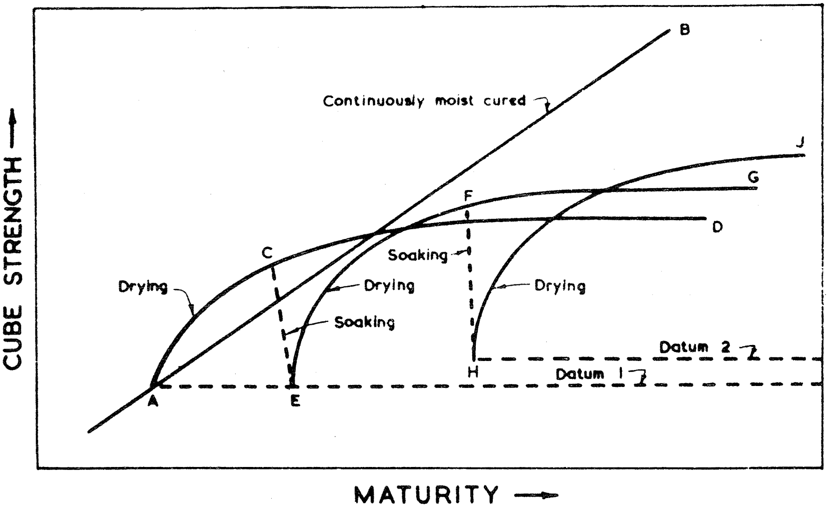


Fig. 33. Mills' [42] figure of the principle involved. "Hypothetical variation of strength for concrete cubes subjected to cycles of wetting and drying".

article by Fitzpatrick. The first extensive study to clarify the dependence of strength on moisture known to the author was Mills' report, published in 1960 [42]. He crystallized his ideas in Figs. 33 and 34, which are reproduced from Mills' report [42]. "The Datum line represents the minimum strength of concrete in which water curing has been interrupted. It is this strength which may be taken as a figure of merit representing the quality of concrete". Mills thus selected water curing as the standard curing method of reference. He found that the relationship between the strength values of a continuously water cured concrete and the same dry concrete (110 °C) was even 1:1.7. His tests showed also that the change in strength with moisture content is reversible.

The dependence of shrinkage on moisture is well-known, but the effect of moisture on creep is not so clear. L'Hermite [46] pointed out that a wet concrete may creep ten times as much as

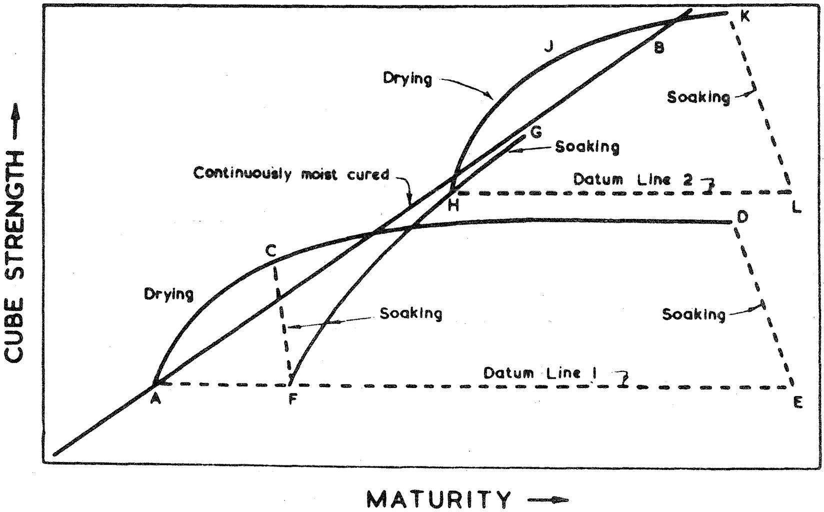


Fig. 34. Mills' [42] figure of the principle involved. "Hypothetical variation of strength for concrete cubes subjected to drying, prolonged re-wetting and re-wetting".

a dry one. Glucklich and Ishai have studied the Creep Mechanism in Cement Mortar [47] and their results showed a close connection between the evaporable water content (moisture) of the specimen on one hand and shrinkage, instantaneous deformation, and creep on the other. The most outstanding phenomena observed were the mutual dependence of the evaporable water and creep, and the almost complete disappearance of creep in specimens from which had been removed most of the evaporable water. One of the main conclusions drawn from the tests of Glucklich and Ishai was that the mechanism of creep is interpreted in terms of water migration within the voids of the specimen, owing to the action of the external load.

In 1963, Campbell-Allen and Thorne presented a report on the thermal conductivity of concrete [48], and concluded that the thermal conductivity of any given concrete varies in an approximately linear fashion with moisture content; the higher the conductivity of a concrete, the greater will be the percentage drop in conductivity resulting from the loss of a given percentage by volume of water.

On the basis of these publications, and of some others, we can conclude that knowledge of moisture content and its distribution (moisture gradient) is of primary importance in concrete technique.

The following chapter gives the results of some tests performed in this laboratory.

8.2. SOME RESULTS CONCERNING THE EFFECT OF MOISTURE CONTENT ON THE PROPERTIES OF FINNISH CONCRETE

8.21. Compressive strength

The effect of moisture content on concrete strength has been treated extensively by Mills [42]. To discover whether the effects are of the same order of magnitude that shown by the findings of Mills, an investigation was made with a test series.

Two concretes were used in the investigation: an ordinary one, w/c = 0.67, cp/a = 1 : 2.4, and a magnetite concrete, w/c = 0.67, cp/a = 1 : 1.9; the maximum particle size of the aggregate was 16 mm. The concretes were the same as those used in the tests presented in Paragraph 6.661. One beam $10 \cdot 15 \cdot 80$ cm^3 of both concretes was available. These beams were four years old at the start of the test, and were then stored continuously in the climate room: RH 95 ··· 100 %, 20 °C. Six prisms of dimensions $10 \cdot 10 \cdot 15$ cm^3 were cut from the beams. 6 + 6 prisms thus obtained were treated and tested as follows:

a) 2 + 2 of the prisms were kept in the climate room, RH 95 ··· 100 %, 20 °C, for two days after the cutting. The specimens were then wrapped in a plastic sheet, excluding the end surfaces (10 cm by 10 cm), which were carefully covered with an ordinary sulphur-clay capping. Load was applied to one hour later after the capping procedure. The capping was

Table 5.

The effect of moisture content on the compressive strength of concrete stored before the tests for four years RH 100 %, 20 °C.

Concrete	Stored at 20 °C and RH 100 %			Dried at 105 °C			Wet		
	Moisture	Strength		Moisture	Strength		Moisture	Strength	
	kg/m^3	kp/cm^2	Ratio	kg/m^3	kp/cm^2	Ratio	kg/m^3	kp/cm^2	Ratio
Ordinary	130	389	1	0	472	1.21	140	273	0.70
Magnetite	158	329	1	0	414	1.26	183	258	0.78

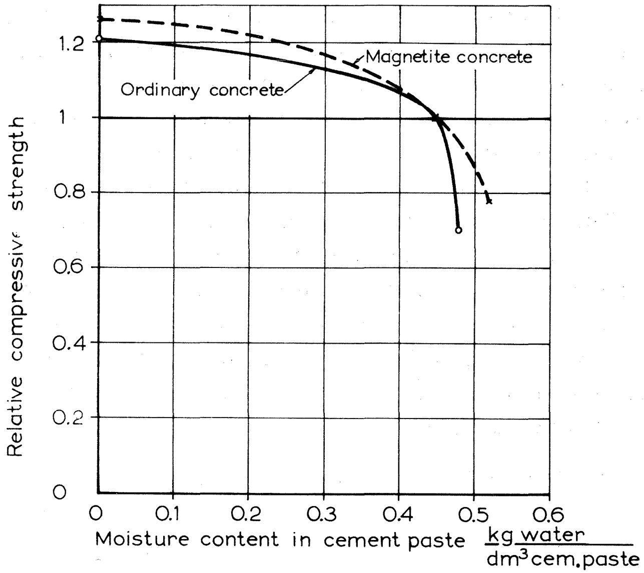


Fig. 35. Effect of moisture content on compressive strength of some concretes. Cf. Table 5.

considered necessary to ensure the smoothness and the similarity of the test surfaces.

b) 2 + 2 of the prisms were dried in an oven at 105 °C after equilibrium had been attained. Following this, the procedure was exactly the same as that applied for the a)-specimens (wrapping, capping, loading).

c) 2 + 2 of the prisms were dried as described in point b). After drying, they were completely immersed in water, and kept in a vacuum box for 48-hours. The pressure was about 10 torr. The wetting was so complete, by reason of the vacuum treatment, that the moisture content in the prisms did not increase during one month's storage in water after the vacuum treatment. The testing procedure (wrapping, capping, loading) was exactly the same as for the a)- and b) - specimens.

The results are presented in Table 5 and in Fig. 35. The values given are averages of the two test values. The average variation range of each two test values was 18 kp/cm^2, and the maximum range 35 kp/cm^2. The relationship between the strength values of completely wet concrete and completely dry concrete was about 1 : 1. 7. The results obtained from the tests support those published by Mills [42].

8.22. Sound velocity

The effect of moisture content of the sound velocity of concrete was investigated with the aid of two concrete prisms (10 · 10 · 50 cm^3, 12 · 12 · 40 cm^3, ordinary concrete compressive strength about 250 ··· 350 kp/cm^2), which were stored in a room (20 °C, RH 25 ··· 70 %) for about one year. The moisture content of the prisms was varied as follows:

a) Drying (105 °C)
b) Water storage (20 °C) 6 months
c) Drying in a room (20 °C, RH 25 ··· 70 %) 8 months

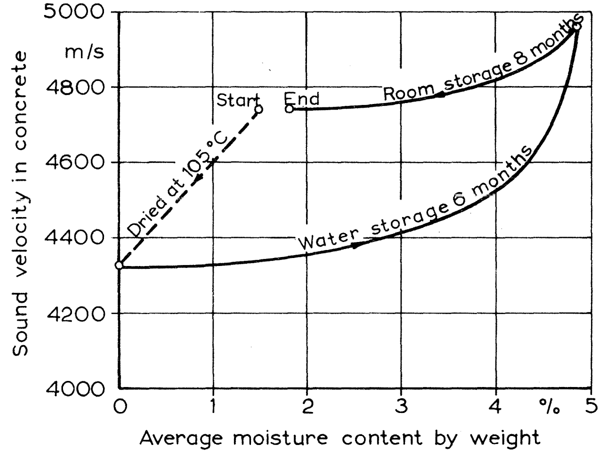


Fig. 36. Relationship of sound velocity and average moisture content of concrete beams. Before the start of the tests, the beams had been stored in a room (20 °C, RH 25 ··· 70 %) for about one year. One weight-% = 2.4 volume-%.

The sound velocity (ultrasonic pulse) was measured by means of an ordinary ultrasonic materials tester (Cawkell Research & Electronics, England, Type UCT 2). The results, given as averages, are to be found in Fig. 36. The results of more extensive tests have been presented in reports [49] [50].

8.23. Shrinkage

The relationship between the moisture content and shrinkage of concrete is one of the phenomena most subjected to study in concrete technique. However, the principle concerning this relationship is presented in Fig. 37 [51].

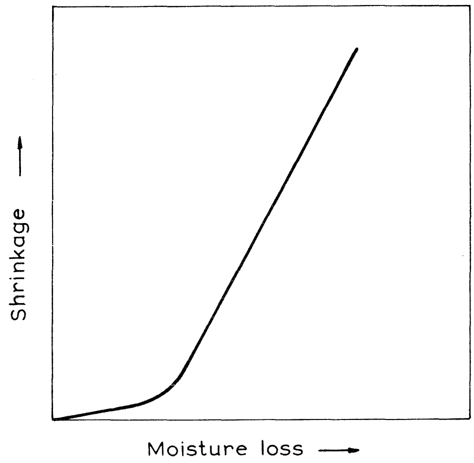


Fig. 37. Relationship of shrinkage and moisture loss of concrete. A figure illustrating the principle involved.

8.24. "Hardness" of a concrete surface

Non-destructive testing with a rebound hammer (Prüfhammer) has indicated that there exists a relationship between the amount of rebound (rebound number) of a light steel bar or hammer ("shot" on concrete with the aid of a steel spring) and other concrete properties such as compressive and flexural strength, and the modulus of elasticity. It is concluded that the instrument may prove a useful supplement in standard compressive strength tests in the hands of persons skilled in its use, and in the interpretation of results. One of the main reasons which has caused a great deal of difficulty in practical interpretation of the results of the rebound hammer has been the effect of the moisture content of a concrete surface on the rebound number. Fig. 38 shows the results obtained in this laboratory [52]. The results indicate the influence of the drying time (1, 2, 6, 24 hours) of 20 cm concrete cubes (or of the

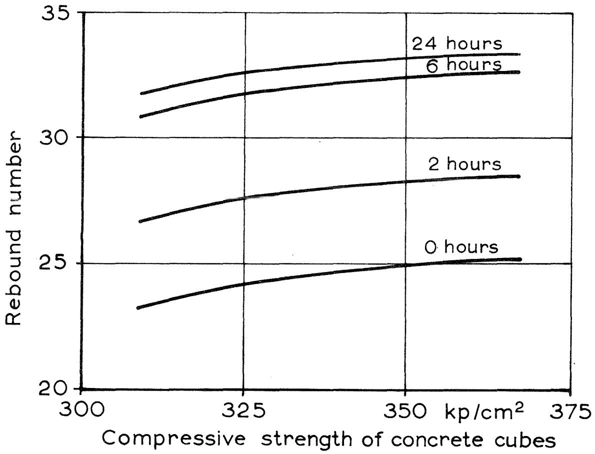


Fig. 38. Effect of moisture content of concrete surface on rebound number (or on "hardness" of concrete surface) [52].

moisture content of a concrete surface) in room air, and stored for a lengthy period in water before testing. During the testing, a load of 5 kp/cm^2 was applied to the cubes. Dependent upon the compressive strength-rebound number relationship, the change in rebound number from 24 to 33 corresponds to an increase of approximately 100 to 150 kp/cm^2 in the compressive strength.

9. SOME GENERAL REMARKS

In the previous text, it has been assumed that water constitutes the movable liquid in concrete. However, if we delve a little deeper into the movement of liquid in concrete, it becomes apparent that strictly speaking a water solution moves in the pores of concrete, viz. water plus dissolved cement minerals. In the drying of concrete, this means that before the water evaporation process (which means an increase in the concentration of the solution), the solution - not the pure water - moves in concrete. This will introduce changes in the moisture conductivity of concrete. According to Powers & Mann & Copeland [53], Verbeck has shown in his unpublished work that soluble materials reduced the rate of flow through cement paste specimens more that could be accounted for by the ordinary effects of solutes on the viscosity of water. Although in Verbeck's tests the effect was caused by the outside water penetrating concrete, the same will in all probability be true in the drying process, in which it is mainly the "original" water in the concrete which moves. It is, nevertheless, probable that in this case the effect will be less.

In the report of Powers et. al. mentioned above two interesting and important results are presented: "All evaporable water appears to be mobile" and "Within the range of paste porosity included in this report, part of the evaporable water, perhaps all of it is adsorbed. Consequently, the viscosity is higher than that of free water. (Also viscosity is increased by the presence of solutes)".

Preliminary studies of thermal moisture transfer have been made by Powers [57] and Swenson & Sereda [58].

Studies of pore size distribution in concrete mortars have been carried out by Kroone & Crook [60] [61] using the method of mercury penetration. This is one way to clarify the highly probable mutual dependence between moisture conductivity, equilibrium moisture content, and pore size distribution.

The phenomena mentioned above, along with others mentioned earlier, show that much research work is needed before a good picture of the drying of concrete is at hand.

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Sähköteknillinen laboratorio *Laboratory of Electrical Engineering*
Radioteknillinen laboratorio *Laboratory of Radio Engineering*
Vuoriteknillinen laboratorio *Laboratory of Mineral Dressing*
Teknillisen fysiikan laboratorio *Laboratory of Technical Physics*

SARJA III — RAKENNUS *SERIES III — BUILDING*

Rakennusteknillinen laboratorio *Laboratory of Building Technology*
Betoniteknillinen laboratorio *Laboratory of Concrete Technology*
Rakennustaloudellinen laboratorio *Laboratory of Building Economy*
Sillanrakennus- ja staattinen laboratorio *Laboratory of Statics and Bridge Building*
Tielaboratorio *Laboratory of Road Construction*
Geoteknillinen laboratorio *Laboratory of Soil Mechanics*
Paloteknillinen laboratorio *Laboratory of Fire Technology*
Lämpöteknillinen laboratorio *Laboratory of Heating Technology*
Maanjakoteknillinen laboratorio *Laboratory of Land Consolidation*

SARJA IV — KEMIA *SERIES IV — CHEMISTRY*

Kemiallinen laboratorio *Chemico-technical Laboratory*
Elintarviketeollisuuslaboratorio *Laboratory of Food Industry*
Turve- ja öljyteknillinen laboratorio *Laboratory of Peat and Oil Research*
Tekstiiliteknillinen laboratorio *Laboratory of Textile Technology*
Panimolaboratorio *Laboratory of Brewing*
Graafinen laboratorio *Graphic Arts Research Laboratory*