

STEADY STATE EFFECTIVE THERMAL CONDUCTIVITY OF WETTED CLOSED POROUS SYSTEM

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by

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ABSTRACT

In this work the steady state heat flux through a closed wetted layer of porous material is studied for the case when the moisture distribution is dependent upon a temperature gradient as well as upon gravity. The basic transport equations of the system are formulated so that the moisture and temperature fields - which must both be known in order to calculate the heat flux through the layer - are presented in terms of the following four quantities: the local value of the effective thermal conductivity of the material, a quantity called the capillary thermal gradient coefficient which is related to that part of the moisture content distribution which is caused by the influence of temperature on surface tension, a quantity called the evaporation thermal gradient coefficient which is related to that part of the moisture content gradient which is caused by evaporation of liquid, diffusion and condensation of the vapour, and capillary return of the liquid, and a quantity which describes the relationship between the moisture content and the capillary potential. All these four quantities are functions of both moisture content and temperature. Expressions, based partly on experimental work, are presented for these four quantities. The transport equations are solved numerically and the moisture content fields so obtained are compared with experimental measurements.

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LIST OF SYMBOLS

b	efficiency coefficient of the cycle of evaporation, diffusion, and condensation of vapour, dimensionless
D	diffusivity, m^2/s
D^T	diffusivity induced by a temperature gradient, m^2/s
c	moisture content, kg water/kg dry material
$C_{\text{cap},T}$	capillary coefficient, at temperature T, m^3/s
$C_{\text{cap},20^\circ\text{C}}$	capillary coefficient, at 20°C , m^3/s
C_h	a constant which relates the capillary drain curve to the capillary rise curve, dimensionless
f_m	mass flux, $\text{kg}/\text{m}^2\text{s}$
f_q	energy flux, W/m^2
h	height of capillary rise or drain from the free liquid surface, m or cm
k_a	molecular thermal conductivity of air, $\text{W}/\text{m}^\circ\text{C}$
k_{cp}	thermal conductivity of the continuous phase in dispersion, $\text{W}/\text{m}^\circ\text{C}$
k_d	equivalent thermal conductivity; the contribution of the cycle of evaporation, diffusion, and condensation of vapour to the effective thermal conductivity of air saturated with water vapour, $\text{W}/\text{m}^\circ\text{C}$
k_{dp}	thermal conductivity of the discontinuous non-solid phase, in dispersion, $\text{W}/\text{m}^\circ\text{C}$

k_e	effective thermal conductivity, $W/m^{\circ}C$
$k_{exp.,dry}$	measured thermal conductivity of a completely dry material, $W/m^{\circ}C$
$k_{exp.,wet}$	measured thermal conductivity of a fully wetted material, $W/m^{\circ}C$
k_g	gas phase thermal conductivity, $W/m^{\circ}C$
k_l	liquid phase thermal conductivity, $W/m^{\circ}C$
k_s	solid phase thermal conductivity, $W/m^{\circ}C$
k_{ser}	series solid conductivity, $W/m^{\circ}C$
K	permeability, m^2
K_{nw}	permeability of the non-wetting phase, m^2
K_r	relative permeability, dimensionless
K_{rnw}	relative permeability of the non-wetting phase, dimensionless
K_{rw}	relative permeability of the wetting phase, dimensionless
l	thickness of layer, m
L_{ik}	coefficient in flux - force equations associated with the flux i induced by a driving force in phase k , see the List of Fluxes at the end of this list
p_c	capillary pressure, N/m^2
r	radius of a capillary tube, m
T	temperature, $^{\circ}C$ or K
T	tortuosity, dimensionless
T_r	relative tortuosity, dimensionless

T_{rw}	relative tortuosity of the wetting phase, dimensionless
T_{rnw}	relative tortuosity of the non-wetting phase, dimensionless
W	velocity of the capillary flow, m/s
x	distance, m
X_k	driving force in the phase k in flux - force equations, see the List of Fluxes at the end of this list.
$X_{l \text{ EDC}}$	driving force in the liquid phase for the return liquid flow in the cycle of evaporation, diffusion, and condensation of vapour, and return liquid flow, m / (kg water/kg dry material)
z	vertical distance of the point studied from the free liquid surface, m
α	thermal diffusivity, m^2/s
γ_1, γ_2	skewness and excess of a distribution, respectively, dimensionless
δ	thermal gradient coefficient, (kg water / kg dry material) / $^{\circ}C$
δ_{cap}	capillary thermal gradient coefficient, (kg water / kg dry material) / $^{\circ}C$
δ_{EDC}	evaporation thermal gradient coefficient, (kg water / kg dry material) / $^{\circ}C$

δ_{EDC}^*	local evaporation thermal gradient coefficient, (kg water/kg dry material)/°C
δ_{EDC}^{*s}	specific local evaporation thermal gradient coefficient, (kg water/kg dry material)/m°C
ϵ	volume fraction of non-solids, dimension- less
ϵ_g	volume fraction of the gas phase, dimensionless
ϵ_s	volume fraction of the solid phase, dimensionless
ϵ_w	volume fraction of water, dimensionless
ϵ_{wnb}	volume fraction of non-bound water, dimensionless
θ	wetting angle, dimensionless
$\kappa_2, \kappa_3, \kappa_4$	cumulants, dimensionless
λ	latent heat of vaporization, J/kg
μ	viscosity, N s/m ²
ξ	(in chapter 6), deviate of a distribution, dimensionless
ρ	density, kg/m ³
σ	(in chapter 2), entropy
σ	surface tension, N/m , or mN/m (dyne/cm)
τ_r	relaxation time for heat conduction
τ_{rm}	relaxation time for liquid flow
χ	weighting function, dimensionless

Ψ	liquid saturation fraction, dimensionless
Ψ_e	effective saturation fraction, dimensionless
Ψ_h	saturation fraction which is a parameter in the expression for the calculation of the capillary rise or drain heights, dimensionless, see equations (6.5) and (6.6)
Ψ_r	residual saturation fraction, dimensionless

The Subscripts of f, L, and X.

0	solid phase
1	liquid phase
2	vapour phase
3	non-condensable gases
m	mass
q	energy

List of Fluxes

$L_{qq}X_q$	flux of energy induced by a temperature gradient.
$L_{q1}X_1$	flux of energy induced by a moisture content gradient.
$L_{q2}X_2$	flux of energy induced by a vapour concentration gradient.
$L_{q3}X_3$	flux of energy induced by a gradient of non-condensable gases.
$L_{1q}X_q$	flux of liquid induced by a temperature gradient.
$L_{11}X_1$	flux of liquid induced by a moisture content gradient.
$L_{12}X_2$	flux of liquid induced by a vapour concentration gradient.
$L_{13}X_3$	flux of liquid induced by a concentration gradient of non-condensable gases.
$L_{2q}X_q$	flux of vapour induced by a temperature gradient.
$L_{21}X_1$	flux of vapour induced by a moisture content gradient.
$L_{22}X_2$	flux of vapour induced by a vapour concentration gradient.
$L_{23}X_3$	flux of vapour induced by a concentration gradient of non-condensable gases.

$L_{3q}X_q$ flux of non-condensable gases induced
by a temperature gradient.

$L_{31}X_1$ flux of non-condensable gases induced
by a moisture content gradient.

$L_{32}X_2$ flux of non-condensable gases induced
by a vapour condensation gradient.

$L_{33}X_3$ flux of non-condensable gases induced
by a concentration gradient of non-
condensable gases.

CHAPTER 1

INTRODUCTION

The objective of this work is to develop a method for the calculation of the steady state heat flux passing through a layer of a wetted porous material which is isolated from the environment with respect to mass transfer but which is subjected to a temperature gradient. The surface temperatures are specified to be below the boiling point of the liquid but above its freezing point.

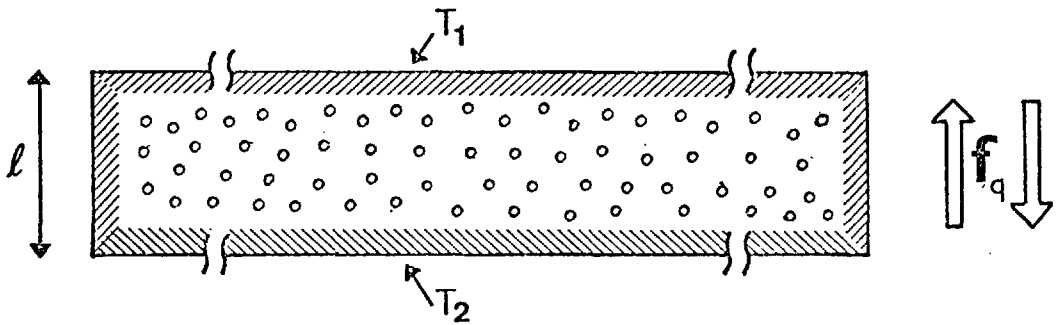


Fig. 1.1. Schematic diagram of the porous system.

A porous material is defined in this work as a material in which the radii of the pores and capillaries are greater than 10^{-7} m. This is the same definition as that used by Luikov (L4, p.220) who classified a material as capillary porous if the pore radii are less than 10^{-7} m.

Vos (V3) used the limit of 0.5×10^{-7} m to distinguish between macropores and micropores. The choice of this radius is based on the relationship between capillary radius and reduction of vapour pressure above the meniscus of a liquid surface known as Thomson's law.

$$p' = p_0 \exp \left(- \frac{2\sigma}{r\rho RT} \right) \quad (1.1)$$

If the capillary radius is greater than about 10^{-7} m and if the liquid is water the quotient p'/p_0 is very close to unity so that vapour pressure is not influenced by capillary radius. The quotient p'/p_0 is not greatly dependent upon temperature.

In equilibrium, the vapour pressure in the surrounding air must equal the vapour pressure above the liquid menisci in the pores. Therefore in a porous material, defined as above, the maximum moisture content which can be achieved by absorption from air at uniform temperature is negligible, even if the relative humidity of the air is very near to 100 per cent. The absence of absorbed liquid simplifies the analysis of the mass transfer flux.

A moist porous material is a multiphase and multi-component system. Typically there are three phases, a solid matrix, a liquid phase, and a gas phase which is usually a mixture of inert gas and vapour. Transfer of moisture occurs in the pore space not occupied by the solid matrix.

A possible method of calculating the energy and mass flows in a moist porous material would be to solve the equations which express the conservation of mass, momentum and energy for each location. The solution would give the temperature and flow fields in all phases and for all components. This might be called a microscopic approach as it deals with purely local quantities.

The irregular and complicated internal geometry of a porous material makes the solution of these microscopic equations a very complicated - if not practically impossible - task. The problem can be simplified by defining macroscopic quantities which are mean values over volume elements. The dimensions of such volume elements are large in comparison with those of the fine structure elements of the material such as granules and pores. A volume element can be called a unit cell of a porous material. To each volume or unit element a value of the thermal conductivity can be assigned which includes all modes of heat transfer, and which may thus be called the effective thermal conductivity. For one-dimensional transfer it is defined as follows in this work:

$$f_q = - k_e \frac{\Delta T}{\Delta x} \quad (1.2)$$

where f_q is the heat flux in the x-direction and Δx is the thickness of the unit element or layer. Thus the effective thermal conductivity in this work is not defined for a point but for a unit element of the material. In a wetted porous material this quantity is a function of the properties of the materials present and is a non-linear function of the moisture content and of temperature.

In order to calculate the heat flux and to present it in a convenient way it is necessary to use the concept of a mean value of the effective thermal conductivity. This quantity is defined as follows:

$$f_q = k_{e \text{ mean}} \frac{(T_2 - T_1)}{l} \quad (1.3)$$

where l is the thickness of the layer of wetted porous material and f_q is the heat flux, see fig. 1.1. The use of the symbol $k_{e \text{ mean}}$ implies that it can be interpreted as a mean value of a number of the effective thermal conductivities of unit elements. Because the effective thermal conductivity, k_e , is, in general, strongly and non-linearly dependent on temperature and on moisture content then in order to evaluate $k_{e \text{ mean}}$ it is necessary to calculate the moisture and temperature fields as well as the effective thermal conductivity of each element.

The flow of fluids and of heat through porous media has been the subject of research for several decades. Nearly all of this work can be classified either as studies of one or more parts of the main problem or as studies of the general theory. Examples of some of the subproblems which have been studied are the flow of liquid in porous media, the effective thermal conductivity of porous media, and the magnitude of capillary forces in porous media. The work published in these fields will be referred to later. The other important field of study has been the development of a more general approach to the theory of moist porous systems. This will be described in chapter 2.

In recent years, the study of heat and mass flows in porous media has entered a new phase partly because the general theory has been successfully developed by the application of irreversible thermodynamics and partly because of a general increase of interest in these phenomena which has been stimulated, in part at least, by the development of a new heat transfer device in the early 1960's; the heat pipe. A recent National Engineering Laboratory publication on the heat pipe (H5) lists 275 references and another publication by Winter and

Barsch (W1) lists 304 references of which many deal with heat and mass transfer in porous media. Chisholm's (C6) recent book on the heat pipe also contains numerous references to works on heat and mass flows in porous media.

Despite the wealth of information on different aspects of heat and mass flows in porous media very little work has been done on the problem described in the beginning of this chapter. In general the theoretical formulations in the literature do not lead to explicit formulae which could be used to calculate temperature and moisture distributions under different conditions. In addition, most of the work done on the subproblems has led to semi-empirical expressions or to equations which contain variables which are unknown and which cannot be calculated.

There is one recent work reported in the literature in which the problem setting is similar to that of this work. This work was done by Hansen, Breyer and Riback (H2) and contains results of experimental measurements of the steady state heat flux through layers of partially wetted porous materials in a closed system. Their work is very valuable because of the comprehensive experimental measurements they made in situ of the moisture content using an X-ray absorption method. They used the results to test the validity of the commonly assumed/relationship between heat flux and driving force and found that their results supported the validity of the relationship. Their predictions of the behaviour of the system were, however, based on some approximations and assumptions that might lead to considerable errors under certain conditions. They used, for example, an equation derived by Riback (R2) for the vapour flux in a porous

medium for which Riback assumed that the porous material consists of parallel straight capillaries. Hansen, Breyer and Riback point out that the weakest link in their method was the use of uncertain data for the capillary pressure. The capillary pressure, or capillary potential, is a function of moisture content as well as - although to a lesser degree - of temperature, and is an important property of a material as it determines the magnitude of the driving force for liquid flow as well as the moisture content distribution caused by gravity. The authors do not present a formula for the capillary potential. It seems that they used measured data points in their calculations.

The work discussed above was published during the course of this study. It made an important contribution and supported some of the results obtained in the course of this work.

CHAPTER 2

DERIVATION OF THE EQUATIONS

2.1 Introduction

From chapter 1, it is clearly necessary to apply the macroscopic approach in the present work. The physical situation can be described in terms of a number of forces and gradients which contribute to the total fluxes of heat and mass. In the most general case any of the forces can give rise to any of the fluxes. The set of basic equations can, however, be simplified; for example in steady state conditions some of the terms vanish. As the problem will be dealt with in terms of abstract phenomenological equations it will be necessary to relate these to the commonly used transfer equations.

2.2 Basic Theory

In the following, a set of fluxes will be studied in a general way by the application of the thermodynamics of irreversible processes. The goals of the study are to acquire deeper insight into the problem and to try to find possible interdependencies between the various fluxes in order to reduce the number of quantities to be determined experimentally. The method of approach is based on the work of de Groot (G7) and Prigogine (P8). These theories have been applied to energy and mass flows in porous materials by several workers of whom Luikov and Mikhailov (L6), Luikov (L2), Taylor and Gary (T3), and Valchar (V1) may be mentioned here.

According to the Gibbs equation:

$$Td\sigma = dU + pdV - \sum_{i=1}^n \mu_i dn_i$$

where μ is the chemical potential defined as follows:

$$\mu_i = \left(\frac{\partial \sigma}{\partial n_i} \right)_{U, V, n_j} \quad \text{where } i \neq j$$

If the internal energy, U , and the volume, V , of the region considered remain constant, the equation becomes:

$$T d\sigma = - \sum_{i=1}^n \mu_i dn_i$$

or

$$d\sigma = - \sum_{i=1}^n \left(\frac{\mu_i}{T} \right) dn_i \quad (2.1)$$

This expression for the entropy increase is valid only for the equilibrium state. However, in his study of non-equilibrium thermodynamics, Prigogine (P8) has shown that when a system is not in equilibrium, its state is often determined by the same variables as if it were. This is not a self-evident fact but is an approximation which, according to Prigogine, is very good if the departure from equilibrium is not very great. In the non-equilibrium case an equation which corresponds to equation (2.1) is:

$$\dot{\sigma} = \frac{d\sigma}{dt} = \sum_{i=1}^n X_i f_i \quad (\geq 0) \quad (2.2)$$

Here the fluxes are denoted by f_i and the thermodynamic driving forces by X_i . For transfer processes the use that has been made of the thermodynamics of irreversible processes,

based on equation (2.2), is limited to the region of validity of the linear phenomenological laws

$$f_i = \sum_{k=1}^n L_{ik} X_k \quad (2.3)$$

The coefficients L_{ik} are assumed to be constants. Equation (2.3) states that all forces may give rise to contributions to all the fluxes. The number of relations L_{ik} may be reduced by application of the reciprocity relation which results from microscopic reversibility and which is known as the Onsager relation:

$$L_{ik} = L_{ki} \quad (2.4)$$

As the meaning of this expression is not easy to see, the following example is given. Assume that an energy flow is induced in a vapour phase by a moisture content gradient. Then the same phenomenological coefficient which describes this energy flow will also describe the vapour flow induced by a temperature gradient. There is experimental verification of this relationship.

De Groot (G7, p. 221 ff.) has shown that the relationships described by equations (2.3) and (2.4) can be applied to unsteady state phenomena of low intensity, although they are normally used for steady transfer processes.

For unsteady transfer processes of high intensity the coefficients in equation (2.3) cannot be considered to be constants. The basic requirement of linearity is therefore violated and equations (2.2) and (2.3) must be modified. According to Prigogine (P8) the change in the rate of entropy

production may be divided into two parts: the first part, $d\dot{\sigma}_X/dt$ arises because of changes of thermodynamic forces, and the second, $d\dot{\sigma}_f/dt$, because changes of the fluxes:

$$\frac{d\dot{\sigma}}{dt} = \frac{d\dot{\sigma}_X}{dt} + \frac{d\dot{\sigma}_f}{dt} = \sum_{i=1}^n f_i \frac{dX_i}{dt} + \sum_{i=1}^n X_i \frac{df_i}{dt} \quad (2.5)$$

Prigogine (P8, p.95) has shown that when the phenomenological coefficients are constant and the Onsager relationships are valid, which is the case if the phenomenological coefficients of the conjugated fluxes and forces are well defined, the portion of the change in rate of entropy production due to changes of thermodynamic forces is equal to the portion due to changes of flux. Thus:

$$\frac{d\dot{\sigma}_X}{dt} = \frac{d\dot{\sigma}_f}{dt} = \frac{1}{2} \frac{d\dot{\sigma}}{dt}$$

and;

$$\sum_{i=1}^n f_i \frac{dX_i}{dt} = \sum_{i=1}^n X_i \frac{df_i}{dt} \quad (2.6)$$

In intense unsteady state processes the fluxes f_i are related to the thermodynamic forces X_k by unknown non-linear equations. However, if the system is not very far from equilibrium, this non-linear dependence can be approximated as follows:

$$f_i = L_i^{(r)} \dot{f}_i + \sum_{k=1}^n (L_{ik} X_k + L'_{ik} \dot{X}_k) \quad (2.7)$$

where $L_i^{(r)}$, L_{ik} and L'_{ik} are constants and $L_i^{(r)}$ describes the response of the system to changes of flux and is usually called the relaxation coefficient, L_{ik} is the basic phenomenological coefficient of the transfer process, and L'_{ik} describes the response of the system to changes of the driving force. In heat transfer this is a function of the specific heat and in mass transfer it is a function of the capacity of the system to accumulate mass.

Under steady state conditions:

$$\dot{X}_i = 0 \quad ; \quad \dot{f}_i = 0$$

and equation (2.7) becomes equation (2.3).

2.3 Equation for Energy Flux

From equation (2.7) the equation for the energy flux, f_q , is:

$$f_q = L_q^{(r)} \dot{f}_q + L_{qq} X_q + L'_{qq} \dot{X}_q + \sum_{k=0}^3 (L_{qk} X_k + L'_{qk} \dot{X}_k) \quad (2.8)$$

where the subscripts 0, 1, 2, and 3 refer to the forces and associated phenomenological coefficients in the solid phase, in the liquid, in the vapour, and in the non-condensable gases, respectively. It may seem strange that the mass fluxes do not seem to appear in equation (2.8). The equation may be interpreted in the following way. The terms of the form $L_{qq} X_q$ represent energy transfer which is not associated with any particular mass flux and the terms:

$$\sum_{k=0}^3 L_{qk} X_k$$

denote energy fluxes associated with the mass fluxes, f_k , induced by the thermodynamic forces X_k , which are functions of the concentration gradients in the phases k . The coefficient L_{q2} , for example includes the conductivity of the vapour in the medium and a term which relates the mass flow to the associated energy flow.

The following simplifications can now be made. There is ample experimental evidence that the relaxation time in most heat conduction situations is very small and that, consequently, the Fourier equation is valid. Only in rarefied gases flowing at high velocities have large relaxation times been found (L2, p. 192).

Hence:

$$L_q^{(r)} \dot{f}_q \approx 0$$

The term $L_{q3} X_3$ represents the energy which is transported with the non-condensable gases. Under the conditions studied in this work the only transport process of the non-condensable gases is natural convection. There is experimental verification by Verschoor and Greebler (V2) that under conditions similar to those studied in this work the contribution made by natural convection in the gas phase is not very great. Their results show that less than three per cent of the total energy flow arises because of natural convection in a material of void fraction of 0.96 at a mean

temperature of about 70°C. If the void fraction is lower, as is the case in most porous materials, or if the gas phase volume is decreased by the presence of liquid, the convective contribution is likely to be still less important. Gorrington and Churchill (G5) reviewed a number of works dealing with this subject and arrived at the conclusion that the contribution by natural convection in porous media is ordinarily small in comparison with the contributions of conduction and radiation.

The solid matrix is assumed to be rigid in this work so that there is no energy flux associated with the flow of solid material.

With the additional assumption that the change of thermodynamic forces with time is not great, equation (2.8) becomes as follows:

$$f_q = L_{qq}X_q + L_{q1}X_1 + L_{q2}X_2 \quad (2.9)$$

This equation can be simplified still further. It is convenient to express the energy transported by vapour in terms of an equivalent thermal conductivity. In order to calculate the effective thermal conductivity of the medium the equivalent thermal conductivity of vapour is used together with the molecular conductivities of the components. The energy flux induced by the vapour concentration gradient is represented by the term $L_{q2}X_2$ in equation (2.9). It will be shown in section 2.4 that the only vapour flux that it is necessary to take into account in a non-hygroscopic state is the flux induced by the temperature gradient. Therefore, it is plausible to apply the following identity:

$$L_{q2}X_2 \equiv (L_{q2} \frac{X_2}{X_q})X_q \equiv L_{q2m}X_q$$

The coefficient L_{q2m} may be combined with the coefficient L_{qq} as follows:

$$L_{qq}X_q + L_{q2m}X_q = (L_{qq} + L_{q2m})X_q = L_{qqe}X_q \quad (2.10)$$

where L_{qqe} is related to the effective thermal conductivity. Equation (2.9) thus becomes:

$$f_q = L_{qqe}X_q + L_{q1}X_1 \quad (2.11)$$

2.4 Equation for Mass Flux

In general the mass flows of the solid, the liquid, the vapour, and the non-condensable gases must be considered. The total mass flux is the sum of the individual mass fluxes, each of which may be calculated by application of equation (2.7). Hence:

$$f_m = \sum_{i=0}^3 f_i = \quad (2.12)$$

$$\sum_{i=0}^3 L_i^{(r)} \dot{f}_i + \sum_{i=0}^3 (L_{iq}X_q + \sum_{k=0}^3 L_{ik}X_k + L'_{iq}\dot{X}_q + \sum_{k=0}^3 L'_{ik}\dot{X}_k)$$

In the previous section it was shown that the heat transferred by natural convection in the gas phase is small and may be ignored. Correspondingly the mass flow associated with this heat transfer, $L_{33}X_3$, is small so that the term $L_{33}X_3$ may be

ignored. The cross terms $L_{31}X_1$ and $L_{32}X_2$ may also be ignored. These terms represent the flux of non-condensable gases because of liquid and vapour concentration gradients. The liquid and vapour fluxes which result from concentration gradients of the non-condensable gases are also small and may be ignored. In addition the system is closed and steady state conditions apply so that, if the solid matrix is rigid, equation (2.12) becomes:

$$f_m = f_1 + f_2 = \quad (2.13)$$

$$\sum_{i=1}^2 L_i^{(r)} \dot{f}_i + \sum_{i=1}^2 (L_{iq} X_q + \sum_{k=1}^2 L_{ik} X_k + L'_{iq} \dot{X}_q + \sum_{k=1}^2 L'_{ik} \dot{X}_k)$$

The vapour flux consists of a flux induced by the temperature gradient, $L_{2q}X_q$; a flux induced by the liquid concentration gradient, $L_{21}X_1$, and a flux induced by the vapour concentration gradient, $L_{22}X_2$. If it is assumed that liquid-vapour equilibrium prevails, the two last mentioned fluxes may be related, i.e. the liquid concentration gradient may give rise to a vapour flux as a consequence of causing a vapour concentration gradient to be established.

It is convenient to study the conditions which give rise to a vapour flux under isothermal conditions. The following expression may be written for this isothermal vapour flux, $f_{2 \text{ iso}}$:

$$f_{2 \text{ iso}} = (L_{21} + L_{22} \frac{X_2}{X_1}) X_1 \quad (2.14)$$

If this flux is greater than zero there is a relationship between the liquid concentration gradient and the partial pressure gradient of the vapour. When the partial pressure of vapour is dependent on the capillary radii of the vapour filled pores such a relationship exists because as the liquid concentration increases the capillaries of smaller radii are filled first. However, if it is assumed that the capillary radii are not smaller than 10^{-7} m as was assumed in chapter 1, then by Thomson's law the partial pressure of vapour becomes independent of the capillary radius and a liquid concentration gradient cannot give rise to a vapour flux. Therefore, for isothermal conditions, the following equations may be written:

$$L_{21}X_1 = 0 \quad (2.15A)$$

$$L_{22}X_2 = 0 \quad (2.15B)$$

Under non-isothermal conditions equation (2.15B) does not apply. In the present study the vapour flux $L_{22}X_2$ arises only because of the imposed temperature gradient and may be incorporated into the term $L_{2q}X_q$.

Thus, if the rate of change of the thermodynamic forces is not great, the simplified formula for the vapour flux is as follows:

$$f_2 = L_{2q}X_q \quad (2.16)$$

The liquid flux, f_1 , in equation (2.13) consists of a flux induced by a temperature gradient, $L_{1q}X_q$; a flux induced

by the liquid concentration gradient, $L_{11}X_1$; and a flux induced by the vapour concentration gradient, $L_{12}X_2$. As discussed in connection with the vapour flux, when the capillary radii are not smaller than 10^{-7} m there is no independent vapour concentration gradient in the material. Thus X_2 is zero. The liquid flux differs from the other fluxes because, as will be discussed in section 2.6, the relaxation term is far greater in the case of the liquid flux than for the other fluxes and it should be taken into account in at least some cases.

All the fluxes have now been discussed and the simplified set of equations becomes as follows:

$$f_q = L_{qqe}X_q + L_{q1}X_1 \quad (2.17)$$

$$f_1 = L_1^{(r)}\dot{f}_1 + L_{1q}X_q + L_{1q}'X_q + L_{11}X_1 + L_{11}'\dot{X}_1$$

$$f_2 = L_{2q}X_q$$

The numerous assumptions made in the derivation of equations (2.15) are collected and presented in the following:

1. The system is never very far from equilibrium.
The only deviation from equilibrium which is taken into account is that in the liquid phase and even then a linear approximation is used.
It is also assumed that vapour-liquid equilibrium prevails.
2. The solid matrix is rigid.
3. No chemical reactions take place.

4. The functions describing the forces are single-valued functions of some - preferably measurable - variables. This poses a very difficult problem because of hysteresis in the capillary potential versus moisture content relationship. This relationship can be reformulated by taking into account the previous wetting history of the material and by combining this information with the wetting/drainage potential functions.
5. The mass fluxes of the non-condensable gases as well as the fluxes induced by a concentration gradient in the non-condensable gases are assumed to be negligible.
6. It is assumed that the fraction of pores with a radius less than 10^{-7} m is negligible. This implies that the maximum moisture content which can be absorbed from the surrounding humid air is also negligible.

2.5 Equations for the Steady State

The temperatures at the boundaries of the layer of wetted porous material are assumed to be specified. The time derivatives are zero, and since the system is closed the total mass flux, $f_1 + f_2$, must be zero. This means that one could expect a continuous cycle of evaporation, diffusion, condensation and return liquid flow to operate in the material. The existence of this cycle is not self-evident but has been shown to exist experimentally from steady state studies of

heat transfer in closed wetted porous systems. An example of such work is that by Hansen, Breyer and Riback (H2). Gurr, Marshall and Hutton (G8) used another method which was based on observing the flow of liquid. They labelled the water in the material by sodium chloride and observed the distribution of water and chlorides after a period of influence of a temperature gradient. Globus and Nerpin (G2) also proved the existence of this cycle by labelling the water radioactively.

The expression for energy flux in equation (2.17) is valid for the steady state. There is, however, an approximation to be made. The term $L_{ql}X_1$ signifies the energy transported by liquid flow. In the steady state there are two mechanisms responsible for this flow: convection in the liquid phase, and the return liquid flow which follows the condensation stage of the cycle of evaporation, diffusion and condensation. In this work natural convection is ignored because in small pores and at temperatures below the boiling point of the liquid it contributes little to the energy transport. Even if it were necessary for it to be taken into account it would be easier for the convective contribution to be incorporated into the thermal conductivity of the liquid. Wooding (W2, W3) has published two papers in which he studied both theoretically and experimentally convective heat transfer in the liquid phase in fully wetted sands. He presented a rather complicated formula by which the convective contribution can be calculated.

If convection is ignored the remaining energy flux by liquid transport is that included in the return liquid flow of the cycle of evaporation, diffusion, and condensation.

Because the total mass flux must be zero, the heat flux, $L_{q1}X_1$, transported with the liquid must be small in comparison with the heat transported in the opposite direction by the vapour mass flux $L_{2q}X_q$. However, provided that enthalpies are appropriately defined the term $L_{q1}X_1$ can easily be incorporated into the term $L_{qqe}X_q$. In the expression for the liquid flow the time derivatives disappear, but the vapour flow equation remains unchanged. Hence, equations (2.17) can be written for the steady state as follows:

$$f_q = L_{qqe}X_q \quad (2.18A)$$

$$f_m = f_1 + f_2 = 0 = (L_{1q}X_q + L_{11}X_1) + (L_{2q}X_q) \quad (2.18B)$$

These are the basic equations for this work.

Equation (2.18A) can be interpreted as the transfer of energy by pure molecular conduction and by the evaporation, diffusion, and condensation of vapour. With the exception of radiation the heat transfer mechanisms which have been ignored have already been discussed. The contribution of radiation to the total conductivity of mineral wool has been studied experimentally by Verschoor and Greebler (V2). They found that radiation contributed only about 2-3 per cent of the total heat flux under the same experimental conditions as those already briefly discussed for natural convection.

Gorring and Churchill (G5) reviewed a number of works dealing with radiation in porous materials. They pointed out that in good insulators, in which conduction is effectively repressed, radiant transfer may be appreciable

even at low temperatures. They mentioned that several investigators have suggested that the radiant transfer far from the boundaries can be expressed in terms of a radiant conductivity which can be added to the true conductivity. Semi-empirical formulae for the radiant conductivity have been presented in the literature referred to by Gorrington and Churchill (G5). In wetted materials the relative contribution of radiant transfer is particularly low because the presence of liquid decreases the volume of the gas phase and because the heat transfer caused by evaporation, diffusion, and condensation of vapour increases very rapidly with temperature and attains a theoretical value that is infinite at the boiling point of the liquid. Radiant transfer, therefore, can safely be ignored in the present work.

Equation (2.18B) represents the sum of the vapour and liquid fluxes. The vapour flux is induced by the temperature gradient, and the liquid flux by both the temperature and moisture content gradients.

The temperature gradient leads to a variation in the surface tension so that a potential gradient is created which leads to a gradient in the moisture content. This topic will be treated in detail in chapter 3.

The moisture content gradient does not necessarily give rise to a liquid flux. The liquid distribution at constant temperature is a function of height from the free liquid surface and is described by functions which in this work are called capillary rise or drain curves. The driving force at a particular moisture content is the difference between the existing moisture content gradient and the moisture content gradient given by the capillary curve.

2.6 The Relationship between the Phenomenological Laws and the Conventional Heat and Mass Transfer Equations

The previous pages deal with the heat and mass fluxes in an abstract way. Use of irreversible thermodynamics does not lead to expressions for the phenomenological coefficients. These can only be found by looking into the mechanisms responsible for the fluxes. Further, the relationships between the phenomenological coefficients and the coefficients in the well-known heat and mass flow equations need careful study. A study of the conventional equations reveals that they are simplified forms of the phenomenological equations. One well-known equation of this simplified type is Fourier's law of heat conduction:

$$f_q = L_{qq} X_q = -k \nabla T \quad (2.19)$$

The basic principle of the phenomenological approach demands that the driving force is separated from the coefficient. Since the coefficient L_{qq} is independent of temperature it is logical to set:

$$X_q = -\nabla \ln T$$

Fourier's law was obtained from an analysis of experimental measurements. However, if it is assumed that the driving force changes very slowly as a function of time, then from equation (2.7) the heat flux becomes:

$$f_q = -k \nabla T - \tau_r \frac{\partial f_q}{\partial t} \quad (2.20)$$

where the relaxation coefficient is denoted by τ_r .

Although the relaxation period is generally short there are, however, special cases where the relaxation term cannot be ignored. Luikov (L2) mentions as an example that the relaxation term is particularly high in the conduction of heat in rarefied supersonic flows. It is interesting to note that equation (2.20) leads to the following hyperbolic equation for the temperature distribution:

$$\frac{\partial T}{\partial t} + \tau_r \frac{\partial^2 T}{\partial t^2} = \frac{\partial}{\partial x} \left(\alpha \frac{\partial T}{\partial x} \right) \quad (2.21)$$

The diffusion of moisture can now be studied in an analogous way. The equations which are equivalent to Fourier's law are called Darcy's law, which relates the flux of fluid to the pressure gradient, and Fick's diffusion equation, which relates the flux of fluid to the moisture content gradient. The latter is as follows:

$$f_m = - D_m \rho_o \nabla c \quad (2.22)$$

where c is the moisture content per unit mass of solid matrix and ρ_o is the bulk density of the solid matrix. According to the work of Luikov (L2) in the case of liquid flow in porous materials the term containing the relaxation period cannot always be ignored. Instead of equation (2.22) the following equation should be used:

$$f_m = - D_m \rho_o \nabla c - \tau_{rm} \frac{\partial f_m}{\partial t} \quad (2.23)$$

which for an one-dimensional moisture content field leads to the following expression:

$$\frac{\partial c}{\partial t} + \tau_{rm} \frac{\partial^2 c}{\partial t^2} = \frac{\partial}{\partial x} \left(D_m \frac{\partial c}{\partial x} \right) \quad (2.24)$$

or, in the case of an intense process:

$$\frac{\partial c}{\partial t} + \tau_{rm} \frac{\partial^2 c}{\partial t^2} + c_m \frac{\partial^2 c}{\partial x \partial t} = \frac{\partial}{\partial x} \left(D_m \frac{\partial c}{\partial x} \right) \quad (2.25)$$

where c_m describes the capacity of the medium to accumulate liquid per unit length measured in the direction of the flow. In the literature the term τ_{rm} in equation (2.24) has been omitted in such works as are those of Philip (P5) and Klute (K1). Experimental verification of the moisture fields predicted from equations (2.24) and (2.25) is not easy because of the difficulty of measuring accurately the local moisture content inside the material. It is particularly difficult if the moisture content changes rapidly as a function of time. This may be one of the reasons why comparisons between experimentally determined moisture fields and those calculated from the simple diffusion equation (2.22) have not led to the replacement of equation (2.22). Because in this work the steady state situation is studied, the term which contains the relaxation coefficient τ_{rm} is zero.

2.7 Derivation of the Equations for the Steady State

Equations (2.18) must now be developed to a usable form. Since the system is at steady state then, by equation (2.17), the liquid flux is:

$$f_1 = L_{1q} X_q + L_{11} X_1$$

Since the system is closed then:

$$L_{1q}X_q = -L_{11}X_1$$

and

$$\frac{X_1}{X_q} = - \frac{L_{1q}}{L_{11}} \quad (2.26)$$

As X_q is related to the temperature gradient and X_1 to the moisture content gradient their ratio can be expressed as follows:

$$\frac{X_1}{X_q} = - \frac{L_{1q}}{L_{11}} = - \frac{L_{1qm}}{L_{11m}} = \frac{\frac{dc}{dx}}{\frac{dT}{dx}} = \frac{dc}{dT} = - \delta \quad (2.27)$$

where the subscripts m denote that the thermodynamic forces have been modified to moisture content and temperature gradients. The quantity $-(dc/dT)$ is called the thermal gradient coefficient by Luikov and is denoted by δ . The thermal gradient coefficient will be studied in more detail in chapter 3.

Taylor and Gary (T3) used a similar formulation and arrived at the following definition of a quantity β^* which they called "a useful transfer coefficient":

$$\frac{dc}{d \ln T} = T \frac{dc}{dT} = - \beta^* \quad (2.28)$$

comparison of equations (2.27) and (2.28) reveals that

$$\delta = \frac{\beta^*}{T} \quad (2.29)$$

It is now assumed that the vapour flux must be taken into account. This is the case when the vapour pressure of the liquid is not very low. Then the vapour transported towards the colder regions condenses and is returned by the capillary forces, i.e. by the flux $L_{11}X_1$. The driving force for the liquid flux can now be separated into two parts. The first part is related to the moisture content gradient that would exist as the result of surface tension gradient even in the absence of vapour flow, and the second part is related to the moisture content gradient which gives rise to the cycle of evaporation, diffusion, and condensation. The liquid flux in equation (2.18) becomes:

$$f_1 = L_{1q} X_q + L_{11} X_1 \text{ cap} + L_{11} X_1 \text{ EDC} \quad (2.30)$$

Equation (2.30) may be written:

$$f_1 = f_1 \text{ cap} + f_1 \text{ EDC}$$

where the subscript cap denotes the contribution caused by the capillary forces. However, under steady state conditions in a closed system:

$$f_1 \text{ cap} = L_{1q} X_q + L_{11} X_1 \text{ cap} = 0 \quad (2.31)$$

so that

$$f_1 = f_1 \text{ EDC}$$

Also, by equations (2.18) and (2.30)

$$f_2 = L_{2q} X_q = -f_1 = -f_1 \text{ EDC} = -L_{11} X_1 \text{ EDC} \quad (2.32)$$

Analogously with equation (2.27) the following quantities are now defined:

$$\delta_{\text{cap}} = - \left(\frac{dc}{dT} \right)_{\text{cap}} \quad (2.33A)$$

$$\delta_{\text{EDC}} = - \left(\frac{dc}{dT} \right)_{\text{EDC}} \quad (2.33B)$$

The quantity δ_{cap} is called by Luikov the capillary thermal gradient coefficient. It will be studied in more detail in chapter 3. The subscript EDC denotes the contribution by the mechanism caused by the cycle of evaporation, diffusion, and condensation of vapour, and return liquid flow. The quantity δ_{EDC} does not appear in the literature. It will be called the evaporation thermal gradient coefficient. By application of equation (2.32) the definition (2.33B) may be expressed as follows:

$$\delta_{\text{EDC}} = - \left(\frac{dc}{dT} \right)_{\text{EDC}} = - \left(\frac{dc}{dX} \right)_{\text{EDC}} \left(\frac{dX}{dT} \right) = - X_1 \text{ EDC} \left(\frac{dX}{dT} \right) = \frac{f_2}{L_{11}} \frac{dX}{dT} \quad (2.34)$$

Calculation of the quantities f_2 and L_{11} in the above equation is a complicated task which will be undertaken in chapter 5. The usable expression for the evaporation thermal gradient coefficient, δ_{EDC} , will be presented in chapter 5.

Next, the influence of a gravitational field will be studied. The effect of a gravitational field does not appear directly in equations (2.18). It is, however, practical to present the influence of gravity as a separate term. It is now assumed that the moisture content gradients caused by these different mechanisms are additive. Hence:

$$\frac{dc}{dT} = \left[\left(\frac{dc}{dx} \right)_{cap} + \left(\frac{dc}{dx} \right)_{EDC} + \left(\frac{dc}{dx} \right)_{gravity} \right] \frac{dx}{dT} \quad (2.35A)$$

or

$$\frac{dc}{dT} = - \delta_{cap} - \delta_{EDC} + \left(\frac{dc}{dx} \right)_{gravity} \frac{dx}{dT} \quad (2.35B)$$

The additivity of the potentials included in equations (2.35) needs consideration. It is logical to assume that these potentials are additive and hence that the gradients of moisture content caused by the various mechanisms are also additive. It will be shown later on that the capillary thermal gradient, δ_{cap} , and the evaporation thermal gradient coefficient, δ_{EDC} , are functions of the local moisture content. However, this is not the case with the gravitational potential gradient. The moisture content field at a uniform temperature must be known, and it can be determined by the following method.

The height $h_T(c)$ from a free liquid surface to which liquid rises in a capillary is proportional to surface tension. Hence in the absence of a temperature gradient the height, $h_T(c)$, to which the liquid rises at a temperature T is related to the height at which the liquid would rise at a temperature of 20°C by the following relationship:

$$h_T(c) = \left(\frac{\sigma_T}{\sigma_{20^\circ\text{C}}} \right) h_{20^\circ\text{C}}(c) \quad (2.36)$$

The total moisture content of a slab subjected to a temperature gradient is the same as the total moisture content in a slab in the absence of a temperature gradient. This condition can be used to determine the moisture distribution in a slab maintained at any uniform temperature provided that the total moisture content is specified.

For any given temperature the curve $h_T(c)$ is known but only with respect to the zero potential level, i.e. with respect to an imaginary free liquid surface. The position of this surface has to be adjusted by repeated integrations so that the total moisture content in the slab ^{is}/~~is~~ preserved. When the moisture content field in the absence of a temperature gradient has been obtained its gradient at any given moisture content is the term $(dc/dx)_{\text{gravity}}$ in equations (2.35A) and (2.35B). Equation (2.35B) may be written as follows:

$$\frac{dc}{dT} = \delta_{\text{cap}}(c,T) + \delta_{\text{EDC}}(c,T) + \left(\frac{\sigma_{20^\circ\text{C}}}{\sigma_T} \right) \left(\frac{dh}{dc} \right)_{c_{\text{iso}}}^{-1} \frac{dx}{dT} \quad (2.37)$$

where (dh/dc) is the derivative of the capillary rise or drain curve depending on whether the moisture content is increasing or decreasing at the point under consideration. The subscript c_{iso} signifies that the derivative (dh/dc) has to be taken at the moisture content which would be the moisture content at the point under consideration at the temperature T in the absence of a temperature gradient.

A procedure for finding the moisture content field c_{iso} has been described above.

The calculation of the moisture content field at a number of different temperatures is time consuming. A simpler, less accurate, method can be used. The search for the position of the zero potential level with respect to the slab may be done at the average temperature of the slab:

$$T_{av} = \frac{1}{2} (T_{x=0} + T_{x=l}) \quad (2.38)$$

An approximate correction can be made for each temperature by the application of equation (2.36) so that:

$$h_T(c) \approx \frac{\sigma_T}{\sigma_{T_{av}}} \left[\left(\frac{\sigma_{T_{av}}}{\sigma_{20^\circ C}} \right) h_{20^\circ C}(c) \right]_{T_{av}} \quad (2.39)$$

The group inside the square brackets is used in the search for the imaginary free liquid surface as discussed above. The approximation given by equation (2.39) is sufficiently accurate if the range of temperatures within the slab is not large. Then the quotient $(\sigma_T / \sigma_{T_{av}})$ is near to unity.

If the temperature range is the maximum which can be experienced for water under atmospheric conditions, i.e. from 0°C to 100°C, the values of the quotient are:

$$\frac{\sigma_{0^{\circ}\text{C}}}{\sigma_{50^{\circ}\text{C}}} = 1.11 \quad ; \quad \frac{\sigma_{100^{\circ}\text{C}}}{\sigma_{50^{\circ}\text{C}}} = 0.87$$

When this method is used the derivative (dh/dc) in equation (2.37) has to be calculated at a temperature of T_{av} .

Equation (2.37) is the mass flux equation (2.18B) in a usable form. The term (dx/dT) can be calculated by taking into account the energy equation (2.18A).

The energy equation (2.18A) was discussed in detail in section 2.5 and has been shown by equation (2.19) to be Fourier's well known law of heat conduction. When the effective conductivity is a function of temperature the differential equation for the conduction of heat in the steady state is as follows:

$$\frac{d}{dx} \left(k_e \frac{dT}{dx} \right) = 0$$

Thus, the following relationship is valid although the effective thermal conductivity, k_e , is a function of temperature:

$$k_e \frac{dT}{dx} = \text{constant} = C = -f_q$$

The constant can be calculated in the ordinary way in integration between the surface temperatures T_1 and T_2 of a slab of thickness ℓ ; that is:

$$\int_{T_1}^{T_2} k_e dT = \ell C \quad (2.40)$$

and,

$$k_e \text{ mean} = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} k_e dT$$

Then

$$C = \frac{(T_2 - T_1) k_e \text{ mean}}{\ell}$$

Hence

$$\frac{dx}{dT} = \frac{\ell}{(T_2 - T_1)} \frac{k_e}{k_e \text{ mean}} \quad (2.41)$$

The moisture field equation (2.37) and the temperature field equation (2.41) must be solved simultaneously, and in fact, (dx/dT) can be eliminated from equation (2.37) by use of equation (2.41). The expression which results is:

$$\frac{dc}{dT} = \delta_{\text{cap}} + \delta_{\text{EDC}} + \left(\frac{\sigma_{20^\circ\text{C}}}{\sigma_T} \right) \left(\frac{dh}{dc} \right)^{-1}_{c_{\text{iso}}} \left(\frac{\ell k_e}{(T_2 - T_1) k_e \text{ mean}} \right) \quad (2.42)$$

Much of the work described in this thesis is devoted to solutions of equations (2.41) and (2.42). The solution procedure which is based on an iterative method is described in appendix 1. The iteration procedure is twofold. There is an inner iterative loop which is used to calculate the moisture content field in the absence of a temperature gradient, i.e. the moisture content field which is caused by gravity. This is needed for the determination of the moisture content c_{iso} . The outer iteration loop is used for the calculation of (dx/dT) . The iteration is continued until the solution of equations (2.41) and (2.42) has converged. The specification of the parameters contained in the equations, i.e. the capillary thermal gradient coefficient, δ_{cap} , the evaporation thermal gradient coefficient, δ_{EDC} , the effective thermal conductivity, k_e , and the derivative of the capillary rise or drain curve with respect to moisture content, (dh/dc) , is an essential part of the procedure. Each of these quantities will be studied in later chapters. The ultimate aim, however, will be to evaluate the mean effective thermal conductivity of a slab, $k_{e \text{ mean}}$, as a function of the total moisture content of the slab. This total moisture content can be calculated when the moisture content field in terms of position is known. Some of the calculated results will be presented in chapter 7 and will be compared with experimental values.

CHAPTER 3

THE CAPILLARY THERMAL GRADIENT COEFFICIENT

3.1 Introduction

In this work a quantity called the capillary thermal gradient coefficient is employed. It is denoted by δ_{cap} and has already been introduced in section 2.7. It also appears in equation (2.42) which is one of the pair of simultaneous equations which is the basis of the analytical treatment of the problem being studied.

The capillary thermal gradient coefficient was originally introduced by Luikov (L5) who defined it as follows:

$$\delta_{\text{cap}} = \frac{D_1^T}{D_1} \quad (3.1)$$

where D_1^T is the liquid diffusivity induced by a temperature gradient and D_1 is the isothermal liquid diffusivity. It will be shown below that Luikov's definition is identical to that of this work. Note that δ_{cap} differs from δ , the overall thermal gradient coefficient, which is defined by Luikov (L3) as follows:

$$\delta = \frac{D_1^T + D_2^T}{D_1 + D_2} \quad (3.2)$$

where the subscripts 1 and 2 refer to the liquid and vapour phases respectively. The diffusion of vapour caused by a temperature gradient in the vapour phase arises from a different mechanism to that of the diffusion of liquid. Therefore, it is logical to separate these diffusivities by the

introduction of δ_{cap} and δ_{EDC} , as in equations (2.33A) and (2.33B).

By application of equation (2.22) the isothermal mass flux is:

$$f_{m \text{ iso}} = D_1 \rho_o \frac{dc}{dx} + D_2 \rho_o \frac{dc}{dx} \quad (3.3)$$

where D_1 and D_2 are the liquid and vapour diffusivities, respectively, and ρ_o is the bulk density of the solid matrix. The mass flux induced by a temperature gradient is then:

$$f_{m \nabla T} = D_1^T \rho_o \frac{dT}{dx} + D_2^T \rho_o \frac{dT}{dx} \quad (3.4)$$

In a closed system at steady state:

$$f_{m \text{ iso}} + f_{m \nabla T} = 0$$

Hence,

$$- \frac{D_1^T + D_2^T}{D_1 + D_2} = \frac{dc}{dT} = - \delta \quad (3.5)$$

Comparison of equations (2.27) and (3.5) shows that in this work the definition of δ is the same as that used by Luikov. For the case studied in the present work D_2 is zero so that δ may be split into two parts. In a manner similar to that used in the derivation of equation (2.27) one uses equations (2.31) and (2.33) to obtain:

$$\delta_{\text{cap}} = \frac{L_{1qm}}{L_{11m}} = \frac{D_1^T}{D_1} \quad (3.6)$$

where the subscript m denotes that the transport coefficients have been modified so that the gradients of the thermodynamic forces may be replaced by moisture content and temperature gradients. Comparison of equations (3.1) and (3.6) shows that in this work the definition of δ is the same as used by Luikov.

Analogously with the derivation of equation (3.6) the following equation is obtained:

$$\delta_{\text{EDC}} = \frac{L_{2qm}}{L_{11m}} = \frac{D_2^T}{D_1} \quad (3.7)$$

From equations (3.2), (3.6) and (3.7) it can be seen that the following relationship applies:

$$\delta = \frac{1}{\frac{1}{\delta_{\text{cap}}} + \frac{D_2}{D_1}} + \frac{1}{\frac{1}{\delta_{\text{EDC}}} + \frac{D_2}{D_1^T}}$$

If D_2 is zero, which is the case when the hygroscopic forces play no role, the following relationship holds:

$$\delta = \delta_{\text{cap}} + \delta_{\text{EDC}} \quad (3.8)$$

3.2 The Capillary Thermal Gradient Coefficient - a Survey of the Literature

In early studies no distinction was made between the thermal gradient coefficient and the capillary thermal gradient coefficient. These early studies were experimental. Smith (S3) expressed the influence of a temperature gradient on the moisture distribution in the steady state by simply presenting the moisture and temperature gradients separately. Dubnitsky (D2) used the concept of the thermal gradient coefficient and found that it is influenced relatively little by temperature. He presented the following empirical expression

$$\delta = A c^2 e^{-Bc}$$

where A and B are constants and in addition B is an integer. For example for diatomite chips A = 9.12 and B = 9. Later, Luikov (L5) distinguished between these two quantities and derived the following equation for the capillary thermal gradient coefficient:

$$\delta_{\text{cap}} = \frac{-\rho_l r' f(r)}{\rho_o \sigma} \frac{d\sigma}{dT} \quad (3.9)$$

where r' is the radius of the largest pore that is filled with liquid and $f(r)$ is the distribution function of the pore radii. Equation (3.9) can be put into a more directly useful form by the use of its relationship with the capillary rise curve. Such a relationship will be studied in detail in chapter 6 but will be applied to the present problem in the following section.

3.3 Calculation of the Capillary Thermal Gradient Coefficient

There is no easily applicable formula in the literature by which the capillary thermal gradient coefficient,

δ_{cap} , may be calculated. Luikov (L5) gives an expression, equation (3.9), which can be used if the distribution of the capillary radii is known. The capillary rise and drain curves used in this work are in fact determined by the distribution of the capillary radii as will be shown in chapter 6. Therefore it should be possible to calculate δ_{cap} from the capillary rise or drain curves. This is accomplished as follows:

The height of rise of liquid in a capillary is as follows:

$$h = \frac{2\sigma \cos \theta}{r g \rho}$$

Thus the capillary rise is directly proportional to the surface tension, i.e.

$$\frac{dh}{h} = \frac{d\sigma}{\sigma} \quad (3.10)$$

other variables being constant.

Thus, at two points that are at different temperatures there are different capillary equilibrium heights. These equilibrium heights are related to the moisture contents by the capillary rise or drain curves. Hence there is a relationship between a temperature gradient and a moisture content gradient. By applying this principle it is possible to

obtain an expression for δ_{cap} .

The following identities may be written:

$$\begin{aligned}\delta\sigma &\equiv \frac{\partial\sigma}{\partial T} \delta T \\ \delta h &\equiv \frac{\partial h}{\partial c} \delta c\end{aligned}\tag{3.11}$$

By substituting equations (3.11) into equation (3.10), rearranging, and using equation (2.33A) the following expression is obtained:

$$\delta_{\text{cap}}(c, T) = - \left(\frac{dc}{dT} \right)_{\text{cap}} = - \frac{h_T}{\sigma_T} \frac{\left(\frac{\partial\sigma}{\partial T} \right)_T}{\left(\frac{\partial h}{\partial c} \right)_T}\tag{3.12}$$

where the subscript T denotes that the quantities concerned are evaluated at a temperature T. It is often necessary to calculate (dc/dT) at different temperatures. The capillary curves, however, are usually measured at a single fixed temperature, e.g. at 20°C.

From equation (2.36) the following equation is obtained:

$$\frac{\partial h}{\partial c} = \left(\frac{\partial h}{\partial c} \right)_{20^\circ\text{C}} \frac{\sigma}{\sigma_{20^\circ\text{C}}}\tag{3.13}$$

By substituting equation (3.13) into equation (3.12) the following expression is obtained:

$$\delta_{\text{cap}}(c, T) = - \left(\frac{dc}{dT} \right)_{\text{cap}} = - \frac{h_{20^\circ\text{C}}}{\sigma_T} \frac{\left(\frac{d\sigma}{dT} \right)_T}{\left(\frac{dh}{dc} \right)_{20^\circ\text{C}}} \quad (3.14)$$

In a pure liquid the surface tension is dependent only upon temperature. Thus in equation (3.14) the terms containing the surface tension are dependent upon temperature only.

Equation (3.14) enables the capillary thermal gradient coefficient to be calculated at any temperature - provided, of course, that the capillary rise or drain curve is known and that its derivative can be calculated. The surface tension of water as a function of temperature and its derivative with respect to temperature are given in appendix 2. It will be shown in chapter 7 that at temperatures significantly lower than the boiling point of the liquid concerned and at moisture contents that are significantly higher than those at which continuous liquid films break down the following relation holds:

$$\delta_{\text{cap}} \gg \delta_{\text{EDC}}$$

Thus when gravitational effects are not important then under the above circumstances $\delta \approx \delta_{\text{cap}}$. Therefore, most of the measured values of $\Delta c / \Delta T$ obtained should be close to the values of the capillary thermal gradient coefficient, δ_{cap} . Fig. 3.1 shows values of δ_{cap} for coarse sand calculated using equation (3.14). The properties of the coarse sand have been given by Luikov (L5) and are included in table 6.2.

Experimental values of the thermal gradient coefficient for quartz sand are also shown in fig. 3.1. These values

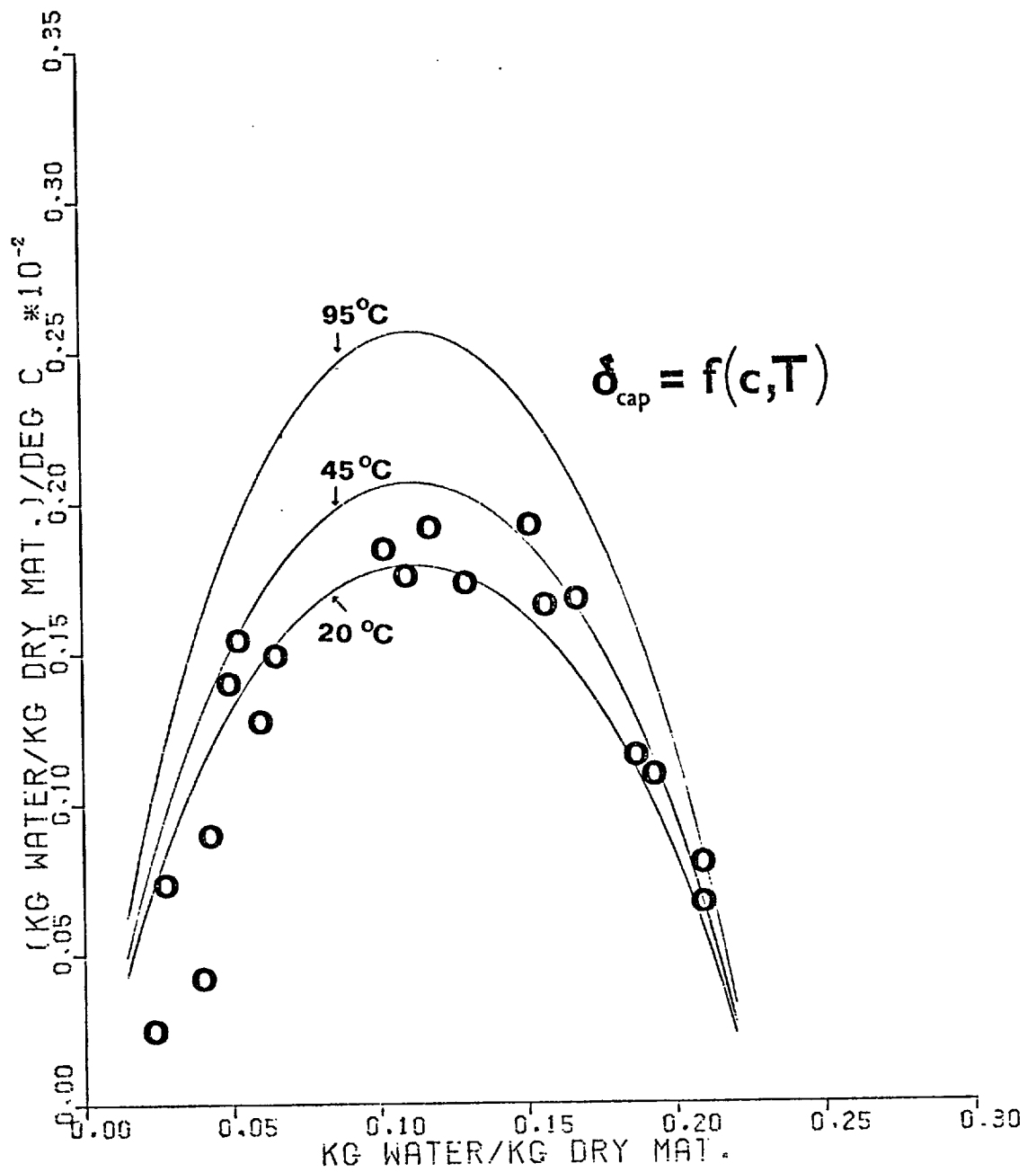


Fig.3.1. Theoretical and experimental values of δ_{cap} .

Solid lines - Theoretical values for a coarse sand with properties given by Luikov (L5).

o - Experimental values for quartz sand, see Luikov (L4, p.287).

are given by Luikov (L4, p. 287). Thus the calculated and experimentally measured values refer to slightly different materials. Further, the measured values are not those of the capillary thermal gradient although, as discussed above, at temperatures not much above room temperature the value of the thermal gradient coefficient is close to that of the capillary thermal gradient coefficient. Unfortunately, there are no experimental values of the capillary thermal gradient coefficient available that are reported together with the capillary rise or drain curves for the same material, so that the validity of equation (3.14) cannot be proved. The close agreement between the calculated and measured values shown in fig. 3.1 is thus of interest.

Equation (3.14) contains expressions for both the capillary rise or drain height and its derivative with respect to moisture content. Because the reproducibility of a capillary rise or drain curve is not perfect, the calculation of the capillary thermal gradient coefficient is subject to considerable error. All the values of δ_{cap} that can be calculated from the experimentally determined capillary rise and drain curves tabulated in appendix 8 are shown in fig. 3.2. The predicted δ_{cap} -values lie within a range of approximately ± 10 per cent about the mean. At low moisture contents the δ_{cap} -values calculated from the capillary drain curves give somewhat lower values than those calculated from the capillary rise curve. The difference is caused by the different behaviour of the capillary rise and drain curves near the dryness. In fig. 3.3 a number of δ_{cap} -curves are shown for a variety of different materials. The curves are based on capillary data as collected from

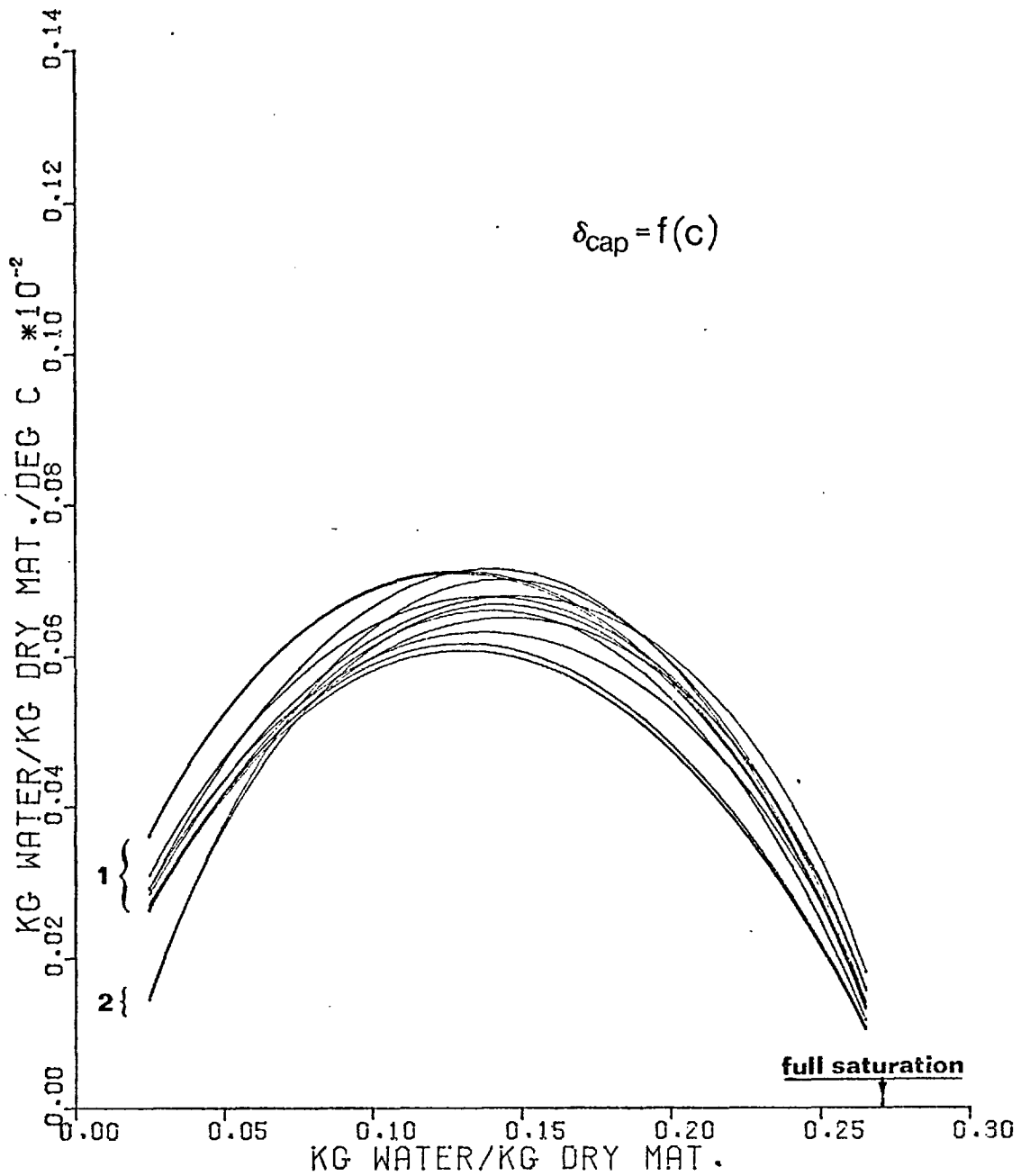


Fig.3.2. The capillary thermal gradient coefficient as a function of moisture content for quartz sand.

The family of curves is obtained by calculating analytical expressions for the capillary curves from series of experimental measurements, appendix 8, and by using the analytical expressions in the formula for δ_{cap} , equation (3.14).

- 1 - calculated from capillary rise data.
- 2 - calculated from capillary drain data.

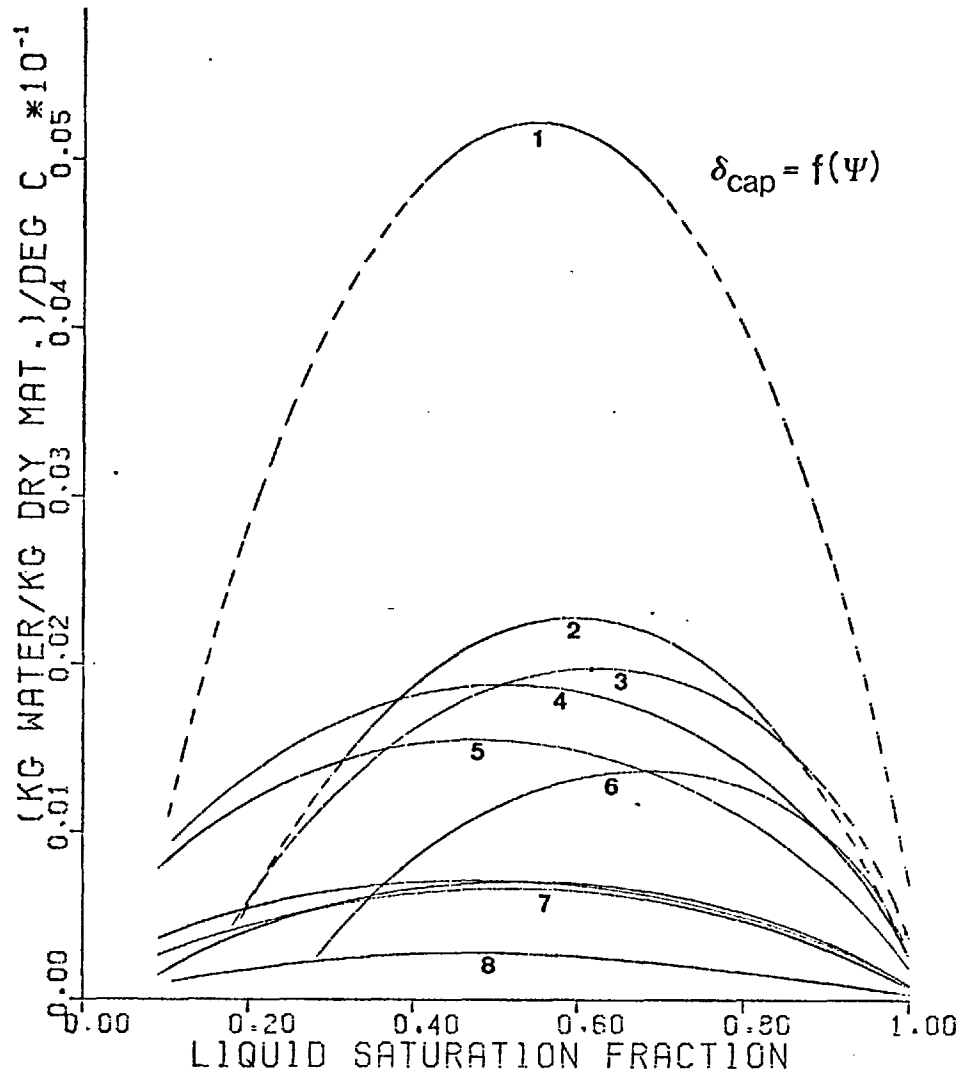


Fig. 3.3. The capillary thermal gradient coefficient as a function of moisture content at 20°C as calculated by equation (3.14) for the various materials the data of which are given in chapter 6, in tables 6.1 - 6.3.

1. Glass beads, Brooks and Corey (B1).
2. Volcanic sands, - " -
3. Fine sand, - " -
4. Coarse sand, Luikov (L5).
5. Fine sand, - " -
6. Silt loam, Brooks and Corey (B1).
7. Quartz sand, this work, three data sets from three experiments.
8. Mixture of sand and clay, Luikov (L5).

various sources and show that values of δ_{cap} are different for different materials. For example, the maximum value of δ_{cap} attained in glass beads is about 0.5×10^{-2} (kg water/kg dry material) / $^{\circ}\text{C}$ whereas in a mixture of sand and clay it has only about five per cent of this value.

Considering these results presented above it seems that the proposed method for the calculation of the capillary thermal gradient coefficient is useful.

3.4 The Influence of Capillary Hysteresis on Experimental Values of the Thermal Gradient Coefficient

As stated previously the thermal gradient coefficient is the derivative $-dc/dT$ ($\approx -\Delta c/\Delta T$) in a steady state closed system. The measured values, however, are influenced by capillary hysteresis. For example, in the method of measurement of the thermal gradient coefficient used by Smith (S3) the material is first evenly moistened, and is then kept under the influence of a small temperature gradient over a period of time in a closed container under the conditions such that the heat flow is in the horizontal direction. When steady state conditions prevail small samples are taken at the same horizontal level. One sample is taken near to the cold surface, the other near to the warm surface. The difference in moisture content between of the two samples is divided by the difference in temperature between them to obtain an approximation to the thermal gradient coefficient. By this method the moisture content of one of the samples increases and the moisture content of the other sample decreases. Thus the change in moisture content of the former sample is in accordance with the capillary rise curve whereas

the change in moisture content of the latter sample is in accordance with the capillary drain curve. The effect of hysteresis is such that the moisture content of one of the samples is different from the value that it would have had if the moisture contents of both samples had been in accordance with the appropriate capillary curve. Since the error occurred by this method may be appreciable the moisture profiles constructed from them by integration may not be reliable. The error may be further increased because, as pointed out by Globus and Nerpin (G2), the moisture field is non-linear. For these reasons it is possible that many of the published values of thermal gradient coefficients are not accurate.

If the method described above is used to measure the thermal gradient coefficient then pairs of samples should be taken such that their moisture contents and moisture contents between the samples either all increase or all decrease from the initial value. In addition, the moisture content and temperature differences between the samples should be small.

CHAPTER 4

THE EFFECTIVE THERMAL CONDUCTIVITY OF WETTED POROUS MATERIALS

4.1 Introduction

The effective thermal conductivity of wetted porous materials under the conditions studied in this work depends on the pure molecular conductivities of the components and on the rate of evaporation, diffusion and condensation of vapour. Obviously it must also depend on the relative abundance of each component and on their geometrical arrangement. Therefore the effective thermal conductivity, k_e , can be expressed as follows:

$$k_e = f(k_s, k_l, k_g, c_s, c_l, c_g, g_i) \quad (4.1)$$

where k_s , k_l , and k_g are the thermal conductivities of the solid, liquid, and gas phases, respectively, and c_s , c_l and c_g are their concentrations. The geometrical factors which describe the arrangement of the phases are denoted by g_i .

The following sections will be devoted to a study of the arguments k_s , k_l , k_g , and g_i .

The molecular thermal conductivities of the solid and liquid phases, k_s and k_l , respectively, appear in equation (4.1). Their values are normally available in the literature or, if not, their measurement is not very difficult. In this work partially wetted quartz sand was studied. The thermal conductivities of water and quartz as functions of temperature are presented in appendices 2 and 3, respectively.

The effective thermal conductivity of the gas phase contains contributions by the molecular thermal conductivity of the gas, denoted by k_a , and by the equivalent thermal conductivity caused by evaporation, diffusion, and condensation of vapour, and denoted by k_d . These contributions are assumed to be additive so that the following equation may be written:

$$k_g = b k_d + k_a \quad (4.2)$$

where k_d corresponds to L_{q2m} and k_a to L_{qq} in equation (2.10). The coefficient b is included to describe the efficiency of the heat transfer mechanism denoted by k_d . In a completely dry material b is obviously zero whereas it is unity if the entire internal surface area of the solid phase is covered by liquid. The prediction of the efficiency coefficient b , and k_d , is relatively complicated, and separate sections will be devoted to both of these terms.

The conductivity k_a in equation (4.2) in the non-hygroscopic region in wetted porous materials is the molecular thermal conductivity of air saturated with water vapour. This value is only slightly dependent on temperature as shown by Krischer (K2, p. 219). The mean value between 0°C and 100°C is 0.026 W/m°C. The molecular thermal conductivity of dry air at 50°C is 0.028 W/m°C (K2, p. 219).

4.2 The Equivalent Thermal Conductivity of Air when Evaporation, Diffusion, and Condensation of Water Vapour Occurs.

The equivalent thermal conductivity of air caused by evaporation, diffusion, and condensation of water, k_d , can be calculated by the following formula presented by Krischer (K2, p. 227). The derivation of this formula is not very difficult:

$$k_d = D_v P \lambda_T \frac{dp_v}{dT} \frac{1}{RT(P-p_v)} \quad (4.3)$$

where D_v is the diffusivity of vapour, P is the total pressure, λ_T is the latent heat of vaporization at the temperature T , R is the gas constant and p_v is the partial pressure of vapour.

In order to verify equation (4.3) experimentally Krischer and Rohnalter (K4) made measurements of the diffusivity of vapour, D_v , and found that it is a little higher in the presence of a temperature gradient than when the diffusion is isothermal. This effect has been studied by other workers and will be surveyed in the following section.

Different expressions for the partial pressure of water vapour as a function of temperature, based on experimental measurements, are surveyed in appendix 2 where calculated values of k_d are also presented. It will be seen that at temperatures near to the freezing point k_d for water is lower than the molecular thermal conductivity of air. With increasing temperature the conductivity k_d increases rapidly attaining the thermal conductivity of water at about 60°C and the theoretical value of infinity at the boiling point.

4.3 The Diffusivity of Water Vapour in Air

In order to use equation (4.3) the diffusivity of vapour, D_v , must be known.

Different expressions for the diffusion coefficient of water vapour in air have been presented in the literature. A detailed comparison of several expressions has been published by de Vries and Kruger (V5). From kinetic theory and from a survey of previously published experimental data they deduced the following expression for the isothermal binary

diffusivity for water vapour in air:

$$D_v = 0.217 \left(\frac{p_o}{p} \right) \left(\frac{T}{T_o} \right)^{1.88} \quad (4.4)$$

where, D_v diffusivity, cm^2/s ,

p_o 1 atm,

T_o 273 K,

and; $273 \text{ K} < T < 373 \text{ K}$

The only experiments quoted by de Vries and Kruger (V5) which were carried out under the influence of a temperature gradient were those of Krischer and Rohnalter (K4) whose expression is as follows:

$$D_v = 0.239 \left(\frac{p_o}{p} \right) \left(\frac{T}{T_o} \right)^{2.3} \quad (4.5)$$

where the notation is the same as for equation (4.4). At a temperature of 0°C equation (4.5) gives values that are 8 per cent greater than those given by equation (4.4): at 90°C the corresponding percentage is 22. It should be noted that the highest temperature in Krischer's experiments was 63°C . The direction of the heat flow in Krischer and Rohnalter's (K4) experiments was vertical, from top to bottom. They state that changing the direction of the heat flow did not alter their results. De Vries and Kruger (V5) investigated the reason for the difference between equations (4.4) and (4.5). They thought at first that the difference could have been due to different experimental situations, i.e. non-isothermal versus isothermal conditions. They showed, however, that the

differences were much larger than could have been accounted for by the effect of thermal diffusion.

In private correspondence Krischer pointed out to de Vries and Kruger (V5) that under non-isothermal conditions supersaturation and/or condensation of water vapour may occur because of the curvature of the saturation vapour pressure versus temperature curve. In a gas between two wet surfaces maintained at different temperatures the vapour pressure rather than the temperature varies linearly between the saturation values at the fixed temperatures. Thus at intermediate temperatures the gas is supersaturated by an amount which depends on the non-linear vapour pressure versus temperature relationship. Krischer suggested that this may be the explanation for the difference between equations (4.4) and (4.5). This led Kruger, Daey Ouwens, te Velde, and de Vries (K6) to the idea of subjecting a capillary tube partly filled with water to a linear temperature variation along the wall and of observing the transport of water in the vapour phase.

Unfortunately, their results still leave uncertain the question of whether to use equation (4.4) or (4.5). In this work equation (4.5) is used as it was obtained in the presence of a temperature gradient and its validity has not been repudiated.

4.4 The Efficiency Coefficient of the Evaporation, Diffusion, and Condensation Cycle.

An efficiency coefficient, b , was introduced in equation (4.2). Krischer (K2, p.229) defines b as a quotient in which the area of the wetted internal surface is divided by the total internal surface. The most obvious definition of the

total internal surface is the gas phase / non-gas phase surface. This kind of definition is, however, unnecessary because b is a quantity which is to be determined experimentally.

The prediction of the efficiency coefficient b as a function of moisture content is a difficult problem on which relatively little work has been done. Krischer (K2, p.232) has presented an equation for the evaluation of b for moisture contents lower than the maximum attainable hygroscopic moisture content. In the present work, however, such moisture contents are not studied. It is not possible at present to predict the way in which the internal surfaces of porous materials become wet. It is also a difficult and time consuming process to determine b experimentally. It is also an inaccurate process because b can only be obtained from measured values of the effective thermal conductivity and it is necessary to use approximate empirical formulae because there is no theoretical formula by which the effective thermal conductivity of a wetted porous material can be calculated from the conductivities of the components.

Krischer (K2, p. 229) presented b as a function of the saturation fraction of water for three different materials: brick, ytong - a sort of concrete - and siporex. Palosaari and Nordén (P2) determined b as a function of moisture content for sulphate pulp, and Nordén and Palosaari (N2) for two different types of mineral wool. In one of the two types of the mineral wool b attained the value of unity at a very low moisture content whereas for the other type, which was difficult to wet evenly, b did not attain the value of unity until a far higher moisture content was attained. Nissan, Hansen and

Walker (N1) presented b as a function of saturation fraction for two different woven fiberglass beds. In the works mentioned above the moisture content is given either as the saturation fraction or as kg water / kg dry material. However, because the process to be studied is the wetting of the internal surfaces as a function of moisture content, it would be more logical, although not very convenient, to express the moisture content as the mean thickness of the liquid layer, i.e. as volume of liquid over unit area of the surface of the internal walls. Unfortunately, none of the workers who has determined values of b has determined the specific internal surface of the materials studied. The value of b is dependent, among other things, on the wetting angle between the liquid and the solid. The wetting angle determines the tendency for dry patches to be formed.

Values of b as available in the literature are shown in fig. 4.1 together with values of b calculated in this work for sand. These calculations were based on experimental measurements of the effective thermal conductivity by de Vries (V4). The method of calculation will be described in section 4.6. The values of b shown in fig. 4.1 are not suitable for further analysis because of the lack of information about the specific internal surface of the materials concerned and because the wetting angles between the liquid and the solid are not known.

4.5 The Thermal Conductivity of Heterogenous Media.

Generally, no perfect method of predicting the thermal conductivity of a heterogenous medium has been developed although a number of formulae have been presented.

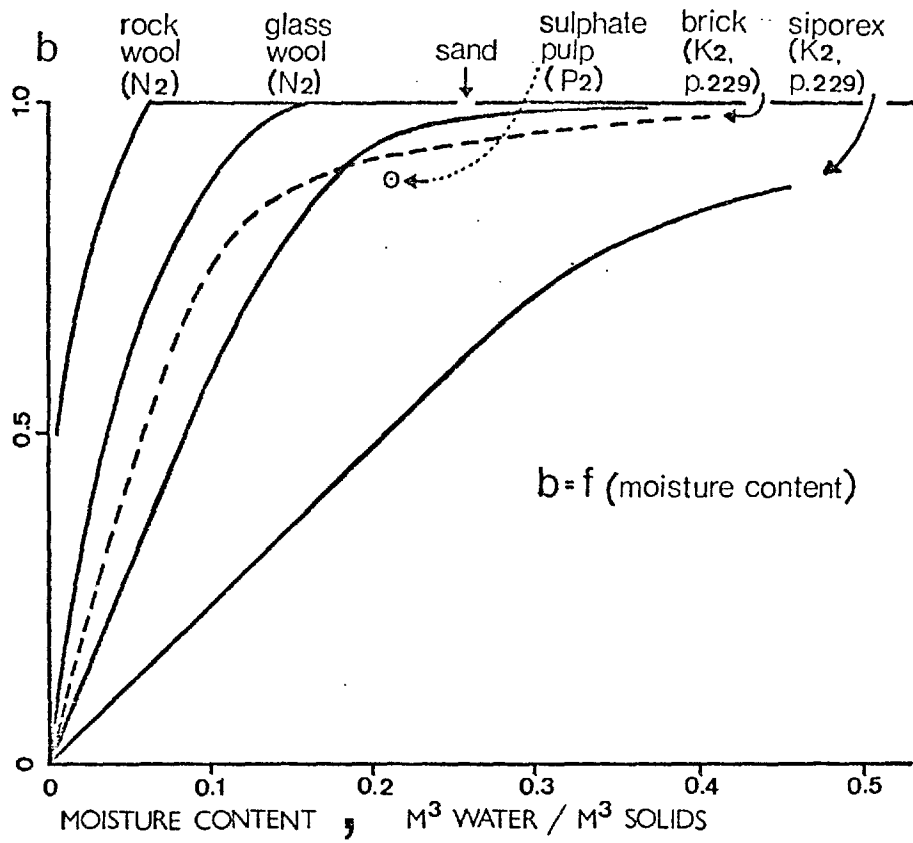


Fig. 4.1. The quantity b as a function of moisture content in various materials.

The values for sand were calculated from the conductivity values measured by de Vries (V⁴). The other values were obtained from the literature references shown.

Each of these formulae can be used successfully only for particular geometrical configurations.

The simplest geometrical arrangement of a number of phases is for them to be stacked in successive plane layers. If the layers are stacked parallel to the direction of heat flow, the thermal resistance is a minimum. If they are stacked normal to the heat flow, the resistance is a maximum. All cases of more complex geometry must fall between these two extremes and may be considered to be equivalent to a combination of parallel and normal slabs. The volume fraction of the slabs normal to the heat flow is an important parameter which must be determined experimentally for each material. Formulae based on this approach are therefore semi-empirical. Krischer (K2, p.224) has used this model to predict the thermal conductivities of porous materials as functions of moisture content and temperature. He has studied materials which have a continuous solid matrix such as various types of concrete in which the solid matrix transfers an important portion of the total heat. Therefore the parameter which describes the fraction of the imaginary slabs that are normal to the heat flow does not change much as a function of moisture content and may be considered a constant.

Another important type of formula is that for which an analytical solution has been derived for the conductivity of a material which consists of a continuous phase and a discontinuous phase in the form of isolated particles of various shapes. If the volume fraction of these particles is large they become so close to each other that their spatial arrangement must be taken into account. Perhaps the simplest formula of this type is that derived by Maxwell (M2) for the

calculation of the conductivity of a medium in which there are spheres so far apart that their spatial arrangement does not influence the total conductivity. According to Maxwell:

$$\frac{k}{k_c} = \frac{1 - 2 \epsilon_1 f_1}{1 + \epsilon_1 f_1} \quad (4.6)$$

where ϵ_1 is the volume fraction of the discontinuous phase and

$$f_1 = \frac{k_c - k_1}{2k_c + k_1}$$

and where

k_1 is the conductivity of the discontinuous phase and,
 k_c is the conductivity of the continuous phase.

Later on, Eucken (E3) extended this formula for a medium which includes discontinuous phases of different conductivities. His formula for the conductivity of a three phase system, which consists of a continuous phase ^{and of} spheres of two different conductivities so far apart that their spatial arrangement does not influence the total conductivity, is as follows:

$$\frac{k}{k_c} = \frac{1 - 2 \epsilon_1 f_1 - 2 \epsilon_2 f_2}{1 + \epsilon_1 f_1 + \epsilon_2 f_2} \quad (4.7)$$

where the notation is the same as for equation (4.6). The subscript 2 refers to the second discontinuous phase. Equation (4.7) reduces to equation (4.6) when there is only one discontinuous phase.

There are slightly different expressions if the particles of the discontinuous phase or phases are not spherical but are, for example, cylindrical or ellipsoidal. Gorring and Churchill (G5) refer to these expressions.

Rayleigh (R1) derived expressions for the conductivities of more densely packed dispersions. His formula for spherical particles is as follows:

$$\frac{k}{k_c} = \frac{1 - 2 \epsilon_1 f_1 - \epsilon_1^{10/3} a f_1 - \dots}{1 + 2 \epsilon_1 f_1 + \epsilon_1^{10/3} a f_1 + \dots} \quad (4.8)$$

where

$$f_1 = \frac{(1 - v_1)^2}{(\frac{4}{3} + v_1)(2 + v_1)}$$

where

$$v_1 = k_1/k_c$$

and where the other notation is the same as that used previously. The coefficient a is a configuration parameter. De Vries (V4) derived values of 1.31, 0.129, and 0.0752 for the coefficient a in simple cubic, body-centred cubic, and face-centered cubic arrays, respectively. This means that at high particle volume fractions the spatial configuration is an important factor. When a is zero equation (4.8) reduces to equation (4.6).

There are a number of other formulae, each of which is suitable for a particular type of porous material.

Recently, Andrea and Ling (A4) showed that the thermal conductivity of composite materials is controlled by probabilistic rather than deterministic laws. They developed a method of calculation based on the random generation of dispersed particles in the space of the continuous phase. The shape of the particles is taken into account analytically. This method requires a considerable amount of computer storage space. Earlier, Cheng and Vachon (C5) used a somewhat similar statistical approach based on the work of Tsao (T7). In their work they assumed that the particle locations were distributed normally and that the normal distribution could be approximated by a portion of a parabola. Cheng and Vachon found that their formula gave values which are very close to those measured experimentally if the volume fraction of the discontinuous phase is not large. They pointed out that their formula becomes unstable and gives erroneous values under certain conditions.

4.6 The Derivation of a Semi-empirical Formula for the Prediction of the Effective Thermal Conductivity of a Wetted Porous Material.

As shown in the previous section no perfect method of predicting the thermal conductivity of a multi-phase medium has been found. The problem is more difficult in the case of wetted porous materials, especially if the solid phase is particulate, as a kind of phase inversion may occur because at low moisture contents the gas phase is continuous whereas at high moisture contents the liquid phase is continuous. A further complication arises because, as discussed in section 4.4, the heat transfer mechanism caused by

evaporation, diffusion, and condensation of vapour is dependent on moisture content in an unknown way. Another feature of the study of the effective thermal conductivity of wetted porous materials is that it is difficult to obtain reliable experimental values. In particular, at temperatures near the boiling point of the liquid the ordinary methods used for the measurement of thermal conductivity are not suitable because they require a steady-state temperature distribution to be established. However, the imposed temperature gradient causes a non-linear moisture content distribution to be set up because of the non-linearity of the thermal conductivity-moisture content - temperature relationships so that the measured values will be erroneous.

Special methods of measurement must be used such as the quasi-stationary method used by Krischer and Esdorn (K3) or the method based on the phase lag of a travelling sinusoidal temperature wave used by Palosaari and Nordén (P1) and Nordén and Palosaari (N2). Another experimental difficulty arises because it is difficult to wet the sample evenly, especially if the moisture content is low.

For the reasons discussed above it was concluded that a comprehensive theoretical treatment of the problem of the effective thermal conductivity of wetted porous materials is not possible at present. Consequently, it was decided to develop a semi-empirical formula for the effective thermal conductivity.

As mentioned earlier in this section, a characteristic feature of a wetted porous medium is that at low moisture contents the liquid forms a discontinuous phase whereas at high moisture contents it forms a continuous phase. The following approximate formula may be written:

$$k_e = (1 - \chi) k^{cg} + \chi k^{cl} + k_{ser} \quad (4.9)$$

where k^{cg} and k^{cl} are the effective thermal conductivities of the wetted porous material when the gas and the liquid phases are assumed to be continuous, respectively. The conductivities k^{cg} and k^{cl} may be calculated, for example, by the use of equation (4.7) where the solid matrix is taken to be one of the discontinuous phases and the conductivity of the gas phase is calculated by equation (4.2). Since the elements of the solid phase are not separated the quantity k_{ser} which denotes the contribution of the series solid conductivity is included in equation (4.9). If the solid phase is particulate k_{ser} is small and it may be added to the contributions of the other conductivities as in equation (4.9). However, if the contribution of the series solid conductivity is large, which is the case if there is a continuous solid matrix which occupies a significant volume fraction and if the conductivity of the solid phase differs much from the conductivities of the other phases then the conductivity k_{ser} cannot be added to the other conductivities without an error being incurred. The quantity χ in equation (4.9) is a function of moisture content and was first used by Palosaari and Nordén (Pl). It is zero in a dry material, it increases with increasing moisture content, and it attains a value of unity in a thoroughly wetted material. The function χ can be expected to be independent of temperature. At very low and very high moisture contents, i.e. when the volume fractions of the liquid and gas discontinuous phases are low the equation should give values of acceptable accuracy even if the thermal conductivities k^{cg} and k^{cl} are calculated by using a simple

formula such as equation (4.7).

The series solid conductivity k_{ser} can be determined by measuring the thermal conductivity of the material in a vacuum, and, in order to keep the contribution by radiation low, at a low temperature. Unfortunately the thermal conductivity of a material in a vacuum is not generally available and the measurement is not easy. In the course of this work k_{ser} was evaluated in the following manner:

$$k_{ser} = k_{exp.,wet} - k(a)_{wet} \quad (4.10A)$$

$$k_{ser} = k_{exp.,dry} - k(a)_{dry} \quad (4.10B)$$

where $k(a)_{wet}$ and $k(a)_{dry}$ are the values of the conductivities obtained by the application of equation (4.8) with the solid taken as the discontinuous phase, and liquid and gas taken in turn as the continuous phase, respectively. The quantities $k_{exp.,wet}$ and $k_{exp.,dry}$ are the experimentally measured values of the conductivity for the fully wetted and completely dry states, respectively. The unknown quantities in equations (4.10A) and (4.10B) are k_{ser} and a . The equations can be solved numerically.

The method presented above was applied to a sand of known wet and dry thermal conductivities and known volume fraction of non-solids. The values are given in table 4.1 together with the calculated values of the quantities a and k_{ser} .

Experimentally measured thermal conductivity of dry sand (C1)	$k_{\text{exp.,dry}}$	W/m °C	0.254
Experimentally measured thermal conductivity of fully wetted sand (V4)	$k_{\text{exp.,wet}}$	W/m °C	2.54
Volume fraction of non-solids, appendix 8	ϵ	-	0.412
Configuration parameter	a	-	0.479
Series solid conductivity	k_{ser}	W/m °C	0.0938

Table 4.1. Properties of a typical sand. The values of the quantities a and k_{ser} were calculated by the use of equations (4.10A) and (4.10B). The values of $k_{\text{exp.,dry}}$, $k_{\text{exp.,wet}}$ were estimated from the given sources for $\epsilon = 0.412$.

When the above method is used for the determination of k_{ser} in equation (4.9) it is necessary to calculate the conductivities k^{cg} and k^{cl} from an expression in which the term containing the quantity a is taken into account. A comparison of equations (4.6) and (4.8) shows clearly the contribution of the configuration term. Equation (4.7) can be modified to incorporate configuration terms for both the solid and the liquid or vapour discontinuous phases. However, the configuration parameter for the solid phase has been evaluated by the method described above whereas the value of the configuration parameter for the liquid or vapour discontinuous phase is unknown and is likely to be a function of moisture content. Thus only the configuration term relating to the solid phase is incorporated in the following modified version of equation (4.7) :

$$\frac{k}{k_c} = \frac{1 - 2 \epsilon_{dp} f_{dp} - \epsilon_s^{10/3} a f_s - \dots}{1 + \epsilon_{dp} f_{dp} + \epsilon_s^{10/3} a f_s + \dots} \quad (4.11)$$

where the notation is the same that used previously. The subscript dp refers to the discontinuous phase which is not the solid phase, and the subscript s refers to the solid phase.

The effective thermal conductivity of a wetted porous material can now be calculated by the use of equation (4.11). This method has been developed for the case when the solid phase is discontinuous, i.e. the material is particulate.

If the solid matrix is continuous it is preferable to apply the two-phase expression, equation (4.6), so that the solid phase is taken to be continuous and the combined vapour and liquid phases are taken to be the discontinuous phase. The conductivity of the combined liquid and vapour phases is taken to be

$$k_{cgl} = (1 - x) k^{cg} + x k^{cl}$$

where the conductivities k^{cg} and k^{cl} are calculated using equation (4.6) with the solid phase ignored and the liquid and gas phases being treated as the discontinuous phase in turn. Since the solid phase is ignored it is necessary to scale up the volume fractions of the liquid and gas phases proportionally so that their sum is unity. This proposed method was not studied in more detail in this work.

A difficult problem in the application of equation (4.9) is the prediction of the quantity x as a function

of moisture content. Even if the necessary experimental values of the effective thermal conductivity at various moisture contents are available, the calculation of values of the quantity χ is difficult because of the existence of another independent function of moisture content, b , which was introduced in equation (4.2). The values of both b and χ are zero in a dry material and increase towards unity with increasing moisture content. The problem was simplified by assuming that there is a simple relationship between the quantities b and χ as follows:

$$b = f(x) \quad (4.12A)$$

$$\chi = f(E\chi) \quad (4.12B)$$

where

$$f(x) = Ax + Bx^2 + Cx^3 \leq 1 \quad (4.13)$$

where

$$x = c - c_{\text{hyg}}$$

and where c_{hyg} is the maximum attainable hygroscopic moisture content, below which the quantity b is small and may be assumed to be zero.

In equation (4.12B) E is a constant and the function f is the same for both equations. Although b and χ are both independent of temperature, their influence on the calculated effective thermal conductivity is, however, different at different temperatures because the quantity b controls only the gas phase conductivity. Therefore, if values of the effective thermal conductivity are known for a range of moisture contents at two different temperatures, it is possible to

construct the functions b and χ by adjustment of the coefficients A , B and C in equation (4.13) and the coefficient E in equation (4.12B) until the difference between the measured and predicted conductivity values at the two temperatures is a minimum. This method was applied to a sand for which experimental conductivity values have been given by de Vries (V4).

The b -function was obtained as follows. The function b was estimated, based on assumed values of the coefficients A , B and C in equation (4.13), and used in equation (4.2) to calculate the equivalent thermal conductivity of the gas phase. This conductivity was used in equations (4.11) and (4.9). In the latter equation the value of the quantity χ was calculated by equation (4.12B) using an assumed value of the coefficient E . In this way equation (4.9) gave a predicted value of the effective thermal conductivity. The process was repeated by adjusting the values of the coefficients A , B and C until the sum of the squares of the deviations between the predicted and experimental values over the range of moisture contents became a minimum. Then the sum of the squares between the experimental and predicted values was minimized at a different temperature by the use of the same values of the coefficient A , B and C but by adjusting the value of the coefficient E in equation (4.12B). The minimization was repeated at the first temperature using the newly found value of E but readjusting the values of A , B and C . Again, a new value of E was searched for at the second temperature.

The process was continued until the sums of the squares of the deviations of the measured values of the

conductivities from the predicted values at both temperatures became acceptably low. For the coefficients A, B, and C in equation (4.13) the values of 2.72, -2.04, and 0.383 were found, respectively. The b-function obtained for the sand referred to above by the use of these values is shown in fig. 4.1. For the coefficient E a value of 2.0 was obtained. Since for this sand the value of E was found to be greater than unity then χ grows faster than b with the increasing moisture content. This is obviously because the capillary forces draw the liquid into the contact points where even a small amount of liquid is able to build a thermal bridge between the particles. On the other hand the liquid is confined to a small region and does not actually wet the surfaces away from the contact points very effectively so causing low rates of evaporation and low values of b.

The effective thermal conductivity of sand can now be calculated as a function of moisture content and temperature by the use of equations (4.9) and (4.11). Calculated values together with experimental values are shown in fig. 4.2. The agreement between the calculated and the measured values is not very good for various reasons.

The use of equation (4.11) incurred an error because the terms containing the configuration parameter for the liquid and gas phases were not taken into account. Even for the solid phase, only the first two terms of the series were taken into account. The experimentally measured values also are suspect because - as discussed earlier in this section - it is difficult to obtain reliable experimental values of the effective thermal conductivity of wetted porous materials; especially at elevated temperatures.

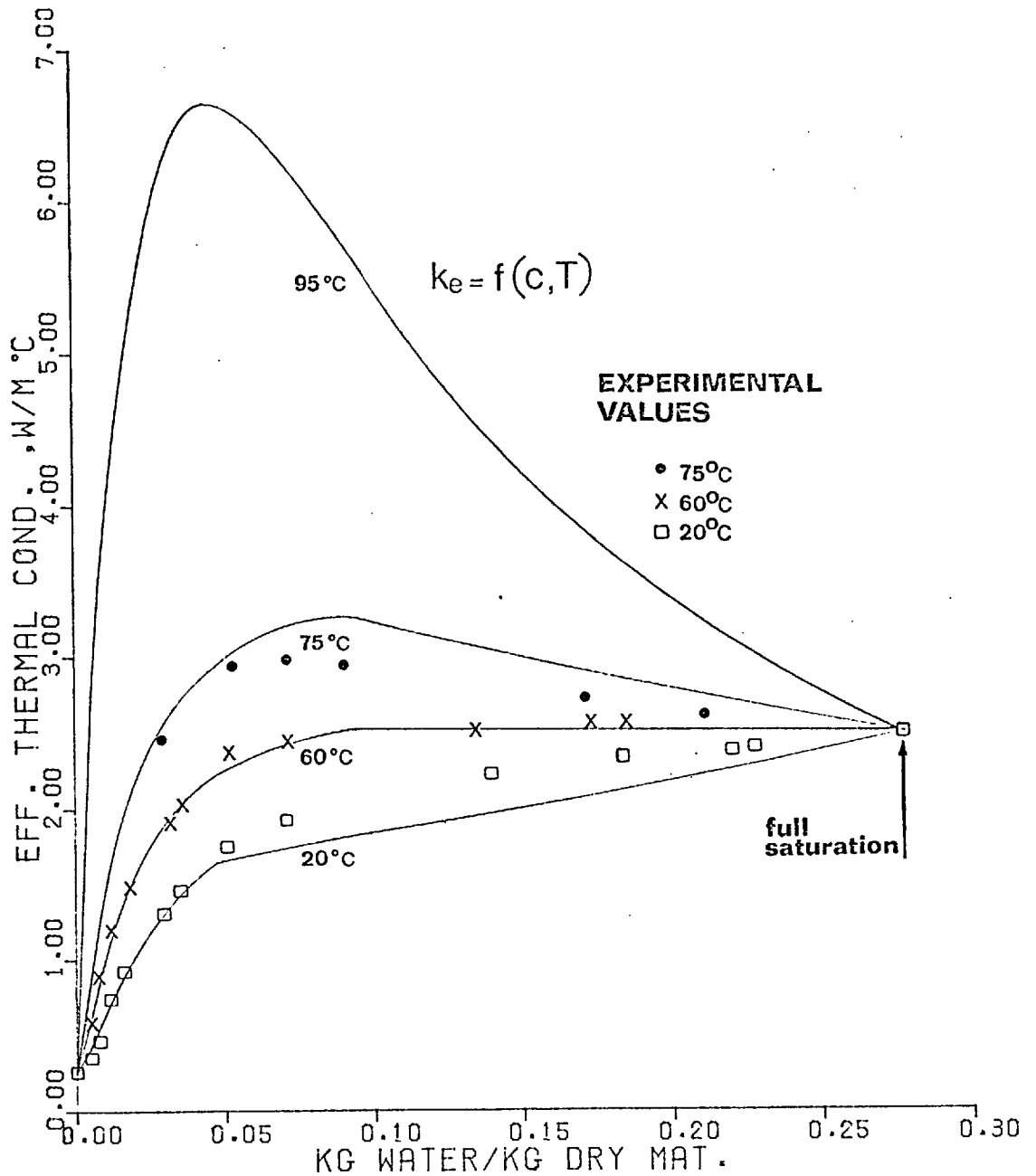


Fig. 4.2. The effective thermal conductivity of sand at various temperatures as a function of moisture content.

The theoretical values (solid lines) were calculated using equations (4.9) and (4.11). The experimental values were measured by de Vries (V4).

To conclude, it is pointed out here, as discussed earlier in this section, that there is no theoretical way of predicting the effective thermal conductivity of wetted porous materials. Formulae, such as equations (4.9) and (4.11), are semi-empirical so that their use may be considered to be good if the deviation of the predicted values from the measured values is less than about 10 per cent and if the conductivity values, as a function of moisture content, form a smooth curve.

CHAPTER 5

THE THERMAL GRADIENT COEFFICIENT CAUSED BY
EVAPORATION, DIFFUSION, AND CONDENSATION OF
VAPOUR

5.1 Introduction

The thermal gradient coefficient caused by the cycle of evaporation of liquid, diffusion, and condensation of vapour, and the return liquid flow induced by capillary forces will now be considered. This coefficient, δ_{EDC} , is defined in equation (2.33B) and appears in equation (2.42). Its value must be known in order to solve the basic transport equations of this work, the simultaneous equations (2.41) and (2.42). From equation (2.34):

$$\delta_{EDC} = - \left(\frac{dc}{dT} \right)_{EDC} = - X_{1\ EDC} \left(\frac{dx}{dT} \right) = \frac{f_2}{L_{11}} \left(\frac{dx}{dT} \right) \quad (5.1)$$

The prediction of δ_{EDC} requires studies to be made of the vapour flux in porous materials, f_2 , and of the characteristic coefficient for liquid flow, L_{11} . The study of both f_2 and L_{11} involves the use of two different concepts, permeability and tortuosity, which must be considered first.

5.2 Permeability

Permeability is a useful concept in the study of the flow of fluids in porous materials. In this work it will be employed in the studies of the vapour and the liquid flows.

The concept of permeability was originally introduced by Darcy in the 1850's (D1). He measured the flow of liquid through a bed of porous material as a function of the pressure difference and arrived at an expression similar to the following equation which is called Darcy's law:

$$f = -\rho \frac{K}{\mu} \frac{dp}{dx} \quad (5.2)$$

The viscosity was introduced into Darcy's law at a later date. Before the common use of the viscosity in this expression it was usual to refer to K as the "specific permeability" whereas the product $K\mu$ was called the "permeability". The introduction of viscosity - popularized by Wyckoff et al around 1933 - was a considerable improvement as the permeability became independent of the properties of the liquid. Its dimension is distance squared. The specific unit of permeability is the Darcy which is equivalent to $9.87 \times 10^{-4} \text{ m}^2$.

Darcy's law is valid only under certain conditions (S1, p. 158, p. 248). Perhaps the most important limitation is that Darcy's law is not valid at high Reynolds numbers. However, there is some confusion regarding the upper limit of the Reynolds number at which Darcy's law is valid. Values from 0.1 to 75 have been proposed by different authors (S1). The reason that different values have been proposed may be result of the difficulty of determining the effective diameter of the flow channels. It is shown in appendix 4 that the liquid velocities likely to occur under the conditions studied in this work are low so that the use of Darcy's law is well substantiated.

A further situation for which Darcy's law is not valid is the very slow molecular flow of gases. This problem does not arise in this work because the vapour flow is described by the diffusion equation.

A vast amount of work has been done on the development of formulae by which the permeability of a porous material can be predicted. This work is surveyed by

Scheidegger (Sl, p. 112 ff.). The earliest attempts were aimed at finding a relationship between porosity and permeability. The relationships of this kind are commonly called "Kozeny" equations of which that incorporated in the Kozeny - Carman equation is perhaps the best known. Later on a large number of different and complicated formulae were developed which can be used to predict the permeability for certain types of materials under certain conditions. These formulae are not, however, of immediate interest because a simple method was developed in the course of this work by which the permeability at the fully saturated state can be predicted easily from measurements made at less than full saturation. For this purpose it is necessary to study the dependence of permeability on moisture content, and to use the concept of relative permeability, K_r , which is defined as follows:

$$K_r = \frac{\text{permeability}}{\text{permeability of the same material when it is fully saturated by liquid}} \quad (5.3)$$

The relative permeabilities of the wetting and non-wetting phases will be denoted by K_{rw} and K_{rnw} , respectively. In this work the non-wetting phase is gas. The relative permeability is dimensionless, its value is zero in a dry material, it increases with increasing moisture content and is unity in a thoroughly wetted material. A paper by Brooks and Corey (Bl) gives a detailed and comprehensive survey of the literature on relative permeability. There are numerous references and the work is relatively recent (1966).

The main objective has been to determine the way in which the relative permeability is dependent on moisture content.

The moisture content of a porous medium is usually expressed as the saturation fraction of non-bound water which is called the effective saturation. It is defined by the following expression:

$$\Psi_e = \frac{\Psi - \Psi_r}{1 - \Psi_r} \quad (5.4)$$

The symbol Ψ_r stands for residual saturation or irreducible saturation. At residual saturation the continuous liquid film is broken down and the removal of the residual liquid normally involves an evaporation process. Generally speaking, the relative permeability is not uniquely dependent on moisture content but is dependent also on the internal geometry of the porous material. Various attempts have been made, however, to express the relative permeability as a function of moisture content only.

Irmay (I3, see also I2) derived such a relationship for soil starting from the assumptions that the driving force for the flow is proportional to the effective saturation and that the viscous resistance to flow is independent of flow rate. He arrived at the following equation:

$$K_r = \Psi_e^3 \quad (5.5)$$

Corey (C7) found experimentally that the following approximation could be used for a variety of consolidated porous rocks:

$$K_r = \Psi_e^4 \quad (5.6)$$

This approximation was also derived analytically by Corey (C7) who assumed that the capillary pressure in porous materials can be approximated by the following expression:

$$\frac{1}{p_c} = C \psi_e$$

where C is a constant.

Averjanov (A5) proposed a relationship which is similar to equations (5.5) and (5.6) but with the difference that his exponent is 3.5.

Another type of empirical expression was developed by Richardson (R3) who used the experimental data reported in the paper by Osoba, Richardson, Kerver, Hafford and Blair (02). Richardson's expression for the permeability of the non-wetting phase is as follows:

$$K_{rnw} = \exp (-5.5 \psi^2) \quad (5.7)$$

where $0 \leq \psi \leq 0.4$

This expression implies that the residual moisture content causes a decrease in the permeability of the non-wetting phase. The permeability of the wetting phase can be obtained from equation (5.7) by application of the symmetry principle which will be described later. The resulting expression is:

$$K_{rw} = \exp \left[-5.5 (1 - \psi)^2 \right] \quad (5.8)$$

Equations (5.5), (5.6), and (5.8) are over simplified. They are, however, useful when estimates of the relative permeabilities are required. Harmathy (H3) used equation (5.7) in

his work on simultaneous heat and moisture transfer in porous media. However, equations (5.5) and (5.6) are better because, as will be shown later, they are approximations of expressions which have been derived on a theoretical basis whereas equations (5.7) and (5.8) are based on empirical data.

The works which will now be discussed have been centred around the development of expressions which incorporate the effects of pore size distribution and the liquid path length as a function of moisture content. One of the first attempts of this kind was made by Rose and Bruce (R4). They proposed the following empirical formula:

$$K_{rw} = \Psi \left(\frac{p_T}{p_c} \right)^2 \quad (5.9)$$

where p_T is called threshold pressure, which is the minimum pressure required for starting the removal of liquid from a fully saturated sample, and p_c is the capillary pressure. This equation takes into account the distribution of the radii of the capillaries around the mean value. If all the radii are the same then the capillary pressure, p_c , would remain constant at all moisture contents and K_{rw} would be equal to the saturation fraction. It can be shown that such a relationship holds only if the material consists of parallel continuous capillaries. Poiseuille's equation is as follows:

$$Q = \frac{\pi}{\mu} \frac{r^4}{8} \frac{\Delta p}{L} \quad (5.10A)$$

which gives for the flux:

$$f = - \frac{pr^2}{8\mu} \frac{dp}{dx} \quad (5.10B)$$

Comparison of equations (5.2) and (5.10B) shows that the permeability is proportional to the square of the capillary radius. The square of the capillary radius is, in turn, proportional to the saturation fraction in a material which consists of straight capillaries of uniform diameter.

In a real porous material, however, the liquid path becomes longer at lower moisture contents. This phenomenon is taken into account by the use of the concept of tortuosity which will be discussed in the following section 5.3. Equation (5.9), however, predicts correctly that decreasing the moisture content leads to progressive lowering of the relative permeability because the liquid first fills the smaller diameter capillaries in which the capillary pressure is higher.

This approach was greatly improved later by various authors. Burdine, Gournay, and Reichertz (B3) modified Poiseuille's and Darcy's equations to accommodate the case when the capillary radii are distributed around the mean value and when each interval of capillary radii has a separate effective capillary length. They arrived at a formula for the permeability which can be converted to an expression for the relative permeability by the application of equation (5.3). Their expression is as follows:

$$K = C\varepsilon \sum_{i=0}^n \frac{\psi_i (\overline{r_i^4})}{x_i^2 (\overline{r_i^2})} \quad (5.11)$$

where C is a constant, and x_i is a length which is proportional to the "effective" capillary length. The summation is taken over the range of wetted capillaries. The proportionality factor, x_i , must be determined empirically.

Burdine et al give a semi-empirical formula for x_i based on experimental studies of porous rocks.

Later, Burdine (B2) found that the proportionality factor, x_i , is equal to the tortuosity and that the following relationship exists between the relative tortuosity and effective saturation:

$$T_{rw} = \Psi_e$$

The above relationship will be discussed in section 5.3.

Wyllie and Gardner (W5) derived a more easily applicable expression for the calculation of relative permeability by starting from Poiseuille's equation, as did Burdine et al, but by using an integral representation. Wyllie and Gardner arrived at the following expression:

$$K_{rw} = \Psi_e^2 \frac{\int_{\Psi_r}^{\Psi} p_c^{-2} d\Psi}{\int_{\Psi_r}^1 p_c^{-2} d\Psi} \quad (5.13)$$

The capillary radii do not appear in this equation because, as will be discussed later, there is a relationship between capillary radius and capillary pressure.

Equation (5.13) is easily applicable, and it seems that no better expression is available. Brooks and Corey (B1) also derived equation (5.13) but with the difference that their integrals have a lower limit to zero moisture content instead that of the residual saturation. This usage is not recommended because the capillary pressure is correctly defined only above the residual saturation where the continuous

liquid film does not break down.

In this work the capillary forces are expressed as capillary rise or drain height instead of as capillary pressure. As shown in appendix 7 equation (5.13) becomes as follows when expressed in terms of capillary rise or drain height:

$$K_{rw} = \Psi_e^3 \frac{(h^{-2})_{\text{mean}}}{(h^{-2})_{\text{mean}, \Psi=1}} \quad (5.14)$$

where

$$(h^{-2})_{\text{mean}} = \frac{1}{h(\Psi) - h(\Psi_r)} \int_{h(\Psi_r)}^{h(\Psi)} h^{-2} dh$$

If all the capillaries and channels in the material are of the same radius then equation (5.14) reduces to Irmay's equation (5.5). In a porous material the radii of the capillaries are not all the same. Since the smaller capillaries are filled first then the higher the moisture content the larger becomes the mean radius of the filled capillaries and the smaller becomes the capillary rise height. Thus the exponent of Ψ_e in equation (5.5) can be expected to be greater than three. This conclusion is supported by experimentally obtained values which, as discussed earlier, range from 3.5 to 4. The relative permeability of the quartz sand referred to earlier was calculated as a function of moisture content by the use of equation (5.14). The result is shown in fig. 5.1 together with the relative permeabilities calculated by the use of

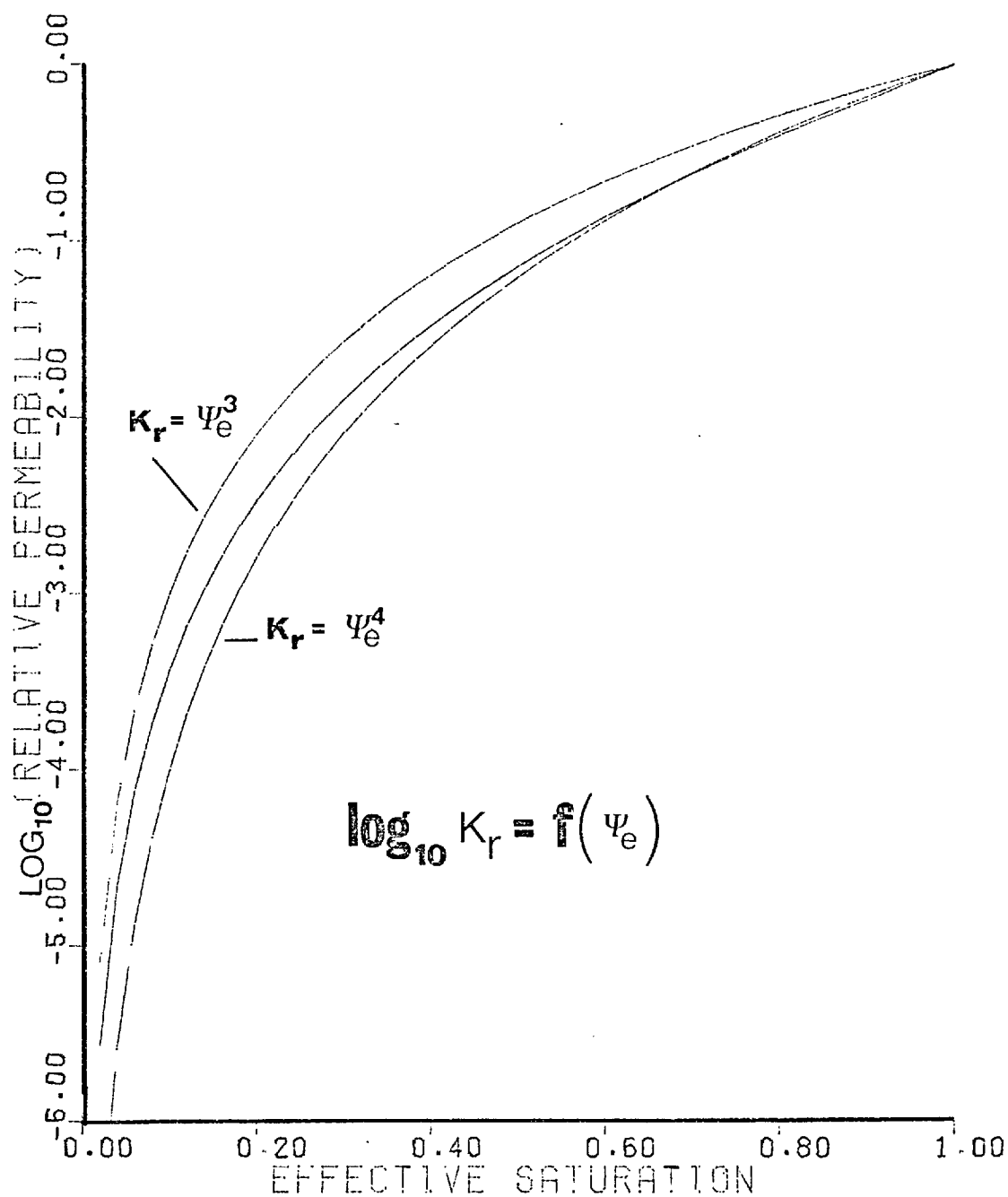


Fig. 5.1. Relative permeability of the wetting phase as a function of effective saturation.

The central curve is calculated by equation (5.14).

The top and bottom curves are calculated by the approximate formulae shown above.

equations (5.5) and (5.6). Fig. 5.1 shows that the results obtained by the application of equation (5.14) are in good agreement with those predicted by equation (5.5) at low moisture contents and are in good agreement with those predicted by equation (5.6) at high moisture contents. At intermediate moisture contents equation (5.14) predicts values approximately midway between those predicted by equation (5.5) and (5.6).

The expression obtained by Wyllie and Gardner (W5) for the permeability of the non-wetting phase is as follows:

$$K_{rnw} = (1 - \psi_e^2) \frac{\int_{\psi}^1 p_c^{-2} d\psi}{\int_{\psi_r}^1 p_c^{-2} d\psi} \quad (5.15)$$

Comparison of equations (5.13) and (5.15) shows that the permeabilities of the wetting and non-wetting phases are symmetric with respect to $(1 - \psi_e)/2 + \psi_r$. Wyckoff and Botset (W4) arrived at this conclusion by analysing their measured permeabilities. By application of this principle to equation (5.5) the following expression is obtained:

$$K_{rnw} = (1 - \psi_e)^3 \quad (5.16)$$

Brooks and Corey (B1) found that above a certain moisture content there is no gas flow through the material. Therefore, equation (5.16) may be modified as follows:

$$K_{rnw} = (\psi_b - \psi_e)^3$$

where Ψ_b is analogous to Brooks and Corey's "bubbling pressure" and may be called the "bubbling saturation". Brooks and Corey provided experimental values of the bubbling pressure for various materials. By use of the relationship between the moisture content and the capillary pressure it is possible to evaluate the bubbling saturation although Brooks and Corey's results do not allow an accurate evaluation. It seems, however, that Ψ_b is in all cases near to unity. Thus, equation (5.16) is a sufficiently accurate approximation.

5.3 Tortuosity

Tortuosity is a useful concept in the study of the flow of fluids in porous media. Various workers in their attempts to describe the flow of a liquid in a porous medium in terms of straight parallel capillaries found that the flow rate was lower than their models predicted. Therefore, the concept of tortuosity was introduced to describe - as it was stated - the extra path length that the fluid must take in order to avoid obstacles in the path. Their definition of tortuosity is as follows:

$$T = \frac{L_a}{L} \quad (5.17)$$

where L_a is the actual length of the fluid path through a layer of porous material of thickness L . This conventional definition of tortuosity may be physically inaccurate as some part of the extra flow resistance attributed to tortuosity may be caused by restrictions in the cross-sectional area available for flow. Therefore, tortuosity can be redefined

as the effective length of the fluid path, L_e , divided by the thickness L . This definition can be generalized as follows:

$$T = \frac{x_e}{x} \quad (5.18)$$

where x_e is a characteristic distance in a fluid channel in a porous material and x is the corresponding distance if the fluid channel is straight and of uniform diameter.

The formal validity of equation (5.18) can be shown as follows. If the distances x_e and x are measured in the direction of the fluid flow, as equation (5.17) presumes, then the following relationships hold if the flow is laminar:

$$W_{\text{linear}} = \frac{1}{T} W_{\text{actual}}$$

and

$$W_{\text{actual}} = C \frac{r^2}{\mu} \frac{\Delta p}{LT}$$

Hence

$$W_{\text{linear}} = C \frac{1}{T^2} \frac{r^2}{\mu} \frac{\Delta p}{L}$$

If the distances x_e and x in equation (5.18) are taken to be the effective radius of the flow channel and the radius of the idealized capillary, respectively, then the velocity of the fluid is by Poiseuille's equation, in this case also, proportional to the reciprocal of the tortuosity squared. Thus, the definition of tortuosity by equation (5.18) is more

general than that of equation (5.17).

Tortuosity is usually used as a correction term in Poiseuille's equation. Since the square of the tortuosity is required, as discussed above, some authors have defined tortuosity as the square of the tortuosity defined by equation (5.18). In this work such usage is avoided and the tortuosity is defined by equation (5.18).

Tortuosity increases with decreasing moisture content. The quotient:

$$T_r = \frac{T_{\Psi=1}}{T} \quad (5.19)$$

was called the tortuosity ratio by Burdine (B2) but in this work it will be called the relative tortuosity analogously with the relative permeability. For the prediction of the liquid flux in a partially wetted porous medium it is important to know the relative tortuosity as a function of moisture content. Early attempts to predict this relationship were based on the assumption that there is a linear relationship between the relative tortuosity and the electrical resistance. According to Thornton (T5) the relative tortuosity for the wetting phase can be expressed as follows:

$$T_{rw} = \frac{R_{\Psi=1}}{R} \Psi \quad (5.20)$$

Later, Burdine (B2) found that the above relationship was not valid at low moisture contents. Gorokhow, Lebedev, and Churaev (G4) found that equation (5.20) is valid in sand from full saturation to about 50 per cent saturation. The direct

measurement of tortuosity is not possible and it must be predicted indirectly by the use of a suitable relationship between the liquid flux and the moisture content. Burdine applied this method using equation (5.11) and arrived at the following relationship between the relative tortuosity and the effective saturation:

$$T_{rw} = \Psi_e \quad (5.21)$$

The above relationship was found to be valid for all the materials which Burdine studied. Equation (5.21) was further verified by Wyllie and Gardner (W5) who used different experimental data.

The relative tortuosity of the non-wetting phase has not been compared with the relative tortuosity of the wetting phase. However, because tortuosity is a function of permeability, as shown by equation (5.11), and because there is a symmetry which allows the relative permeability of the non-wetting phase to be calculated from the relative permeability of the wetting phase it seems plausible to assume that this symmetry principle is also valid for tortuosity. Therefore, by analogy with equations (5.5) and (5.16):

$$T_{rnw} = 1 - \Psi_e \quad (5.22)$$

Tortuosity was evaluated in this work by the method shown in appendix 6 using an experimentally measured quantity, the capillary coefficient, C_{cap} .

5.4 The Vapour Flux in a Porous Medium Induced by a Temperature Gradient

The vapour flux appears in equation (5.1) and its value must be known in order to calculate the evaporation thermal gradient coefficient, δ_{EDC} , which is a parameter in the basic transport equations of this work, equations (2.41) and (2.42).

Before the vapour flux in a porous material can be predicted it is necessary to predict the vapour flux induced by a temperature gradient in a typical single pore. This can easily be done by dividing the heat flux transported with the vapour flux by the latent heat of vaporization evaluated at the temperature of the point studied. The heat flux can be calculated by the application of equation (4.2), and equation (2.11) expressed in the form of equation (2.19). The vapour flux in the pore becomes:

$$f_{2p} = - \frac{b k_d}{\lambda_T} \left(\frac{dT}{dx} \right) \quad (5.23)$$

where k_d and λ_T are evaluated at the same temperature.

The vapour flux in a porous medium is less than that predicted by equation (5.23) and it is necessary to introduce a correction factor which takes into account the restrictions between the pores. However, it must be established first whether the flow between pores is controlled by diffusion or by the resistance to flow caused by the other phases.

Krischer (K2, p. 172, p. 227, ff.) studied the diffusion of vapour in porous media in considerable detail and presented equations for the vapour flux in which the flux is

controlled by diffusion in the non-condensable gas. Krischer did not state the basis of his implicit conclusion that the flow resistance caused by the other phases is unimportant but it can be justified in the following way. The vapour flux in a wetted porous medium induced by a temperature gradient can be interpreted as caused by the gradient of the partial pressure of vapour. Application of equation (5.2) gives the following expression:

$$f_2 = - \rho_2 \frac{b K_d}{\mu_2} \frac{dp_{H_2O}}{dx} \quad (5.24)$$

where K_d is not necessarily a permeability in the sense of being a property of the material but is a formal concept and may depend on the diffusivity of vapour. The "permeability" K_d can be compared with the actual permeability of the material at the appropriate moisture content:

$$\xi = \frac{K_d}{K_{nw}} \quad (5.25)$$

If the quotient ξ is small it can be concluded that diffusion is the controlling factor in the flow. The permeability of the material to the vapour flow is equal to or lower than it would be in completely dry material. The permeability of a completely dry material to a gas is the same as the permeability of a completely wetted material to a liquid. The efficiency coefficient of evaporation, b , is less than or equal to unity. Thus the substitution of equation (5.25) into equation (5.24) followed by the replacement of K_{nw} by $K_{\psi=1}$ and b by unity

gives an expression for the maximum attainable value of the quantity ξ :

$$\xi = \frac{\mu_2 k_d}{\rho_2 \lambda_T K_{\Psi=1}} \left(\frac{dp_{H_2O}}{dT} \right)^{-1} \quad (5.26)$$

The viscosity and density of the vapour phase, i.e. the viscosity of air saturated by water vapour, is given by Krischer (K2, p.220).

The quantity ξ is much less than unity up to temperatures very near to the boiling point. Its value at 20°C is 0.7×10^{-4} , and ^{at} 99.6°C it is 0.01. These results show that diffusion is the controlling factor in vapour flow induced by temperature gradient.

Krischer (K2, p.160) expressed the correction factor to be applied to a diffusion flux in a dry porous medium as follows:

$$C_T = \frac{\epsilon}{T} \quad (5.27)$$

The above equation must be modified for wetted materials. The porosity must be replaced by the volume fraction of the vapour phase, which is:

$$\epsilon_g = \epsilon(1 - \Psi) \quad (5.28)$$

The tortuosity can be expressed as a function of the moisture content by equation (5.19). Substitution of equations (5.19), (5.22), and (5.28) into equation (5.27) yields:

$$C_T = \frac{(1 - \Psi_e) (1 - \Psi) \epsilon}{T_{\Psi=1}} \quad (5.29)$$

The correction factor, C_T , is applied to equation (5.23) to yield the following expression for the vapour flux in a porous material:

$$f_2 = - \frac{(1 - \Psi_e) (1 - \Psi) \epsilon b k_d}{T_{\Psi=1} \lambda_T} \left(\frac{dT}{dx} \right) \quad (5.30)$$

5.5 The Liquid Flux Induced by a Moisture Content Gradient

The phenomenological coefficient for liquid flow induced by a moisture content gradient appears in equation (5.1) and its value must be known in order to calculate the evaporation thermal gradient coefficient, δ_{EDC} , which is a parameter in the basic transport equations of this work, equations (2.41) and (2.42).

From equation (2.18B) the isothermal liquid flux arising from capillary forces is given by:

$$f_{1 \text{ iso}} = L_{11} X_1 \quad (5.31)$$

This equation is often interpreted as a "diffusion" equation and is usually called Fick's law. It can be written as follows:

$$f_{1 \text{ iso}} = - D_{\text{cap}} \rho_o \frac{dc}{dx} \quad (5.32)$$

where D_{cap} is the capillary diffusivity of the liquid in the porous medium and is the same quantity as Krischer and Sommer's

(K5) "Flussigkeitsleitzaht" (liquid conductivity number).

The concept of a diffusivity for a liquid flow induced by capillarity is misleading because there is no diffusion in the molecular sense. Equation (5.32) is, however, the customary way of expressing the capillary flow of liquid in a porous medium because the total mass flow, regardless of the nature of the transport phenomenon concerned, is conveniently expressed in the form of a diffusion equation.

Values of diffusivity can easily be calculated from experimental measurements.

Luikov (L4, pp. 284-286) reviewed a considerable amount of the experimental work done on the mass diffusivity in porous materials and presented a number of empirical formulae. He also presented a theoretical formula which will be discussed later.

Krischer and Sommer (K5) derived the following theoretical formula using Poiseuille's equation (5.10A), and the expression for the capillary rise height in a single capillary, equation (6.1):

$$D_{\text{cap}} = \frac{\sigma \cos \theta}{4 T_{\Psi=1} r_{\text{max}}^4 f_s(r_{\text{max}})} \int_{r_{\text{min}}}^{r_{\text{max}}} r^4 f_s(r) dr \quad (5.33)$$

where $f_s(r)$ is the distribution function of the number of pores about the mean pore radius. Krischer and Sommer compared values of the capillary diffusivity predicted by their equation with measured values obtained at a number of different moisture contents in several materials of different types. For each material they obtained good agreement for the range of moisture

contents studied after they had adjusted the value of

$T_{\Psi=1}$.

Krischer and Sommer's practical application of equation (5.33) was difficult because they did not use an explicit mathematical expression for the distribution function but they resorted to a cumbersome method of evaluating the integral graphically on the basis on a number of experimentally determined values of the distribution function.

Luikov (L5, p.29) presented a theoretical expression for the calculation of the capillary diffusivity. It is slightly different from equation (5.34) as the terms r^4 and $r_{\max}^4$ are replaced by r^2 and $r_{\max}^2$. This difference may be the result of the use of different definitions of the distribution function. Unfortunately, Luikov's definition is not clear. Also, Luikov's equation differs from that of Krischer and Sommer's because he assumed the tortuosity to be unity which is only valid for straight capillaries of uniform diameter.

Equation (5.31) can also be interpreted in terms of Darcy's law, equation (5.2), but the pressure must be interpreted as a capillary pressure or as a capillary potential. As will be shown in chapter 6 the capillary pressure can be calculated from the capillary rise height. It may seem that the use of the diffusion equation offers an advantage over the use of Darcy's law because information about the capillary forces is not required. However, the prediction of the liquid flux by the use of the diffusion equation requires the distribution of the capillary radii to be known; but, as will be shown in chapter 6, this distribution also enables the capillary pressure to be predicted.

The use of Darcy's law has the advantage over the use of the diffusion equation that the results of studies of

permeability can be applied to the prediction of the liquid flux in a porous medium. Another advantage of the use of Darcy's law is that the actual driving force for the capillary flow, the capillary pressure, can easily be separated from the rest of the expression for the calculation of the phenomenological coefficient of the flux. For these reasons it was decided not to treat capillary flow as a diffusion problem in this work.

The liquid flux can be calculated by the use of the following expression, first introduced by Dupuit (D3) in 1863:

$$f_1 = \epsilon_{wnb} \rho_1 W_{mean} \quad (5.34)$$

where ϵ_{wnb} is the volume fraction of non-bound liquid, ρ_1 is the density of the liquid, and W_{mean} is the mean linear velocity of the capillary flow.

The mean linear velocity of the liquid can be calculated from an expression for the velocity in a single capillary which has been adapted to include all the capillaries of the material.

Consider a single capillary. According to Greinacher (G6) the velocity at which a liquid rises or falls in a vertical capillary of uniform diameter can be expressed as follows:

$$W = \frac{r^2 \rho_1 g}{8 \mu} \left(\frac{h}{z} \pm 1 \right) \quad (5.35)$$

where z is the distance of the liquid meniscus from the free liquid surface. The above equation is not valid if z is near to zero. It is convenient to define the driving force in equation (5.35) in terms of the height h so that the di-

dimensionless driving force becomes:

$$X_1 = \frac{h}{z} \pm 1 = \frac{h \pm z}{z} \quad (5.36)$$

The plus sign is used when the liquid flows downwards and when the liquid surface is above the capillary meniscus. When the liquid is rising and when the capillary meniscus is above the free liquid level, the minus sign is used. When the liquid flows horizontally at the level of the free liquid surface the driving force becomes:

$$X_1 = \frac{h}{z} \quad (5.37)$$

When the liquid flows downwards above the height h the following expression is obtained:

$$X_1 = \frac{z - h}{z} = - \frac{(h - z)}{z} \quad (5.38)$$

It may appear to be strange that the numerical value of the driving force is the same in the upward flow version of equation (5.36) as it is for downward flow in equation (5.38). The reason for this is that the gravitational pull in downward flow is expended in overcoming the extra flow resistance which arises because of the longer wetted distance.

The capillary radius, r , of equation (5.35) can be eliminated by the use of the relationship between the capillary radius and the height of rise in a capillary, equation (6.1), so that the following expression is obtained:

$$W = \frac{\sigma^2 \cos^2 \theta}{2 \rho_l g \mu} \frac{1}{h^2} \left(\frac{h}{2} \pm 1 \right) \quad (5.39)$$

The above equation is valid for a single capillary only. For a bundle of capillaries of different diameters the mean height h_{mean} must be substituted for the height and $(1/h^2)$ must be replaced by the mean value of this quantity. The resulting velocity of the flow may be called the mean velocity, W_{mean} . Because there is a relationship between the rise height h and the moisture content the mean velocity can be calculated as a function of the moisture content. This may be done as follows: Assume that there is a situation such as that shown in fig. 5.2.

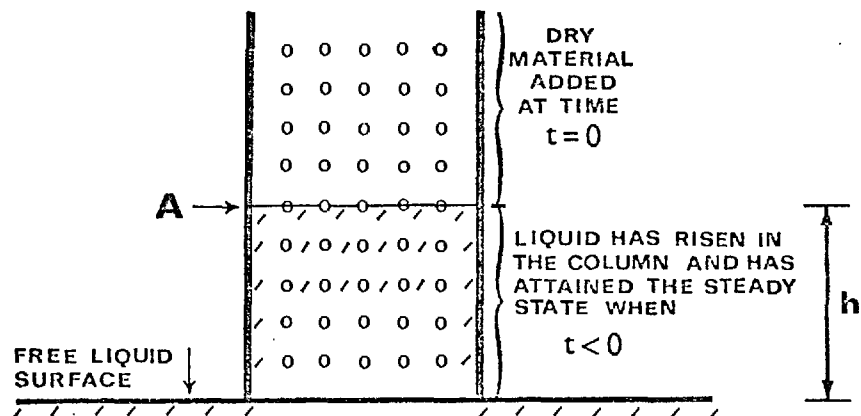


Fig. 5.2. Capillary flow of liquid into a layer of dry material.

The moisture content at the boundary A in steady state conditions is determined by the relationship between the capillary pressure (capillary rise height) and the moisture content.

The capillaries of large diameter cannot be filled above the boundary A if the rise height in them is equal or less than the distance from the free liquid surface to the boundary A. For the calculation of the mean velocity of the liquid penetrating into the material above the boundary A it is not necessary to know the position of A if the equilibrium moisture content at A is known so that the distance z in equation (5.39) may be replaced by $h(\Psi_A)$. Equation (5.39) becomes:

$$W_{\text{mean}} = \frac{\sigma^2 \cos^2 \theta (h^{-2})_{\text{mean}}}{2 \rho_1 g \mu} \left[\frac{h_{\text{mean}}}{h(\Psi_A)} \pm 1 \right] \quad (5.40)$$

where the mean values are defined as in equation (5.14). Equation (5.40) can be adapted to a porous material by the application of the concept of tortuosity as discussed in section 5.3. Then, in equation (5.40) both the tortuosity and the wetting angle must be determined experimentally although the latter may in some cases be available in the literature. In this work, however, a simple experiment was used which allowed both the wetting angle and the tortuosity to be incorporated into a single coefficient.

It has been observed that liquid rises into a layer of dry porous material behind a clearly visible frontier. When Luikov (L5) plotted the rise velocities at various heights from the free liquid surface against the reciprocals of the heights he found that over a certain range of heights the resulting curve was linear as shown in fig. 5.3. The reason for this phenomenon may be that the liquid velocity in the larger capillaries exceeds that in the smaller capillaries so that the rate at which the wet frontier advances

is controlled by the larger capillaries which represent a relatively narrow range of capillary radii.

Application of equation (5.39) to the linear region of liquid velocities discussed above gives the following expression:

$$W = \frac{\sigma^2 \cos^2 \theta}{2 \rho_l g \mu} \frac{1}{(h_{\text{ext}})^2} \left(\frac{h_{\text{ext}}}{z} - 1 \right)$$

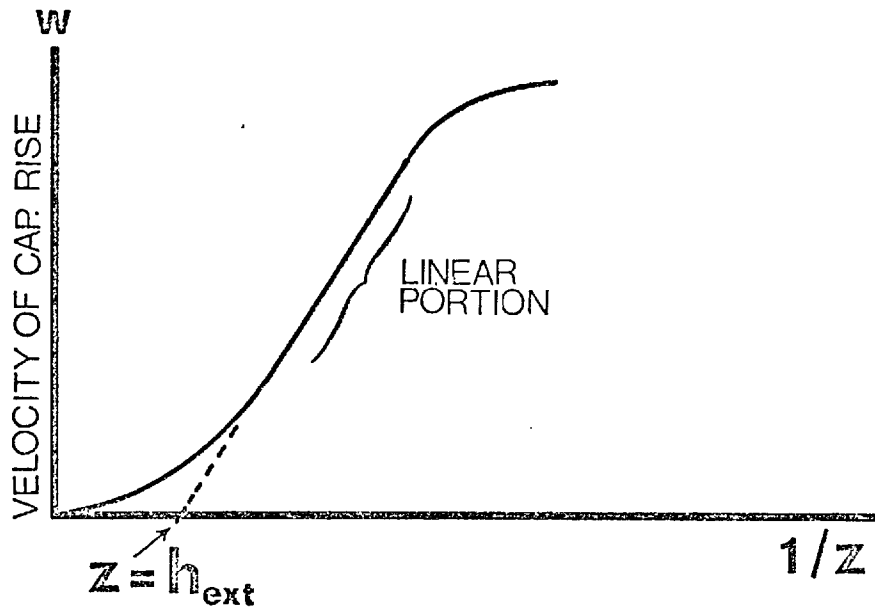


Fig. 5.3. The velocity of the advance of the wetting frontier into a porous layer as a function of the reciprocal of the height from the free water surface.

Since the capillaries are not straight the square of the tortuosity must be introduced as shown in section 5.3:

$$W = \frac{\sigma^2 \cos^2 \theta}{2 (T_{\Psi_{\text{ext}}})^2 \rho_l g \mu} \frac{1}{(h_{\text{ext}})^2} \left(\frac{h_{\text{ext}}}{z} - 1 \right) \quad (5.41)$$

where $T_{\Psi_{\text{ext}}}$ is the tortuosity evaluated at the moisture content Ψ_{ext} which corresponds to the rise height h_{ext} introduced in fig. 5.3. This equation can be rearranged as follows:

$$\frac{\sigma^2 \cos^2 \theta}{2 (T_{\Psi_{\text{ext}}})^2 \rho_l g \mu} \frac{1}{(h_{\text{ext}})^2} = W / \left(\frac{h_{\text{ext}}}{z} - 1 \right) = \text{constant}$$

The above equation can only be used in the linear region, see fig. 5.3.

The group on the left hand side of the above equation is dependent on the quantities h_{ext} and Ψ_{ext} and it is convenient to remove these quantities from the group. Thus, by the application of equation (5.21) and rearranging the following expression is obtained:

$$C_{\text{cap}} = \frac{\sigma^2 \cos^2 \theta}{2 (T_{\Psi=1})^2 \rho_l g \mu} = \left[W / \left(\frac{h_{\text{ext}}}{z} - 1 \right) \right] \frac{(h_{\text{ext}})^2}{(\Psi_{\text{ext}})^2} \quad (5.42)$$

At a given temperature the left-hand side of equation (5.42) is a constant which will be called the capillary coefficient, C_{cap} . Normally the velocity, W , is measured at room temperature, e.g. at 20°C . The capillary coefficient can be evaluated at a temperature T by the application of equation (5.42) as follows:

$$C_{cap,T} = C_{cap, 20^{\circ}\text{C}} \left(\frac{\mu_{20^{\circ}\text{C}}}{\mu_T} \right) \left(\frac{\sigma_T}{\sigma_{20^{\circ}\text{C}}} \right)^2 \quad (5.43)$$

Equation (5.42) was used to calculate values of C_{cap} at 20°C for various materials for which experimental data were available. The results are shown in table 5.1.

Table 5.1 shows that the three different sands studied have capillary coefficients of the same order of magnitude whereas a mixture of sand and clay has a value that is only about 1/1000 of those of the sands.

Equation (5.42) shows that there is a relationship between the tortuosity and the capillary coefficient. The tortuosities given in table 5.1 were calculated by the use of this relationship. There is also a relationship between the permeability and the capillary coefficient. The derivation of this relationship is given in appendix 7. The permeabilities given in table 5.1 were calculated by the use of this relation.

In order to enable values of the capillary coefficient to be obtained from experimental measurements various methods were developed in the present work for the measurement of the velocity of the capillary rise. These methods are described in appendix 8. It was concluded that sufficiently

material	$h_{ext},$ m	$\Psi_{e ext},$ dimension- less	$C_{cap, 20^{\circ}C}$ m^3/s	$T_{\Psi=1},$ dimension- less	$K_{\Psi=1},$ m^2
A	0.10	0.837	0.852×10^{-5}	6.70	1.25×10^{-11}
B	0.10	0.872	0.244×10^{-5}	12.0	8.95×10^{-11}
C	0.418	1.00	0.528×10^{-5}	7.13	0.533×10^{-11}
D	0.00466	0.936	0.349×10^{-8}	296.	0.140×10^{-11}
A Quartz sand studied in this work - data given in appendix 8. B Fine sand, Tanaeva (T2), also (L5). C Coarse sand, Tanaeva (T2), also (L5). D Mixture of sand and clay in proportion 5:2, Tanaeva (T2), also (L5).					
<u>Table 5.1. Values of capillary coefficients, tortuosities, and permeabilities.</u> The values of the capillary coefficients were calculated by the use of equation (5.42). The residual moisture contents needed for the calculation of the effective moisture contents were not available for the materials studied by Tanaeva. A value of 0.02 kg water/kg dry material was assumed for all the three materials. The tortuosities were calculated as shown in appendix 6, and the permeabilities as shown in appendix 7.					

accurate values of the velocity were obtained by visual observation of the rising wet frontier through a transparent wall.

Substitution of equation (5.43) into equation (5.41) and incorporation of the tortuosity by the use of equations (5.19) and (5.20) gives the following expression:

$$W_{\text{mean}} = C_{\text{cap},T} (h^{-2})_{\text{mean}} \psi_e^2 \left[\frac{h_{\text{mean}}}{h(\psi)} \pm 1 \right] \quad (5.44)$$

where $C_{\text{cap},T}$ is given by equation (5.43).

An expression for the liquid flux induced by capillary forces is obtained by the substitution of equation (5.44) into equation (5.34). However, this equation incorporates a dimensionless driving force and, consequently, the phenomenological coefficient for the liquid flow obtained by the use of this equation is not the same as that required in equation (5.1). Therefore, it is necessary to redefine the driving force in terms of the moisture content.

This can be done by multiplication of the dimensionless driving force by the reciprocal of the derivative of the capillary curve with respect to the moisture content and by multiplication of the phenomenological coefficient by the same derivative. The derivative must be estimated at the moisture content at the point studied. The obtained expression is as follows:

$$f_1 = \epsilon_{\text{wnb}} \rho_l (C_{\text{cap},T}) (h^{-2})_{\text{mean}} \psi_e^2 \left(\frac{dh}{dc} \right) \left[\left(\frac{dh}{dc} \right)^{-1} \left(\frac{h_{\text{mean}}}{h(\psi)} \pm 1 \right) \right] \quad (5.45)$$

By means of this equation the liquid flux induced by capillary forces can be calculated as a function of moisture content for the case presented in fig. 5.2. From equations (5.31) and (5.36) it can be seen that the group of quantities in the above equation in front of the square brackets is the

phenomenological coefficient for the liquid flux, L_{11} , and that dimensionally it has the form required in equation (5.1). This coefficient will be used in the following section in which an expression will be developed for the calculation of the evaporation thermal gradient coefficient.

5.6 The Evaporation Thermal Gradient Coefficient

An expression for the local evaporation thermal gradient coefficient, δ_{EDC}^* , is obtained by the substitution of equation (5.30) and the phenomenological coefficient from equation (5.45) into equation (5.1). The following expression is obtained:

$$\delta_{EDC}^* = \frac{(1-\Psi_e) (1-\Psi) \epsilon b k_d}{\underbrace{\Psi_e^2 \lambda_T T_{\Psi=1} \rho_l (C_{cap, 20^\circ C})}_{\epsilon_{wnb} (h^{-2})_{mean}}} \frac{\mu_T}{\mu_{20^\circ C}} \left(\frac{\sigma_{20^\circ C}}{\sigma_T} \right)^3 \left(\frac{dh}{dc} \right)^{-1} \quad (5.46)$$

The local evaporation thermal gradient coefficient is specific for the material concerned and is a function of the moisture content and temperature. However, it is not necessarily related to physical situations other than that for which it was derived as shown in fig. 5.2, p.115.

It is necessary to derive an expression for the evaporation thermal gradient coefficient for a more general physical situation. Assume that in fig. 5.2 there is a temperature gradient imposed which causes vapour to be transported in the steady state situation downwards towards the boundary A.

The vapour flux will be compensated for by the liquid transported by the capillary forces for which the driving force, in terms of the moisture content, may be described by the following expression which is analogous to equation (5.36):

$$X_{1 \text{ EDC}} = \frac{h_{\text{mean}} - z}{z} \left(\frac{dh}{dc} \right)^{-1} \quad (5.47)$$

If the evaporation in fig. 5.2 is so intense that above the boundary all the liquid is evaporated so that the material above the plane A remains dry and if the resistance to flow is small the height z in fig. 5.2 can be replaced by $h(\Psi_A)$. If the flow resistance is not small then z will deviate from $h(\Psi_A)$. If the evaporation is of low intensity then there is liquid above the boundary A and the boundary no longer represents the frontier between wet and dry material. In this situation the height z is meaningless and must be replaced by a quantity z_{mean} as follows:

$$X_{1 \text{ EDC}} = \frac{h_{\text{mean}} - z_{\text{mean}}}{z_{\text{mean}}} \left(\frac{dh}{dc} \right)^{-1} \quad (5.48)$$

where

$$h_{\text{mean}} = \frac{1}{h(\Psi) - h(\Psi_r)} \int_{h(\Psi_r)}^{h(\Psi)} h \, dh$$

and

$$z_{\text{mean}} = \frac{1}{z(\Psi) - z(\Psi_r)} \int_{z(\Psi_r)}^{z(\Psi)} z \, dz$$

The difference between h_{mean} and z_{mean} is caused by evaporation and when the intensity of evaporation is low the difference is small. Hence the following approximation can be made:

$$X_{1 \text{ EDC}} \approx \frac{h_{\text{mean}} - z_{\text{mean}}}{h_{\text{mean}}} \left(\frac{dh}{dc} \right)^{-1} \quad (5.49)$$

The approximation made in the above equation is plausible at low moisture contents even at intense evaporation rates because at low moisture contents h_{mean} and h approach each other and z_{mean} lies in between these quantities. At high moisture contents the total moisture content gradient is controlled by the capillary thermal gradient coefficient, as will be shown later, so that the error caused by the approximation made in equation (5.49) is insignificant. Hence, it may be assumed that this approximation is plausible under all conditions.

If the direction of the heat flux is from the bottom to the top the definition of the driving force for the liquid flux is not simple in all cases. If the vapour flux causes a moisture content gradient so small that there is more liquid in the bottom layers than in the top then equation (5.38) would be suitable. In some cases, however, the bottom layers may become completely dry but even then there is usually no free liquid surface in the slab above the meniscus so that equation (5.36) may not describe the actual situation. Instead, equation (5.38) may be a better approximation. Thus, regardless of the direction of the heat flux the numerical value of the driving force is the same and only the sign changes.

An important difference between the previously studied general case of the capillary rise and the present case of the return flow for the evaporation, diffusion, and condensation cycle is as follows: In the latter case the vapour condenses everywhere along the length of the capillaries so that the liquid flux is not a constant along the length of the capillaries. Therefore, because a linear relationship exists between the length of a capillary tube and the evaporation thermal gradient coefficient it is reasonable to express the evaporation thermal gradient coefficient as the mean value along the length of the capillary of the local evaporation thermal gradient coefficient:

$$\delta_{EDC} = \frac{1}{h_{mean}} \int_0^{h_{mean}} \delta_{EDC}^* dz \quad (5.50)$$

where h_{mean} can be calculated by the use of equation (5.49). In an actual material it may happen that when the heat flow is from the bottom to the top of a slab the maximum moisture content may be located between the point of study and the free liquid surface. Because there cannot be a capillary flow of liquid from a region of lower moisture content towards a region of higher moisture content then the capillary path of the liquid becomes shorter. Another reason for a shorter fluid path is that a free liquid surface may not exist in the bed studied. It is therefore necessary to study how the shortened fluid path influences the value of the thermal gradient coefficient. Equation (5.1) shows that the thermal gradient coefficient is proportional to the driving force for the liquid

flux, $X_{1 \text{ EDC}}$; and equation (5.48) shows that this driving force, in turn, is proportional to the reciprocal of h_{mean} , the length of the fluid path. Thus, equation (5.50) may be written as follows:

$$\delta_{\text{EDC}} = \frac{1}{h_{\text{mean}}} \int_{x_0}^{x_{\psi \text{max}}} \delta_{\text{EDC}}^* dx \quad (5.51)$$

where the integration is taken from the location of study, x_0 , to the location of the maximum moisture content regardless whether this maximum is attained at the free liquid surface or not. In order to use the above equation it may be recalled that the local evaporation thermal gradient coefficient, δ_{EDC}^* , may be calculated by the use of equation (5.46).

Equation (5.51) leads to the definition of the following quantity:

$$\delta_{\text{EDC}}^{*s} = \delta_{\text{EDC}}^* / h_{\text{mean}} \quad (5.52)$$

where the quantity δ_{EDC}^{*s} may be called the local specific evaporation thermal gradient coefficient. It incorporates all the quantities specific to a material which are needed for the calculation of the evaporation thermal gradient coefficient. The quantity δ_{EDC}^{*s} is dependent upon the local temperature and moisture content and it is shown in fig. 5.4 as a function of moisture content at different temperatures for the quartz sand introduced earlier. As may be expected it is strongly dependent upon moisture content.

As equation (5.51) shows the evaporation thermal gradient coefficient is dependent on the conditions imposed

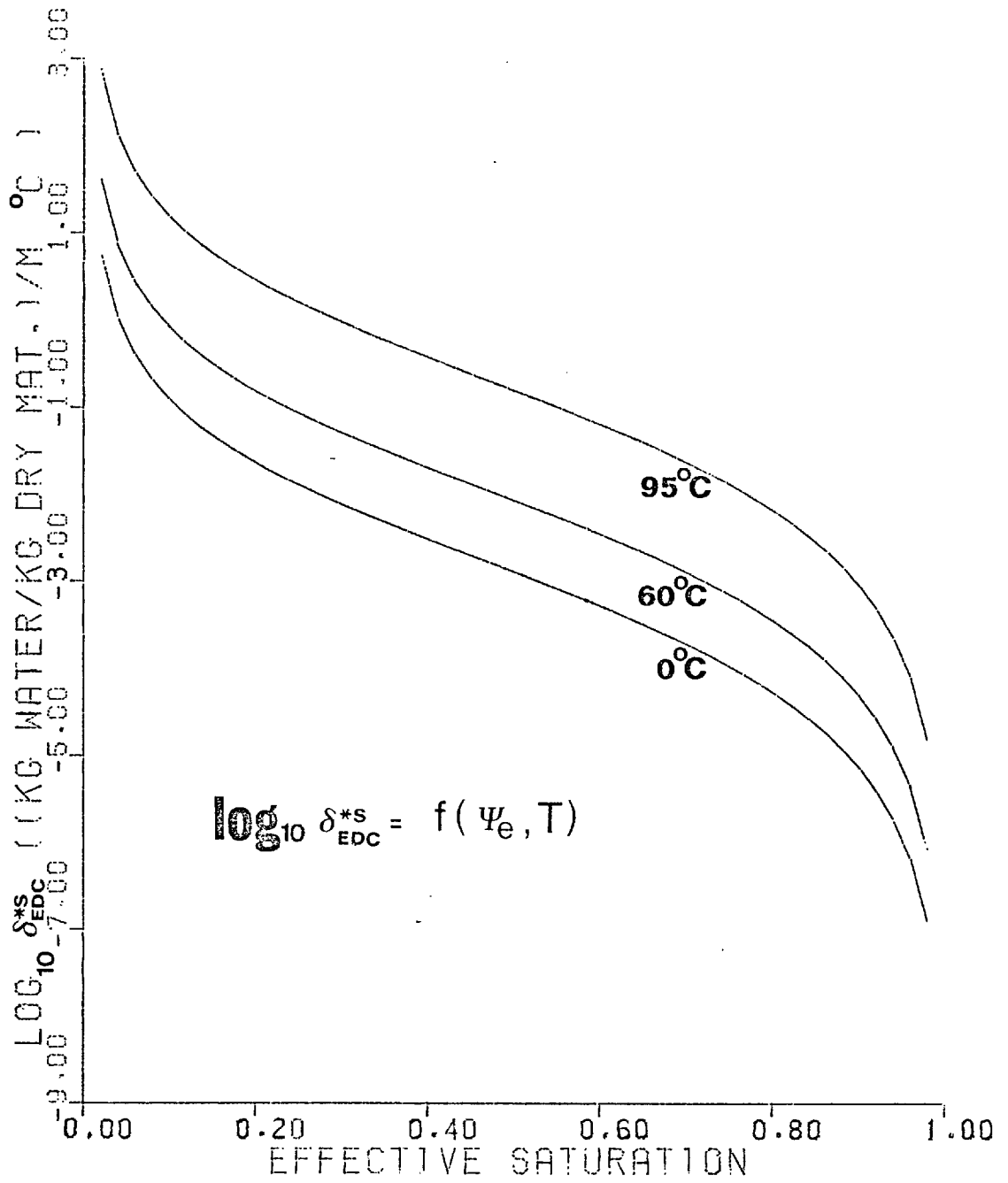


Fig. 5.4. The quantity δ_{EDC}^{*s} as a function of moisture content at three temperatures as calculated by the use of equation (5.46). For δ_{EDC}^{*s} the logarithmic scale is used.

on the system being studied. It is a parameter in the basic equations (2.41) and (2.42) and it must be specified in order for a solution of those equations to be obtained. However, its value depends upon the moisture content and temperature profiles which can only be determined from the solution of the equations (2.41) and (2.42). The solution procedure is, therefore, iterative. The method of solution, which was described in chapter 2, will be used in chapter 7 to obtain values of the evaporation thermal gradient coefficient for a bed of quartz sand described previously.

CHAPTER 6

CAPILLARY PRESSURE AS A FUNCTION OF
MOISTURE CONTENT IN POROUS MATERIALS

6.1 Introduction.

In order to solve the basic transport equations of this work, equations (2.41) and (2.42), the equilibrium rise and drain moisture contents must be known for the porous material being studied as functions of height from a free liquid surface.

If a layer of porous material is partially wetted then in the steady state there is normally more liquid in the bottom layers. The moisture content can be represented as a function of height by a continuous curve such as that shown in fig. 6.1. From certain practical points of view it is, in fact, more convenient to express height as a function of moisture content rather than vice versa. The importance of this function, which will be denoted by h , is twofold. First, the function h must be known in order to determine the steady state distribution of liquid caused by gravity. For this purpose, the derivative of the function h with respect to moisture content is needed in the basic transport equation (2.42). Secondly, as was discussed in chapter 5, the derivative of the function h with respect to moisture content is an important driving force for the liquid flow in unsaturated porous materials. It is convenient to obtain an explicit analytical expression for the function h . In this chapter an attempt will be made to find such an expression, and consideration will be given to various analytical and experimental properties of the function h .

The pores of a porous material can be considered to be bundles of capillary tubes. Liquid is held in them by surface tension and the equation for capillary rise in a single capillary can be applied to each capillary. The

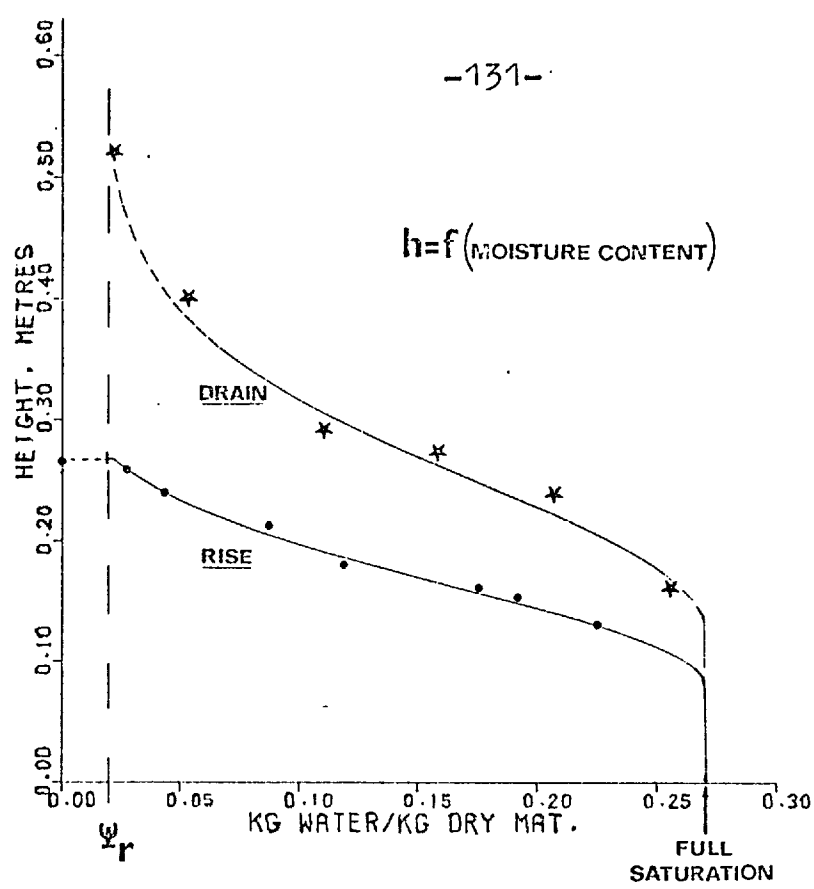


Fig. 6.1. The capillary rise and drain curves of a quartz sand.

Dots and stars - experimentally measured values of rise curve A and drain curve B, table 6.1., respectively.

continuous lines - predicted curves by equation (6.15).
The parameters used are shown in table 6.1.

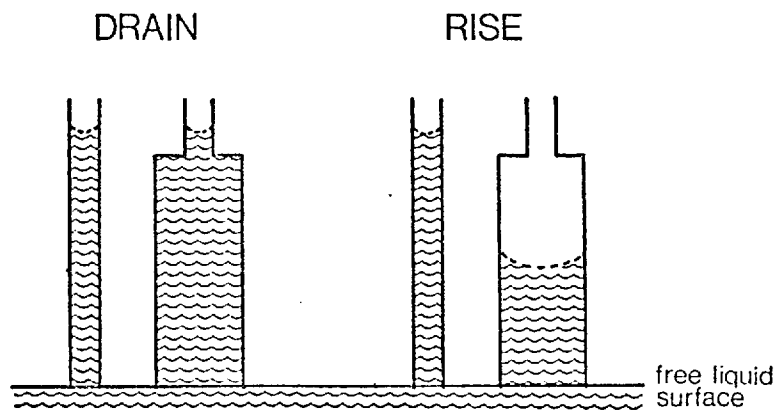


Fig. 6.2. Illustration of a basic law of the capillary rise and drain.

equation for capillary rise is as follows:

$$h = \frac{2 \sigma \cos \theta}{r \rho_l g} \quad (6.1)$$

If a material were to consist of capillaries of the same radii, the capillary rise height would be the same at all moisture contents. In real materials, however, there are capillaries and channels of different radii. In an open structure all the capillaries that are narrower than or equal to a certain radius at a certain height are filled with liquid. The capillary drain curve is obtained if the material is initially thoroughly wetted and is then left to drain. The reason for the capillary hysteresis, shown in fig. 6.1, is that liquid is retained at higher levels in the porous material by the occurrence of a meniscus in restricted parts of the capillary structure. This phenomenon is due to the basic law of capillary rise as illustrated by fig. 6.2, p.131.

The capillary forces are not, however, the only forces which support a liquid close to a solid wall. In addition there are adsorption, osmosis, and possibly other forces acting. In soil science all these forces are usually considered together as discussed by Yong and Warkentin (Yl, p. 132). Between the capillary and adsorption forces there is an important difference. Adsorption takes place between gas and solid phases whereas capillarity is an interaction between a liquid and solid phases. Therefore, these forces must be treated separately. In this work, as discussed in chapter 1, only the capillary forces will be taken into account, i.e. only a small amount of liquid is assumed to be present

as the result of the action of forces other than capillary forces.

Perhaps the simplest way to measure the strength of the capillary forces is to let liquid rise into a layer of material and to determine the moisture content versus height as soon as the steady state has been attained. For materials with very narrow capillaries the heights involved are very large. Then the capillary curves can be better measured by pressure cells or tensiometers. In a pressure cell, the pressure in the porous material is increased in order to balance the tendency of liquid to enter the material. In a tensiometer, the negative pressure caused by suction in a porous material is measured. In a tensiometer the material is in a closed space in a container which has one wet porous wall. The material imbibes liquid through the porous wall from a closed space filled with water. The reduced pressure in this latter space is measured. Some of the commonly used terms for the pressure obtained are: moisture potential, water potential, suction potential, capillary potential, and capillary pressure. It is emphasized here that the obtained pressure is the sum of the pressures caused by capillarity, adsorption, and other forces. Only the pressure which exceeds that attained in an ambient relative humidity of 100 per cent is caused by capillary forces. In this work the terms capillary rise curve and capillary drain curve are used to emphasize that only capillary forces are taken into account. Both the rise and the drain curves are expressed in units of height. The capillary pressure and the capillary potential can be calculated from the capillary height by the use of the following expressions:

$$p_c = g \rho_l h \quad (6.2)$$

$$\Delta H_c = gh$$

where p_c is the capillary pressure and ΔH_c is the capillary potential.

6.2 Analytical Formulations of the Capillary Curves.

In the previous section it was shown that the relationship between the moisture content and the capillary rise is determined by the distribution of the capillary radii about the mean value. Consequently, there is no possibility of constructing a capillary curve from knowledge of some easily measurable properties of the material such as void fraction or density. It is, however, appropriate to describe some of the most useful work done in this field.

A well-known early attempt to describe the capillary curves was that of Leverett (L1) in 1941. He introduced the following dimensionless expression which is known as the "Leverett function":

$$J(\psi) = \frac{p_c}{\sigma} \sqrt{\frac{K}{\epsilon}} \quad (6.3)$$

The relationship between the Leverett function and the saturation fraction is based on the relationship between moisture content and permeability. It has been found that values of the Leverett function for a number of unconsolidated porous media fall near two curves, one for wetting, and the other for drainage. Thus the Leverett function can be used to approximate

the capillary curves for materials for which the parameters contained in the Leverett function are known. Because of the inaccurate nature of the Leverett function it is unsuitable for the purposes of this work.

Mason (M1) developed a method by which he could approximate the capillary rise and drain curves for a bed of spheres of equal size. Mason approximated the pore spaces between the spheres by considering them to be tetrahedra. In real materials the particle or pore sizes vary so that Mason's method may not be useful.

Brooks and Corey (B1) developed an empirical method of describing the capillary pressure versus liquid saturation relationship. They found that in case of drainage the relationship:

$$\log (p_c) = f [\log (\psi)] \quad (6.4)$$

is approximately linear over a considerable range of moisture contents. Brooks and Corey studied nine different materials and found that the linear region extended from the lowest measured moisture contents up to saturation fractions of 0.75-1.0. They called the negative slope of the linear region the "pore size distribution index", and the point obtained by extrapolation of this line to the intercept at the saturation fraction of unity the "bubbling pressure". These quantities together with the residual saturation were enough, according to Brooks and Corey, to enable the construction of an approximate capillary curve. Although the linear relationship found by Brooks and Corey seems to provide a valid approximation for some materials there seems to be no physical

reason which supports the assumption that it is of general validity. In the present work, equation (6.4) was applied to the quartz sand introduced earlier. The results are shown in fig. 6.3. The linearity is not very satisfactory. Nevertheless, a linear form of equation (6.4) is quoted in a book by Yong and Warkentin (Y1, p. 378). Still another method of describing the capillary curves is that developed by Tanaeva (T2) and quoted by Luikov (L5). In this method the capillary curve is obtained from the unsteady-state distribution of moisture for the limiting case of infinite time. The use of the method requires empirical knowledge of the velocity of the capillary flow as a function of height from the free liquid surface. If only the steady state distribution of moisture is of interest, as in this chapter, it is easier to measure the capillary rise curve than to determine it from the velocity of the liquid flow induced by capillary forces. Further, Tanaeva's method is not suitable for the prediction of the complete capillary curve from a few experimental measurements.

Tabuchi (T1) presented in 1971 a semi-empirical method of describing capillary curves. He derived theoretically the following expression for the moisture content in regular arrays of particles:

$$\psi_e = \exp \left[- \frac{f(h) - \gamma}{\alpha} \right]$$

where Tabuchi gave the coefficients α and γ for two different particle packings. For the function f he gave the following expression:

$$f(h) = a d h + b$$

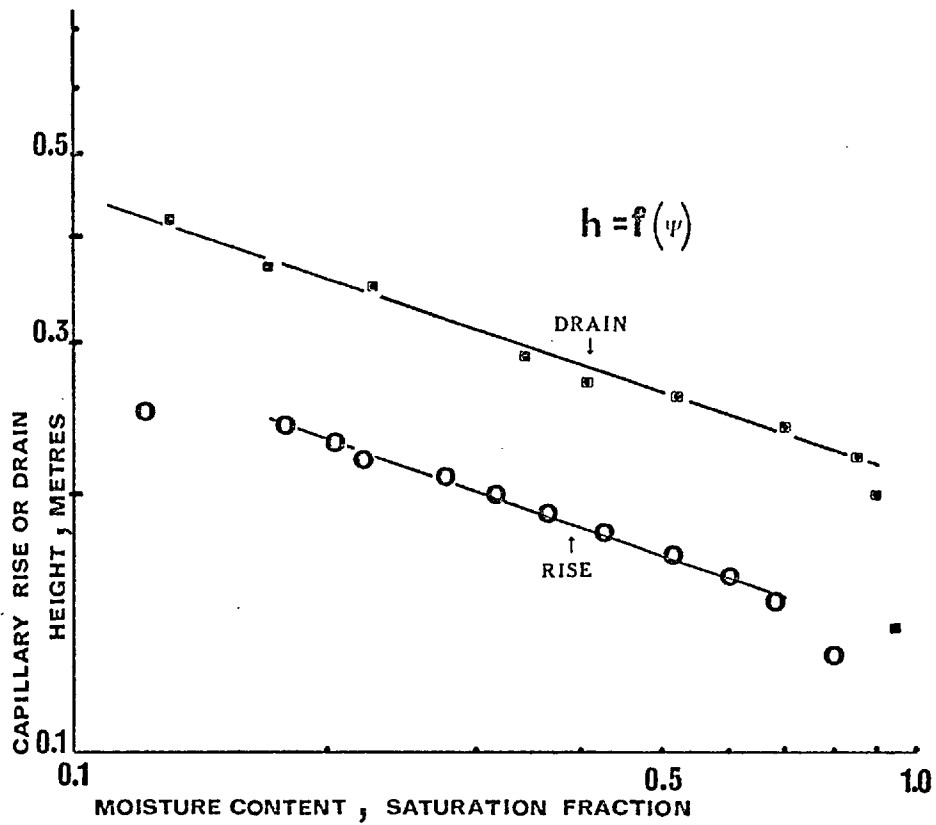


Fig. 6.3. Study on the linearity of the relationship $\log(h) = f[\log(\Psi)]$ for quartz sand.

The data of the upper line are those of the drain curve A and the data of the lower line are those of the rise curve G, both from appendix 8.

where d is the diameter of a particle in a packing of particles of equal size, and a and b are empirical constants. Tabuchi did not study how successfully his formula could be applied to materials of varying particle size. Besides this disadvantage, a capillary curve constructed by the use of his expression is exponential, i.e. the rise height has a non-zero value at full saturation from which point the height increases exponentially with decreasing moisture content. In fact, however, capillary curves are S-shaped, as shown in fig. 6.1, although in some cases, as shown by the curves presented by Brooks and Corey (B1), the shape of the curve is not far from exponential.

There has also been some purely theoretical attempts to describe the capillary rise and drain curves. These works are mainly centred around the problem of predicting the capillary rise curve if the drain curve is known and vice versa. These works will be discussed in section 6.5. The results obtained have not been very encouraging.

Thus, because the available expressions for the capillary curves are unsatisfactory it was decided to develop an expression for the relationship between rise height and moisture content. This problem will be treated in the following section.

6.3 Prediction of a Capillary Curve.

As seen from section 6.1 a capillary curve is determined by the distribution of the effective radii of the pores or channels in a material. The experimental prediction of this distribution function is best obtained by measurement of at least some of the points of the capillary curve itself.

The simplest way of obtaining values at points other than at the measured points is by the use of some form of interpolation procedure such as that based on the use of polynomials. Among the other methods available there is also a novel method developed by Akima (A3) which yields a particularly smooth curve which passes through all the data points.

These methods are formal in the sense that the predicted values are not based on any physical or statistical knowledge of the phenomenon described. Another disadvantage of interpolation methods is that the derivative of the curve so found tends to have discontinuities at some of the experimentally determined points. As mentioned in section 6.1 the derivatives of the curve are needed in this work. The derivatives can be made continuous for example, by the use of the well-known least squares method in which a suitably chosen function is fitted to go near to each of the measured points so that the sum of the squares of the distances from the curve to the points is minimized. It is important to choose the function to be used on an understanding of the nature of the phenomenon studied and not on purely mathematical grounds. For example, if it is found that the phenomenon studied can be described by a Gaussian distribution it is obviously better to use this function in the fitting procedure instead of using some less suitable function. For these reasons the nature of the capillary curve will be studied in more detail.

In a real material there are capillaries and channels of different radii. In an open structure where all the capillaries are equally accessible to liquid the only capillaries

which are filled are those which are narrower than or equal to a certain radius which is dependent on the height from the free liquid surface. Thus the relationship between the distribution function of the capillary radii, $f_d(r)$, and the moisture content may be expressed as follows:

$$\Psi_h = \int_0^{r_{\max}(h)} F[f_d(r)] dr \quad (6.5)$$

where $r_{\max}(h)$ is the radius of the largest capillary which is filled at rise height h .

The moisture content, Ψ_h , in the above equation is expressed as a saturation fraction which is related to the capillary rise or drain heights from the free liquid surface.

In the case of drain the pores which hold the liquid called the residual saturation do not take part in the distribution of the liquid which is influenced by capillary forces. Experimental studies have shown that even at considerable heights above the free liquid surface the moisture content increases continuously with decreasing height as shown in fig. 6.1. Thus the quantity Ψ_h may be taken to be the effective saturation, Ψ_e .

In case of rise the situation is different. The material is not originally wetted and the continuous liquid film breaks down at the residual moisture content thus preventing the liquid entering the small pores which otherwise would be filled. The distribution of the available pore radii becomes therefore truncated and it is seen in the rise curve that the moisture content decreases continuously with

the increasing height until the height corresponding to the residual saturation above which height there is no more liquid. This situation is shown in fig. 6.1.

Thus, the h-saturation fraction, Ψ_h , can be defined as follows:

$$\Psi_h = \Psi_e = \frac{\Psi - \Psi_r}{1 - \Psi_r} \quad \text{in case of drain} \quad (6.6)$$

$$\left. \begin{aligned} \Psi_h &= \Psi, & \text{if } \Psi \geq \Psi_r \\ \Psi_h &= \Psi_r, & \text{if } \Psi < \Psi_r \end{aligned} \right\} \quad \text{in case of rise}$$

In equation (6.5) the function F describes the distribution of liquid volume into the capillaries of various radii. The function F is related to the function f_d as follows:

$$F = C(r) \cdot n(r) \cdot f_1(r) \cdot f_d(r) \quad (6.7)$$

where the function f_1 relates the capillary radius to the volume of liquid inside the capillaries. In a material consisting of straight capillaries of uniform diameter:

$$f_1(r) = r^2$$

and for spherical pores:

$$f_1(r) = r^3$$

In equation (6.7), $n(r)$ denotes the number of pores of radius r , and $C(r)$ denotes the coefficient needed for the calculation of the volume if the effective radius is known. For a

material consisting of capillaries of circular cross-section C is a constant and is πx . In a porous material, however, C may be a function of the radius.

Equation (6.7) is not, however, very important in the present work and it is enough to know that there is a relationship between the function F and the capillary radius r . Equation (6.5) suggests the use of a cumulative distribution function. Thus, equation (6.5) may be written as follows:

$$\Psi_h = F_c(r) \quad (6.8)$$

Because there is a relationship between the capillary radius and the capillary rise height it is possible to predict the moisture content distribution if the capillary radii distribution or the capillary height distribution is known. Although capillary radii and capillary heights range from zero to infinity it is more convenient to use distributions which range from minus infinity to plus infinity as these have been studied extensively. One method of doing this is to study either the distribution of the logarithms of the capillary radii or, preferably, the logarithms of the capillary rise heights. Equation (6.8) becomes:

$$\Psi_h = F_c(\ln h) \quad (6.9)$$

which can be expressed as follows:

$$\ln h = \xi(\Psi_h) \quad (6.10)$$

where ξ is the deviate of the cumulative distribution function F_c . It is now assumed that the distribution function

is unimodal. It has been found empirically that many unimodal distributions which cover the range from minus infinity to plus infinity can be described adequately by distribution functions which are related to the Gaussian or normal distribution and that only four independent parameters are needed. These parameters describe the mean, the variance, the skewness, and the excess of the distribution function and are usually denoted by the symbols m , σ^2 , γ_1 , and γ_2 , respectively. Hence equation (6.10) may be written as follows:

$$h = \exp \left[\xi (\Psi_h, m, \sigma^2, \gamma_1, \gamma_2) \right] \quad (6.11)$$

An analytical expression which is suitable for the present purpose is an asymptotic expansion of the Gaussian distribution function obtained by the exact cumulant method. The principle of this method is shown by the following formula known as Edgeworth's series (C8, p.228) which relates the probability p to the deviate ξ :

$$\begin{aligned} dp = \exp \left[- \frac{(\kappa_1 - m)}{1!} \left(\frac{d(\beta(x))}{dx} \right) + \frac{(\kappa_2 - \sigma^2)}{2!} \left(\frac{d^2(\beta(x))}{dx^2} \right) \right. \\ \left. - \frac{\kappa_3}{3!} \left(\frac{d^3(\beta(x))}{dx^3} \right) + \frac{\kappa_4}{4!} \left(\frac{d^4(\beta(x))}{dx^4} \right) - \dots \right] d\xi \end{aligned} \quad (6.12)$$

where

$$\beta(x) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left[- \frac{(x-m)^2}{2\sigma^2} \right]$$

where x is the deviate of the Gaussian distribution of the density $\beta(x)$, and

where the cumulants $\kappa_1, \kappa_2, \kappa_3$ and κ_4 can be removed by the use of their relationship with the mean, variance, skewness, and excess, respectively. The inverse distribution needed in equation (6.11) was presented by Fischer and Cornish (F4), and it is commonly known as Cornish-Fischer asymptotic expansion. The expansion is as follows when terms involving cumulants higher than the fourth order are left out:

$$\begin{aligned} \xi = & m + x + \frac{1}{6} \kappa_3 (x^2 - 1) + \frac{1}{2} b x \\ & - \frac{1}{36} \kappa_3^2 (2x^3 - 5x) + \frac{1}{24} \kappa_4 (x^3 - 3x) \\ & - \frac{1}{6} b \kappa_3 (x^2 - 1) - \frac{1}{24} \kappa_3 \kappa_4 (x^4 - 5x^2 + 2) \quad (6.13) \\ & + \frac{1}{324} \kappa_3^3 (12x^4 - 53x^2 + 17) \\ & - \frac{1}{8} b^2 x - \frac{1}{16} b \kappa_4 (x^3 - 3x) + \frac{1}{72} b \kappa_3^2 (10x^3 - 25x) \quad ** \\ & - \frac{1}{384} \kappa_4^2 (3x^5 - 24x^3 + 29x) + \frac{1}{288} \kappa_3^2 \kappa_4 (14x^5 - 103x^3 + 107x) \quad ** \\ & + \frac{1}{7776} \kappa_3^4 (252x^5 - 1688x^3 + 1511x) \quad ** \\ & + \dots \end{aligned}$$

(** All these terms are of the same order of magnitude)

where

$$b = \kappa_2 - \sigma^2$$

In the above equation, terms of the same order of magnitude are on the same line. A computational simplification of the above equation can be made by noting that the quantity b can be made to be zero by choosing the variance

$$\sigma^2 = \kappa_2 \quad (6.14)$$

If equation (6.14) is to be used the deviate x must correspond to the variance of the magnitude of κ_2 and may be denoted by x_b . The capillary rise height can now be predicted by the use of equation (6.10) and the simplified form of equation (6.13). The equations to be used are as follows:

$$h = \exp (\xi) \quad (6.15)$$

where

$$\begin{aligned} \xi = & m + x_b + \frac{1}{6} \kappa_3 (x_b^2 - 1) \\ & - \frac{1}{36} \kappa_3^2 (2x_b^3 - 5x) + \frac{1}{24} \kappa_4 (x_b^3 - 3x_b) \\ & - \frac{1}{24} \kappa_3 \kappa_4 (x_b^4 - 5x_b^2 + 2) \\ & + \frac{1}{324} \kappa_3^3 (12x_b^4 - 53x_b^2 + 17) \end{aligned}$$

cont...

$$\begin{aligned}
 & - \frac{1}{384} \kappa_4^2 (3x_b^5 - 24x_b^3 + 29x_b) \\
 & + \frac{1}{288} \kappa_3^2 \kappa_4 (14x_b^5 - 103x_b^3 + 107x_b) \\
 & - \frac{1}{7776} \kappa_3^4 (252x_b^5 - 1688x_b^3 + 1511x_b) \\
 & + \dots
 \end{aligned}$$

 ↑ All these terms are of the same order of magnitude.
 ↓ -----

where the quantity x_b can be calculated as follows:

$$x_b = \sqrt{\kappa_2} x_n \left[= \sigma x, \text{ by the use of equation (6.14)} \right]$$

where x_n is the deviate of the Gaussian distribution function which has the variance of unity.

It may be recalled here that, according to equation (6.8), the value of the cumulative distribution function equals to the moisture content, Ψ_h . Thus, the value of x_n can be determined by the use of the following equation:

$$\Psi_h = Q(x) = \frac{1}{\sqrt{2\pi}} \int_{x_n}^{\infty} \exp(-t^2/2) dt$$

where Ψ_h is given by equation (6.6).

The elimination of the quantity b in equation (6.13) reduces the number of terms which have been truncated. However, the truncation error is not necessarily reduced since the quantity x_b occurs in every term of the series, and x_b includes the cumulant κ_2 . If the value of κ_2 is greater than unity

then the convergence of the series in equation (6.15) becomes slower than it was in its original form in equation (6.13). It was found, however, that in the materials studied the value of κ_2 was always less than unity.

The Cornish-Fisher expansion, which is the basis of equation (6.15), has been presented in a slightly different form by Abramowitz (A1, p.935), namely:

$$\xi = m + \sigma w \quad (6.16)$$

where w denotes the right hand side of the expression for the deviate ξ in equation (6.15) but without the first term m and with the normalized deviate x_n used instead of the transformed deviate x_b . Abramowitz's approximation can be used if the cumulants κ_3 and κ_4 are small. In the present work, the convergence of Abramowitz's approximation and the series presented in equation (6.15) were compared using different values of the parameters.

It was found that equation (6.15) converges more rapidly than Abramowitz's approximation.

A minor modification of equation (6.15) can be useful if the function to be fitted consists of experimentally determined values. The calculation proceeds by finding successively optimum values of the parameters m , σ^2 , κ_3 , and κ_4 . In order to avoid unnecessary evaluations of the function it is necessary to replace κ_3 and κ_4 by skewness, γ_1 , and excess, γ_2 , respectively. The skewness and excess are independent of the variance, σ^2 . The relationships required are as follows (A1, p. 928):

$$\kappa_3 = \gamma_1 \sigma^3$$

$$\kappa_4 = \gamma_2 \sigma^4$$

In the general case, equation (6.15) is unsatisfactory in two ways. First the values of the cumulants must be less than unity for convergence. Fortunately, in the present work, it was found that the capillary curves could be described successfully by the use of low values of the cumulants. Secondly, the series becomes divergent when deviate values greater than unity occur such as when the moisture content is very low or very high. A reasonably good convergence is obtained if the deviate x_b is unity or less. If the variance is 0.5 then, as required, the deviate x_b is less than unity if the probability, or in this case the effective saturation, has a value between 0.046 and 0.954. Because in the materials studied here the variance was about 0.5 or less, these limits were chosen to be used in such a way that the entire effective saturation range from zero to unity was transformed linearly to be between the values 0.046 and 0.954. This transform causes small deviations from the actual distribution near dryness and near full saturation.

The limitations on the usefulness of the Edgeworth's series have been known for a long time and have led to the development of other distribution functions. These will now be discussed.

Felch and Shuck (F2) used the modified Maxwellian distribution to describe the pore size distribution. This distribution is as follows:

$$dn_i = A \left(\frac{r_p}{r_o} \right)^a \exp \left[- \left(\frac{r_p}{r_o} \right)^2 \right] dr_p \quad (6.17)$$

where n is the number of pores within the radii interval from r_p to $r_p + dr_p$. The coefficients A and a describe the variance and skewness respectively, and r_o is the mean capillary or pore radius. As shown in section 6.3, the inverse of the integral of the distribution function is needed in order to describe the capillary curves. Analytical integration of equation (6.17) leads to the incomplete gamma function as can be seen from the following formula (A1, p. 260):

$$\gamma(a, x) = \int_0^x e^{-t} t^{a-1} dt \quad (6.18)$$

Evaluation of the inverse of the incomplete gamma function is a lengthy process. The result, however, is not satisfactory because the excess of the distribution is not taken into account. A well-known distribution which includes parameters which describe both the skewness and excess is the incomplete beta function:

$$I_x(a, b) = \frac{\int_0^x t^{a-1}(1-t)^{b-1} dt}{\int_0^1 t^{a-1}(1-t)^{b-1} dt} \quad (0 \leq x \leq 1) \quad (6.19)$$

$$\begin{pmatrix} a > 0 \\ b > 0 \end{pmatrix}$$

where a and b are related to the skewness and excess of the distribution, see Abramowitz (A1, p. 930). The incomplete

beta function can be transformed to cover the range of the distributed variable from minus infinity to plus infinity by the following transformation:

$$\xi = \frac{1}{2} \ln \left[\frac{a(1-x)}{bx} \right] \quad (6.20)$$

where x is the distributed variable of the incomplete beta function. According to Pearson in a prefatory note to a paper by Thompson (T4) this transformation was first used by Fisher in 1938. In case of zero skewness and zero excess the quantities a and b are both unity and the resulting distribution obtained from equation (6.19) approximates the Gaussian distribution. The inverse form of equation (6.20) is:

$$x = \frac{a}{a + be^{2\xi}} \quad (6.21)$$

A serious drawback with the use of the incomplete beta function is that, as shown in the introduction to Pearson's book (P3), no completely satisfactory method has been discovered for evaluating it numerically for all values of a and b .

For the prediction of the capillary curves the inverse of the incomplete beta function is needed. The approximation for the inverse given by Abramowitz (A1, p. 945, equation 26.5.22) was tested in this work. Abramowitz's approximation was developed originally by Carter (C4) for a variable interval from minus infinity to plus infinity. The resulting formula was then transformed by use of equation (6.21) to describe the incomplete beta function. Comparison of Carter's formula and equation

(6.15) showed that the latter converges more rapidly. Thus, since the distribution on which equation (6.15) and Carter's formula is based are almost identical there appears to be no advantage in using Carter's formula in preference to equation (6.15).

A relatively recent and more accurate approximation of the incomplete beta function was developed by Peizer and Pratt (P4). Their approximation is also cited by Pearson (P3, p. XXX). In as much as it appears that there is a need for a better approximation than that provided by equation (6.15), Peizer and Pratt's formula may be worth exploring. The formula requires a series of recursive approximations to be made so that calculation of the function is a lengthy procedure. Because of the nature of the functions concerned, the capillary curve must be found by a minimization method and function must be, therefore, evaluated a large number of times. The computer time required to carry out this process would be so large that it would make the application of this approximation impracticable. Thus equation (6.15) was used in this work.

Equation (6.15) was used in the preparation of fig. 6.4 for which the values of κ_3 and κ_4 were varied within the limits ± 0.75 . Both parameters were found to have a distinct influence on the shape of the curve obtained.

The parameters m , σ^2 , κ_3 , and κ_4 in equation (6.15) were determined for various capillary curves which were determined experimentally in the present work, see appendix 8, and for curves obtained from the literature. The results are shown in tables 6.1, 6.2 and 6.3. The computer programme used

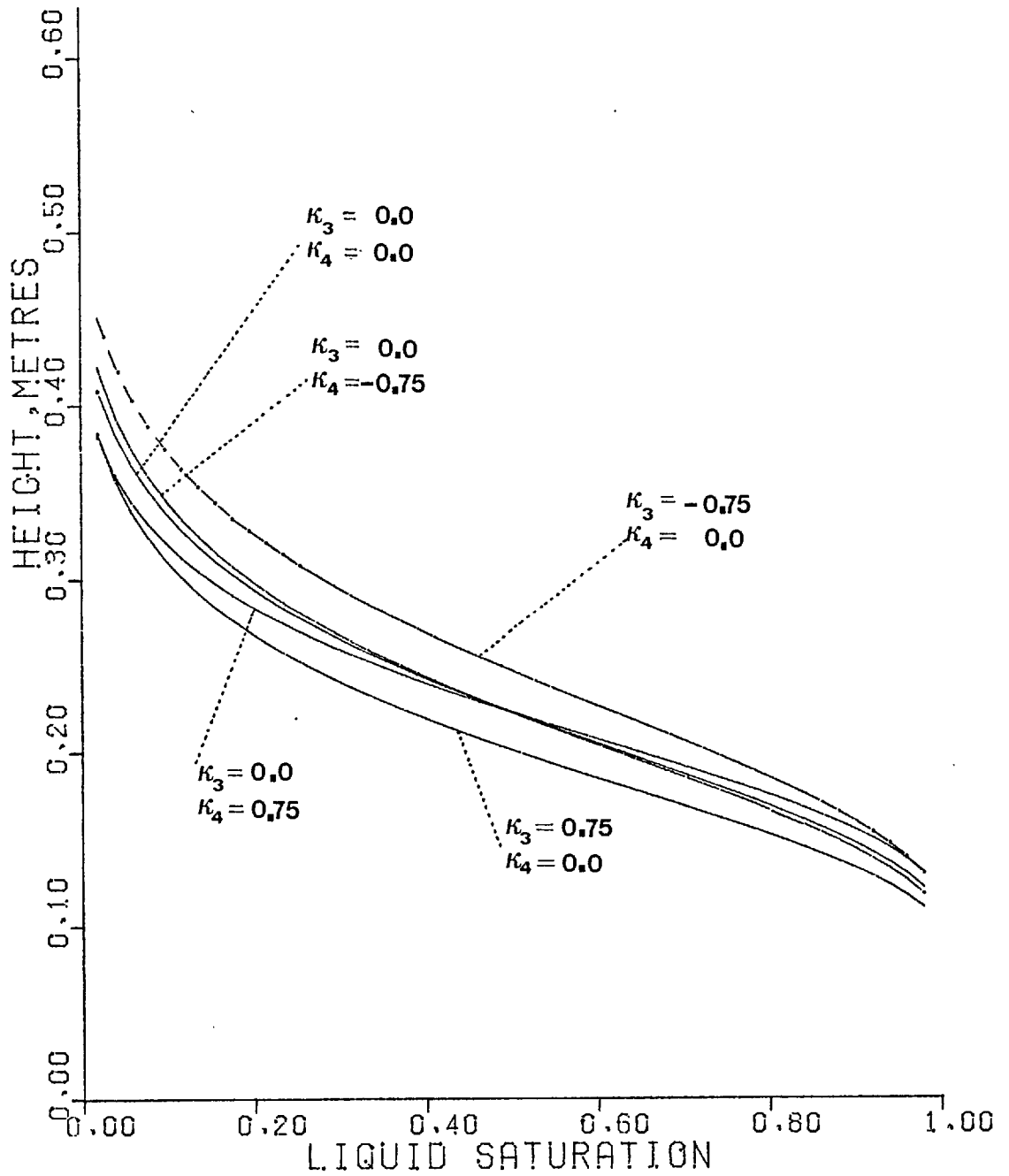


Fig. 6.4. Study of the influence of parameter values of the analytical expression of the capillary rise curve, equation (6.15).

The values of m and σ^2 , chosen arbitrarily, were -1.5 and 0.35 , respectively.

Table 6.1. Values of the parameters m , σ^2 , κ_3 , and κ_4 in equation (6.15) for the quartz sand introduced in appendix 9, and the drain or rise heights calculated by the use of these parameters.

c %	$h_{\text{meas.}}$ cm	$h_{\text{pred.}}$ cm	Parameters in equation (6.15)			
			m	σ^2	κ_3	κ_4
2.68	26.0	26.0	-1.83	0.325	-0.618	0.225
4.40	24.0	24.0	Rise curve A, 7 point data set, maximum step length of the variables in the minimization programme 0.04			
8.70	21.0	20.6				
11.9	18.0	18.7				
17.5	16.0	15.8				
19.1	15.0	14.9				
22.5	13.0	13.1				
2.68	26.0	26.1	-1.80	0.332	-0.427	0.261
4.40	24.0	24.0	Rise curve A, 7 point data set, maximum step length of the variables in the minimization programme 1.0			
8.70	21.0	20.5				
11.9	18.0	18.6				
17.5	16.0	15.8				
19.1	15.0	14.9				
22.5	13.0	13.1				
2.68	26.0	25.9	-1.82	0.367	-0.385	0.750
3.50	25.0	24.8	Rise curve A, 16 point data set, maximum step length of the variables in the minimization programme 0.04			
4.40	24.0	23.9				
5.25	23.0	23.0				
5.40	22.0	22.9				
8.70	21.0	20.4				
10.5	20.0	19.3				
11.0	19.0	19.1				
11.9	18.0	18.5				
13.7	17.0	17.6				
17.5	16.0	15.6				
19.1	15.0	14.8				
21.5	14.0	13.4				
22.5	13.0	12.8				
23.8	12.0	12.0				
23.9	11.0	11.9				
3.60	25.0	24.8	-1.71	0.395	0.384	0.750
4.90	23.0	23.1	Rise curve B			
7.00	21.0	21.0				
10.9	18.0	18.2				
14.5	16.0	16.2				
19.8	14.0	13.5				
24.2	11.0	11.2				

Table 6.1 continued.

c	$h_{\text{meas.}}$	$h_{\text{pred.}}$				
%	cm	cm	m	σ^2	κ_3	κ_4
3.90	24.0	24.1	-1.76	0.367	0.202	-0.119
7.50	21.0	20.5				
10.5	18.0	18.4				
12.5	17.0	17.2	Rise curve C			
16.6	15.0	15.0				
20.8	13.0	12.8				
23.8	11.0	11.1				
3.90	25.0	25.0	-1.72	0.416	0.705	-0.750
5.60	23.0	22.8				
8.60	20.0	20.2				
12.9	17.0	17.3	Rise curve D			
17.5	15.0	14.7				
22.1	12.0	12.0				
3.70	24.0	23.8	-1.70	0.364	0.542	0.750
5.60	22.0	21.6				
7.90	19.0	19.6				
10.7	17.0	17.8	Rise curve E			
17.3	15.0	14.4				
21.2	13.0	12.6				
24.0	11.0	11.6				
2.90	24.0	24.3	-1.87	0.362	-0.750	-0.750
4.30	23.0	22.4				
7.20	20.0	19.9				
10.8	17.0	17.6	Rise curve F			
18.8	14.0	13.9				
22.8	12.0	11.9				
3.30	25.0	25.3	-1.71	0.345	0.293	0.036
4.80	24.0	23.4				
6.20	22.0	22.1				
9.90	19.0	19.3	Rise curve G			
13.9	17.0	17.0				
18.4	15.0	14.8				
23.5	12.0	12.1				
2.90	43.0	42.7	-1.36	0.360	-0.0369	0.750
4.60	37.0	37.3				
6.10	35.0	34.5				
9.30	29.0	30.5				
14.1	26.0	26.2	Drain curve A			
19.0	24.0	22.5				
24.4	20.0	17.9				
25.6	14.0	16.4				
2.60	51.0	51.2	-1.39	0.325	-0.75	-0.128
5.40	40.0	39.1				
10.9	29.0	31.0				
15.8	27.0	26.5	Drain curve B			
20.7	24.0	22.3				
25.6	16.0	17.0				

Table 6.1 continued.

c	$h_{\text{meas.}}$	$h_{\text{pred.}}$				
%	cm	cm	m	σ^2	κ_3	κ_4
3.00	44.0	43.2	-1.32	0.352	0.0180	0.750
4.10	40.0	39.5				
5.10	36.0	37.2				
7.30	32.0	33.6				
12.2	29.0	28.5	Drain curve C			
18.4	25.0	23.7				
23.7	21.0	19.4				
25.8	15.0	16.8				

Table 6.2. Values of the parameters m , σ^2 , κ_3 , and κ_4 in equation (6.15) for various materials. The experimentally determined rise heights are given by Tanaeva (T2) and quoted by Luikov (L5). The heights were calculated by the use of equation (6.15) using the values of the parameters shown.

Parameters in equation (6.15)						
c	$h_{meas.}$	$h_{pred.}$	m	σ^2	κ_3	κ_4
%	cm	cm				
1.5	5.25	5.23	-2.97	0.104	0.588	0.750
5.61	4.76	4.84				
7.35	4.82	4.74				
16.2	4.21	4.27				
16.4	4.08	4.27				
17.4	4.43	4.20				
Coarse sand, relative density of solid 2.66, $c_{max} = 0.22$ kg water/kg dry material						
1.5	16.0	16.8	-2.13	0.150	-0.684	0.750
3.07	15.7	16.1				
10.6	15.2	14.1				
11.9	14.9	13.9				
14.8	14.0	13.3				
18.5	13.8	12.8				
17.8	12.3	12.7				
20.6	11.8	12.2				
22.4	10.1	11.8				
Fine sand, relative density of solid 2.61, $c_{max} = 0.27$ kg water/ kg dry material						
4.8	2.46	2.44	-4.18	0.760	0.750	-0.750
6.8	2.02	2.02				
9.0	1.61	1.69				
11.1	1.50	1.44				
13.6	1.21	1.19				
16.5	0.887	0.903				
Mixture of sand and clay, relative density of solid 2.65, $c_{max} = 0.22$ kg water / kg dry material						

Table 6.3. Values of the parameters m , σ^2 , κ_3 , and κ_4 in equation (6.15) for various materials. The experimentally determined values of the drain capillary pressures, given by Brooks and Corey (B1), were converted to capillary heights by the use of equation (6.2).

ψ	$\frac{p_c}{\rho g h_1}$	$\frac{p_c}{\rho g h_1}$	Parameters in equation (6.15)			
	meas. cm	pred. cm	m	σ^2	κ_3	κ_4
0.424	1.78	1.70	0.304	0.457	0.741	0.750
0.495	1.43	1.47	Touchet silt loam, $\psi_r = 0.270$			
0.645	1.07	1.15				
0.713	0.975	1.04				
0.825	0.875	0.867				
0.956	0.785	0.653				
0.262	0.745	0.736	-0.740	0.351	-0.750	-0.750
0.308	0.695	0.680	Fine sand, $\psi_r = 0.167$			
0.398	0.570	0.606				
0.625	0.480	0.485				
0.788	0.425	0.413				
0.930	0.342	0.335				
0.125	0.430	0.408	-1.19	0.168	-0.75	-0.75
0.187	0.380	0.384	Glass beads, $\psi_r = 0.085$			
0.262	0.342	0.365				
0.500	0.316	0.327				
0.700	0.304	0.301				
0.930	0.278	0.264				
0.275	0.354	0.343	-1.33	0.368	0.699	0.75
0.480	0.240	0.256	Volcanic sand, $\psi_r = 0.157$			
0.636	0.202	0.216				
0.861	0.175	0.166				
0.950	0.157	0.142				

in this work is described in appendix 9 where the application of equation (6.15) is discussed. The conclusion may be drawn that equation (6.15) is easily applied and that five measured points from a capillary curve are enough for a reasonably good description of the curve to be obtained. An increase in the number of measured points does not significantly improve the result.

6.4 Relationships between Capillary Rise and Drain Curves.

If a layer of porous material is thoroughly wetted and is then allowed to drain while its bottom layer is in contact with a free liquid surface it is found that the steady state liquid distribution differs from the distribution obtained by allowing liquid to rise into an originally dry layer of material. There are two reasons for this kind of behaviour. First, according to the laws of capillary rise, rise heights are controlled by the large diameter regions in a capillary whereas the drain heights are controlled by the small diameter regions. This phenomenon is illustrated by fig. 6.2. Secondly, the rise height is directly proportional to the cosine of the wetting angle, see equation (6.1), and it may be that there is a hysteresis effect associated with the wetting angle. The existence and the nature of this effect is not known, and it is assumed in the literature that only restrictions in the capillary channel need be taken into account in the study of capillary hysteresis.

In addition to the hysteresis between a completely wetted material draining and a completely dry material wetting there are intermediate states when the material is partially wetted and is then left to dry or when liquid is rising into

a layer of a material which has been partially wetted previously. Thus a whole family of "redry" and "rewet" curves is created.

It would be useful to have a method of predicting the capillary drain curve from the capillary rise curve or vice versa as well as a method of predicting the "redry" and "rewet" curves. The work centred around this problem is based on the independent domain theory developed by Everett (E4, E5), Enderby (E2) and various other workers referred to by Topp and Miller (T6). In this theory the pore space is divided into domains which empty and refill in jump transitions which are specific to each domain and which are independent of the state of wetting of the other domains. The analysis of the changes of the total moisture content caused by the changes in the total capillary pressure can be made graphically. Poulouvasilis (P6) applied the independent domain theory in order to predict the magnitude of capillary hysteresis in a bed of sintered glass beads. However, when Topp and Miller (T6) later applied the independent domain theory to beds of glass beads they found that the predictions obtained from the application of this theory were in very poor agreement with the experimental data measured by themselves and by Morrow and Harris (M4). The usefulness of the independent domain theory is therefore questionable.

An attempt to derive an analytical treatment of the hysteresis phenomena in wetted materials is outside the framework of this study. Therefore, only an approximate method was developed in the present work.

Assume that a porous material consists of volume units of material of different pore sizes but of the same internal

geometry so that one proportionality factor is needed to describe the dimensional differences. This situation exists for similar arrays of particles of the same shape but of different dimensions, i.e. when any array can be made identical with any other array by multiplication of all linear dimensions by a constant.

The difference between the rise and drain curve in a capillary channel of varying diameter is determined, as shown in fig. 6.2, by the difference between the smallest and the largest radii. In a porous material of the assumed type of ratio between the smallest and the largest capillary radii remains constant regardless of variations in overall sizes of the particles. Thus in such a material the ratio of the heights of the capillary rise and drain curves is independent of moisture content and it is only necessary to determine the ratio at one moisture content. It may seem that this reasoning cannot be applied successfully to an actual porous material. However, as shown in table 6.4, it was found that when the above idealization was applied to a quartz sand it enabled a very accurate prediction of the drain curve to be obtained from the rise curve. The expression which may be used in applying the method described above is as follows:

$$h_{\text{rise}}(\psi_h) = C_h h_{\text{drain}}(\psi_h) \quad (6.22)$$

where C_h is a constant.

For convenience the rise and drain heights should be obtained at the h -saturation values of 0.5. At these moisture contents the slopes of the capillary curves are near to their minimum values and their heights can be obtained with maximum accuracy.

It would be interesting to study the validity of equation (6.22) for other materials. Unfortunately, suitable rise and drain curve pairs are not available and no further experimental study of the validity of equation (6.22) was carried out.

Moisture content, $\frac{\text{kg water}}{\text{kg dry mat.}}$ per cent	Measured height, drain curve B, appendix 9, metres	Predicted height from equation (6.22), and from the rise curve A, table 6.1, metres
2.49	0.480	0.475
5.42	0.381	0.381
10.3	0.313	0.313
15.2	0.268	0.268
20.1	0.227	0.226
25.1	0.177	0.176
26.5	0.152	0.150

Table 6.4. Values of the capillary drain heights predicted from the rise heights by the use of equation (6.22) and compared with the measured drain heights. The value of the coefficient C_h was 0.629. The full saturation moisture content was 27 per cent.

CHAPTER 7

SOLUTIONS OF THE BASIC TRANSPORT EQUATIONS AND DISCUSSION

The basic transport equations (2.41) and (2.42) were solved numerically after substituting into them the expressions which have been developed for the effective thermal conductivity of the porous material, k_e ; the capillary thermal gradient coefficient, δ_{cap} ; the evaporation thermal gradient coefficient, δ_{EDC} ; and the derivative of the capillary rise or drain curve with respect to the moisture content, (dh/dc) .

The method of solution of equations (2.41) and (2.42) was described briefly at the end of chapter 2 and is discussed in detail in appendix 1.

Mean values of the predicted effective thermal conductivities in a layer of quartz sand are presented in figs. 7.1 and 7.2. These figures show that the conductivity at intermediate moisture contents is dependent on the direction of the heat flux. An analysis of the predicted moisture content fields given in figs. 7.3 and 7.4 shows that the reason for this is that when the heat flux is downwards the top parts of the layer are dry. Fig. 7.2 also shows that the mean effective thermal conductivity has a maximum at intermediate moisture contents if the other surface temperature is near to the boiling point of the liquid, as it is in the case of Fig. 7.2. This maximum is caused by the high values of the local effective thermal conductivity at temperatures near to the boiling point of the liquid as shown in fig. 4.2 on p.89. The maximum is higher if the heat flow is downwards than it is when the heat flow is upwards. Fig. 7.4 shows that the reason for this is the relatively complete wetting of the colder bottom layers even if the mean moisture content is relatively low.

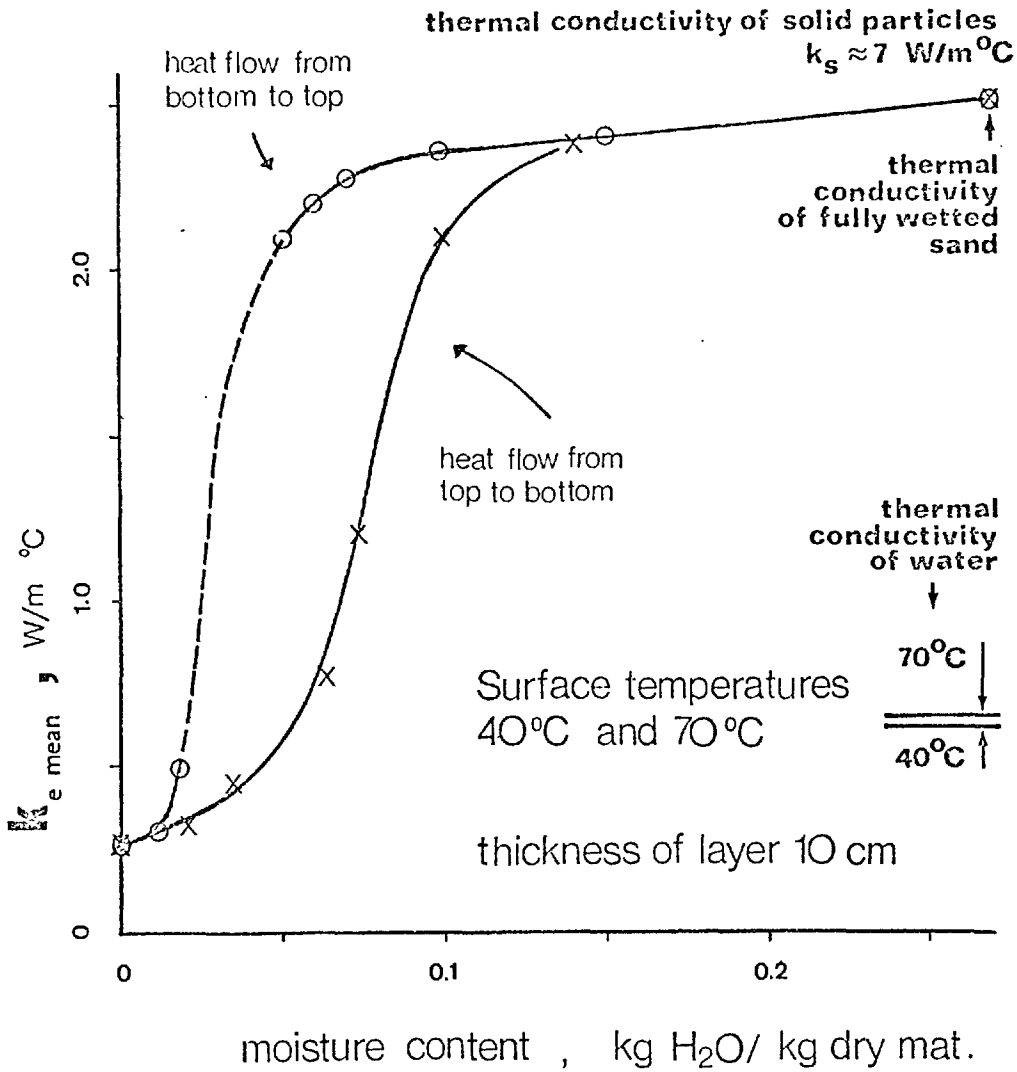


Fig. 7.1. The mean effective thermal conductivity of a layer of quartz sand, surface temperatures 40°C and 70°C.

The dashed line denotes the region where the method of solution did not converge.

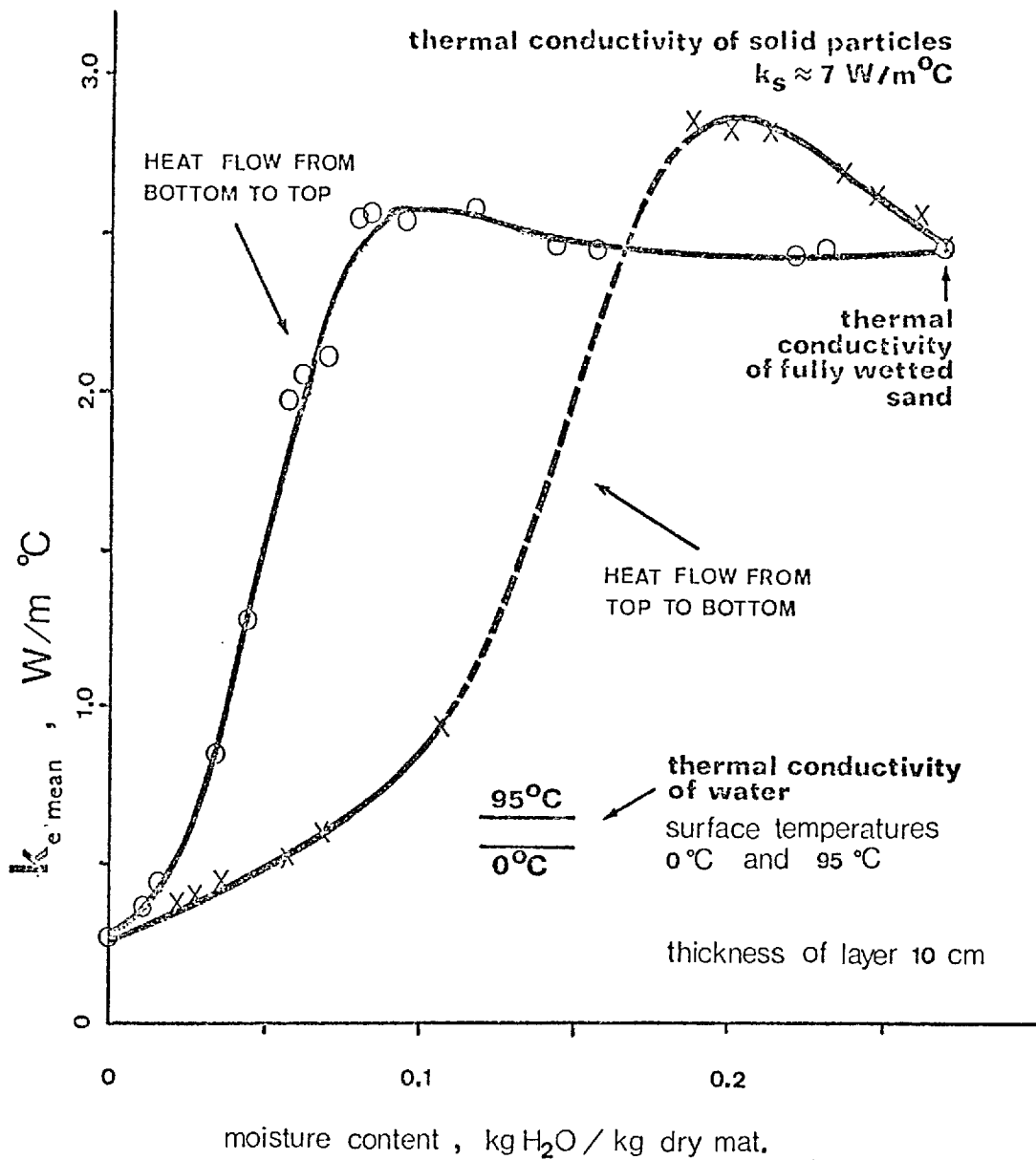


Fig. 7.2. The mean effective thermal conductivity of a layer of quartz sand for surface temperatures 0°C and 95°C .

The dashed line denotes the region where the method of solution did not converge.

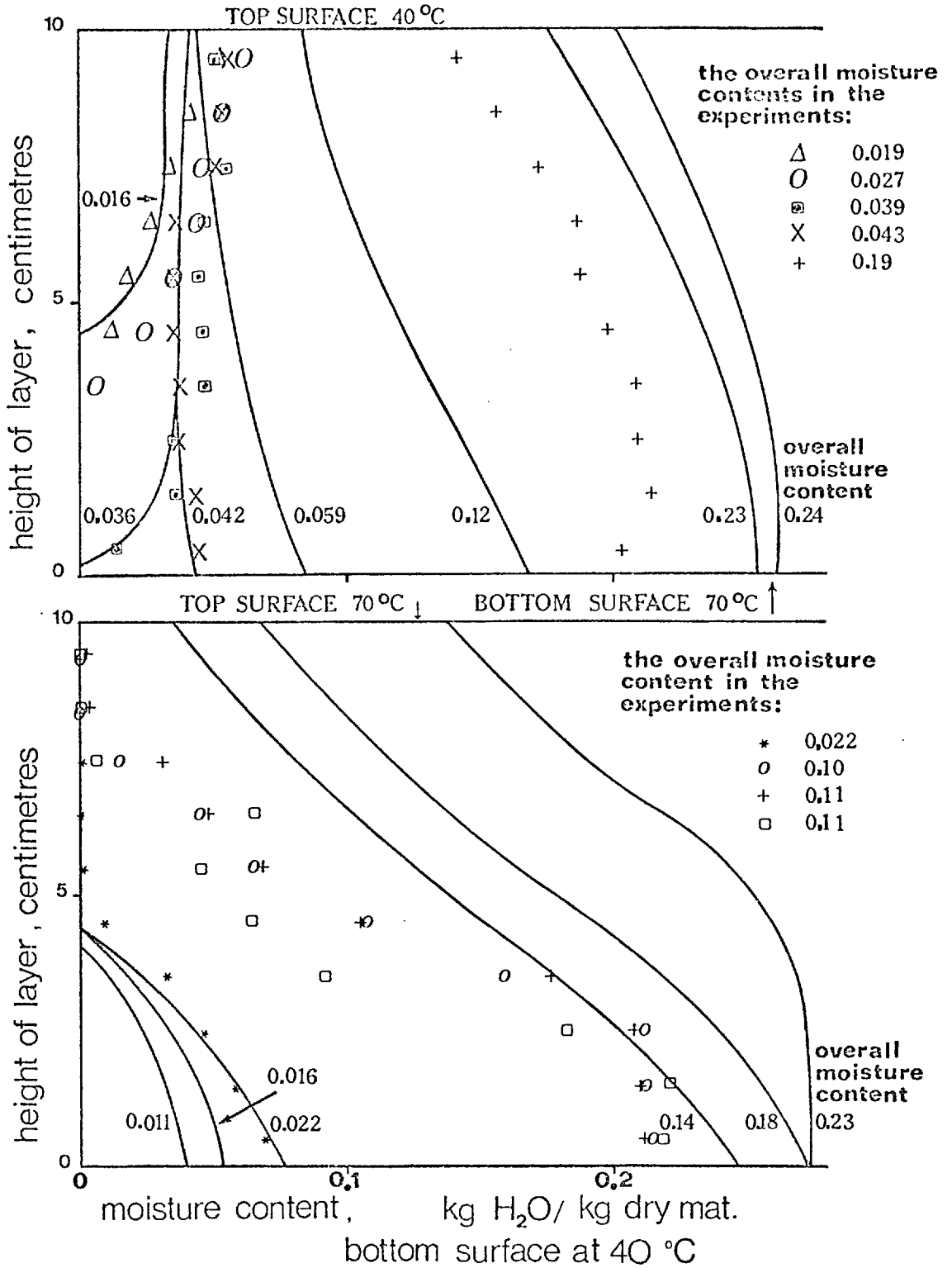


Fig. 7.3. Moisture content fields in a layer of quartz sand for surface temperatures of 40°C and 70°C.

The total moisture content was varied and each set of symbols corresponds to an experimentally measured moisture content distribution obtained at a particular total moisture content. The continuous lines represent predicted moisture content fields at various total moisture contents.

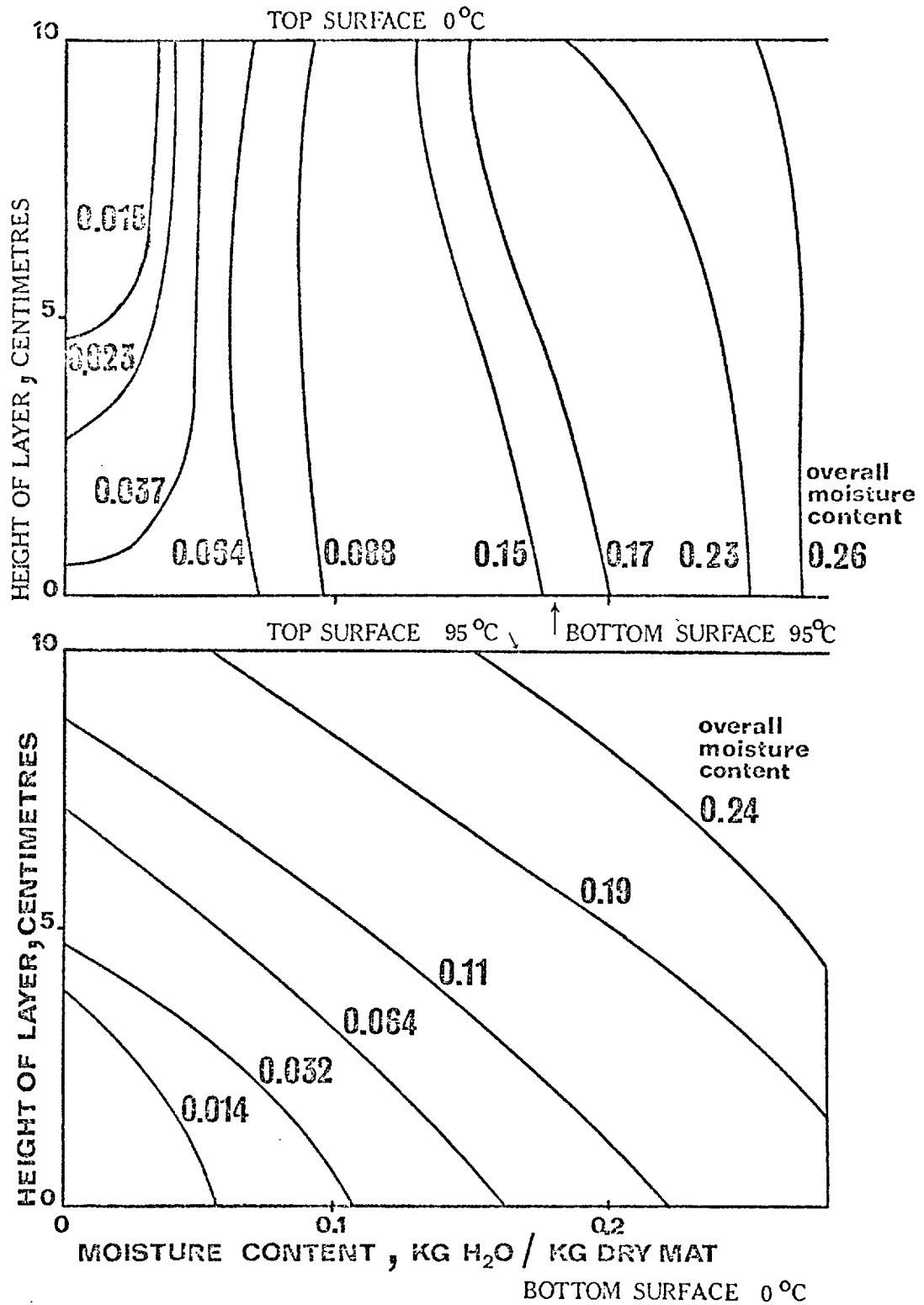


Fig. 7.4. Theoretically predicted moisture content fields in a layer of quartz sand. No experimental measurements were obtained.

In the cold region the effective conductivity remains relatively high as shown in fig. 4.2, p.89.

In the calculation of the effective thermal conductivity of a porous system the moisture fields are generated and, as was discussed above, they determine the mean effective thermal conductivity of the layer in a crucial way. For the experimental verification of the predicted mean values of the effective thermal conductivity it is more useful to determine the moisture content fields experimentally than to measure the mean conductivity itself. It should be mentioned that it is difficult to obtain reliable values of the thermal conductivity of wetted porous media. Hence, experiments were carried out to check that the moisture content fields calculated by the use of equations (2.41) and (2.42) agreed with experimentally determined moisture fields. The material studied was chosen to be quartz sand because it is the only material for which sufficient data are available for the estimation of the parameters required in the calculation. The experimental procedure used in these experiments is given in fig. 7.5.

In fig. 7.3 the predicted and the experimentally determined moisture content fields are compared. The agreement between these fields is generally good. In the case of downwards heat flow the experimentally determined moisture contents were unreliable at the higher mean moisture contents but it can be seen that the general trend of the measured values was in agreement with the predicted values. For this case of downwards heat flow it was found that moisture contents

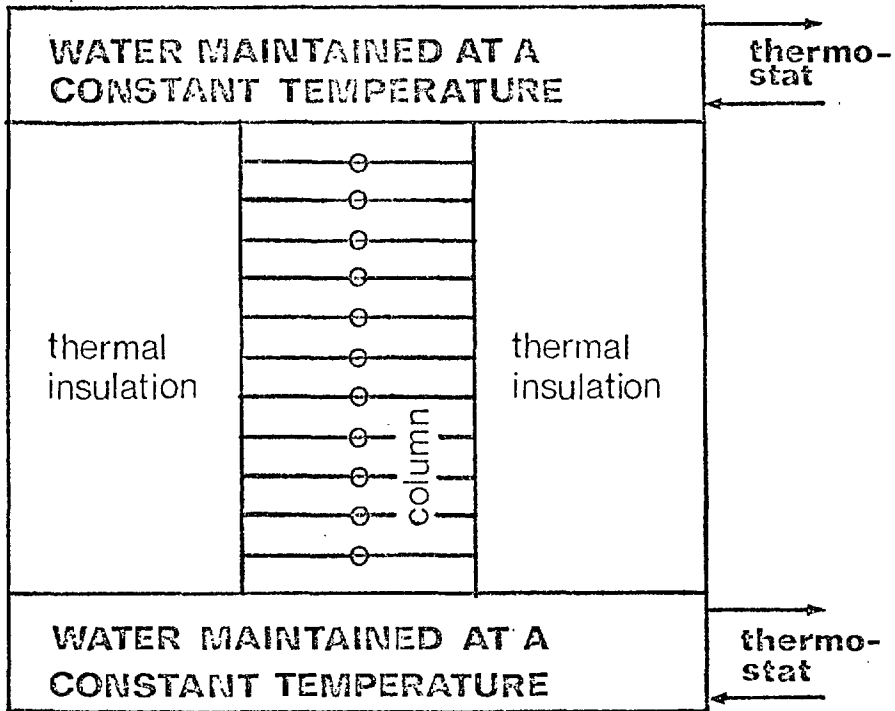


Fig. 7.5. Schematic illustration of the experimental equipment.

The material studied was placed in the column. The column consisted of plastic rings of ten centimetres internal diameter and one centimetre in height. The column together with the material studied was placed in a double plastic bag in order to prevent moisture escaping from the column. Temperatures were measured at one centimetre intervals in the vertical direction using copper - constantan thermocouples connected to a multi-channel data logger. After the steady state temperatures were attained the column was dismantled and the moisture content of the material contained in each ring was determined by weighing, drying, and reweighing.

greater than 22 per cent could not be obtained although full saturation corresponded to 27 per cent. This phenomenon may be accounted for by the presence of air bubbles entrapped in the closed system.

The effective thermal conductivity of a wetted porous system is determined by the parameters in the basic transport equations (2.41) and (2.42), and it is necessary to compare the relative contributions of these parameters to the effective thermal conductivity.

The mean value of the effective thermal conductivity in a layer is crucially determined by the moisture distribution in the layer and particularly by the location of the wet boundary. This is because the effective thermal conductivity of a dry material is very much lower than that of a wetted material as shown in fig. 4.2 on p. 89. Knowledge of the moisture content field is sufficient for the estimation of the mean effective thermal conductivity of the system. From what has been said above it appears that the most important quantity for the prediction of this conductivity is the evaporation thermal gradient coefficient, δ_{EDC} , because it alone is responsible for the presence of dry regions in the material. The value of this quantity increases very rapidly with decreasing moisture content as shown in fig. 5.4 on p.127 where the quantity δ_{EDC}^{*s} , which is the determining factor for the evaporation thermal gradient coefficient as shown by equations (5.52) and (5.51), is given as a function of moisture content at various temperatures. The value of the quantity δ_{EDC}^{*s} increases by about one-thousandfold when the

moisture content decreases from 15 per cent to three per cent. In a layer of a material this means that below a certain moisture content the moisture content gradient becomes very high and only a short distance is needed for the transition from wet material to dry material. This phenomenon is shown in fig. 7.6 where the contributions of the evaporation thermal gradient coefficient, δ_{EDC} ; the capillary thermal gradient coefficient, δ_{cap} ; and gravity on the total thermal moisture content gradient are compared. The strong increase of the contribution of the evaporation thermal gradient coefficient with decreasing moisture content is noticeable. In the case shown in fig. 7.6 even a tenfold increase in the value of δ_{EDC} would only slightly change the position of the wet boundary, and thus would only slightly change the mean value of the effective thermal conductivity in the layer. Consequently, the accurate prediction of δ_{EDC} , and still less the prediction of the effective thermal conductivity k_e , is not very important. Instead, the derivative of the capillary curve with respect to the moisture content, (dh/dc) , is important as it appears not only in the basic transport equations but also in the expressions for the capillary thermal gradient coefficient, δ_{cap} , and evaporation thermal gradient coefficient, δ_{EDC} , as shown in equations (3.14) and (5.51) respectively.

The study of the capillary curves is incomplete in this work because, ^{was} as discussed in section 6.5, the whole family of hysteresis curves between the pure drain situation and the pure rise situation should be taken into account. However, only the limiting cases of pure drain and pure rise were considered. In order to obtain information about the behaviour, and especially about the effective thermal conductivity, of

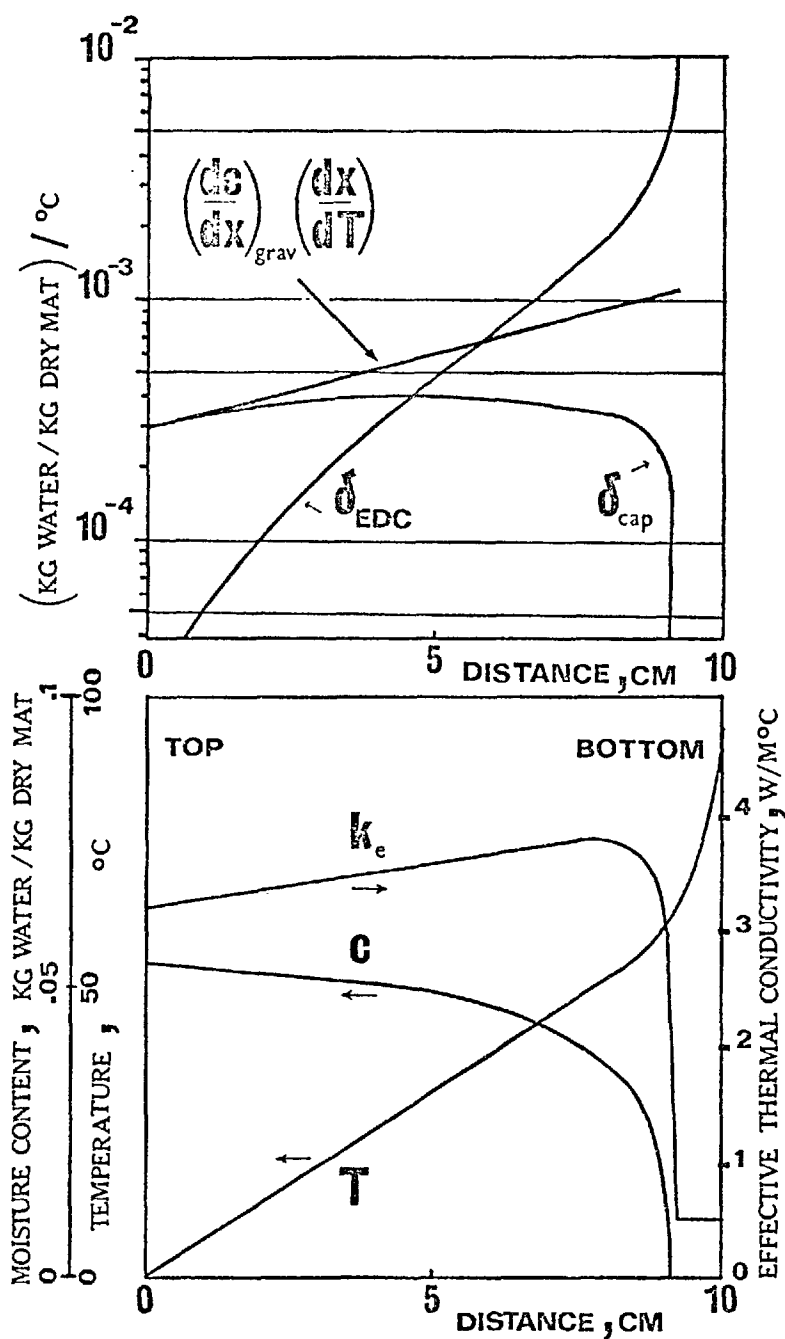


Fig. 7.6. Predicted moisture content and temperature fields in a horizontal layer of quartz sand in the steady state.

The values were calculated by solving the basic transport equations (2.41) and (2.42). In the upper graph the derivative of the moisture content with respect to temperature is analysed into parts as shown in equation (2.35B).

the system under the conditions when these intermediate capillary curves are important a series of experiments were carried out to determine the steady state moisture content distribution when only the top part of the bed was wetted initially.

Experimentally determined moisture content fields are shown in fig. 7.7 for the case when the direction of the heat flow was downwards. Moisture was transferred from the part of the bed which was initially wetted so that in order to predict the moisture content field theoretically a knowledge of the degree of initial wetting of the entire bed would have been required as well as a knowledge of the appropriate hysteresis capillary curves. Thus the moisture content fields shown in fig. 7.7 cannot be predicted theoretically. However, an analysis of these moisture content fields provides information about the behaviour of wetted porous systems under the influence of a temperature gradient as well as enabling the mean effective thermal conductivity to be calculated. In the situation corresponding to fig. 7.7 it could be expected that the temperature gradient would eventually cause a steady state situation to be established in which liquid would be transported by vapour transfer and condensation to the vicinity of the colder surface. However, as shown in fig. 7.7, this does not always happen and relatively large amounts of moisture may remain in the initially wetted regions. This behaviour may be explained as follows. In a wetted porous material the distance over which an evaporation - condensation cycle may exist is much less than the total thickness of the layer, and, as was discussed in the development of equation (5.51), the intensity of the evaporation, diffusion, and condensation

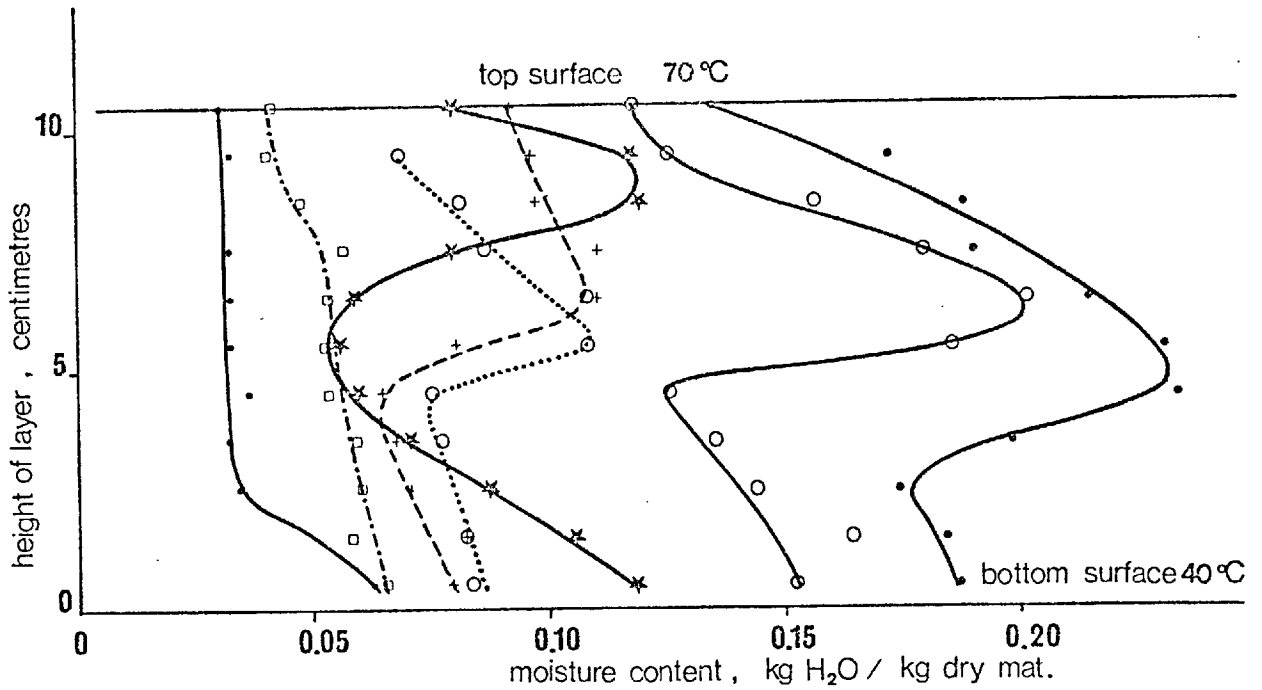


Fig. 7.7. Experimentally determined moisture content fields in a layer of quartz sand. Initially the top layers were wetted and the bottom layers were dry. The moisture content corresponding to full saturation was 0.27 kg water/kg dry material. The solid and dotted lines have been drawn to approximate the experimental values.

The mean moisture contents of the layer and the initial moisture distributions were as follows: (from left to right)

symbol	mean moist. content, kg water/kg dry material	Initial wetting condition.
•	0.036	top 2 cm fully wetted
□	0.053	top 3 cm fully wetted
○	0.086	top 5 cm fully wetted
+	0.086	top 5 cm fully wetted
★	0.086	top 2 cm fully wetted and additional water added
○	0.15	top 6 cm fully wetted
•	0.19	top 7 cm fully wetted

cycle varies from point to point. These local variations create moisture content gradients which are dependent on the local values of the derivative of the capillary curve with respect to moisture content as shown by equation (5.46). This derivative is dependent on the previous wetting history of the material at the point studied. Thus the system is able to maintain such apparently unnatural moisture content distributions as those shown in fig. 7.7. It is interesting to note that at low overall moisture contents for the conditions shown the effective thermal conductivity of the system in fig. 7.7 must be higher than it would have been if the bottom of the layer had been initially wetted. This is a result of moisture remaining in the top of the layer whereas the moisture would have been concentrated in the bottom part of the layer if only the bottom part had been initially wetted and other conditions had been the same as those shown in figs. 7.3 and 7.4 for downwards heat flow.

It is interesting to compare the magnitudes of the capillary and the evaporation thermal gradient coefficients. In fig. 7.8 some points where the evaporation thermal gradient coefficient, δ_{EDC} , is ten per cent of the capillary thermal gradient coefficient, δ_{cap} , are shown at various moisture contents and temperatures. The results do not represent a single valued function but rather a zone because the evaporation thermal gradient coefficient, which is a local quantity, is dependent on the moisture content of the system as shown in equation (5.51). The values in fig. 7.8 were taken from solutions of equations (2.41) and (2.42) for the bed thickness of ten centimetres of quartz sand for various surface temperatures and for both upwards and downwards heat flow. According to fig. 7.8, situations in

which the evaporation thermal gradient coefficient is greater than ten per cent of the capillary thermal gradient coefficient and cannot thus be ignored are to be found at low moisture contents and at high temperatures. At low temperatures and high moisture contents the evaporation thermal gradient coefficient is less than ten per cent of the capillary thermal gradient coefficient and its effect is unimportant. In different materials the location of the points in fig. 7.8 would be different. The contributions of the capillary and the evaporation thermal gradient coefficients can be compared on the basis of a theoretical analysis only from solutions of equations (2.41) and (2.42) for each case. The contributions of these two quantities can also be compared experimentally because, as shown in chapter 3, the capillary thermal gradient coefficient is not strongly dependent on temperature whereas, as shown in chapter 5, the evaporation thermal gradient coefficient is strongly dependent on temperature. This conclusion can be applied to an analysis of Dubnitsky's (D2) experimental work on the thermal gradient coefficient. His work was introduced in chapter 3. Dubnitsky determined experimental values of the thermal gradient coefficient, which, according to equation (3.8), in the non-hygroscopic region is the sum of the capillary thermal gradient coefficient and the evaporation thermal gradient coefficient. He found the measured values to be practically independent of temperature. It may be concluded, therefore, that the values measured by Dubnitsky were those of the capillary thermal gradient coefficient.

A general conclusion about the behaviour of the system studied as regards to the maximum attainable heat flux may be drawn as follows. According to chapter 5 the magnitude of the

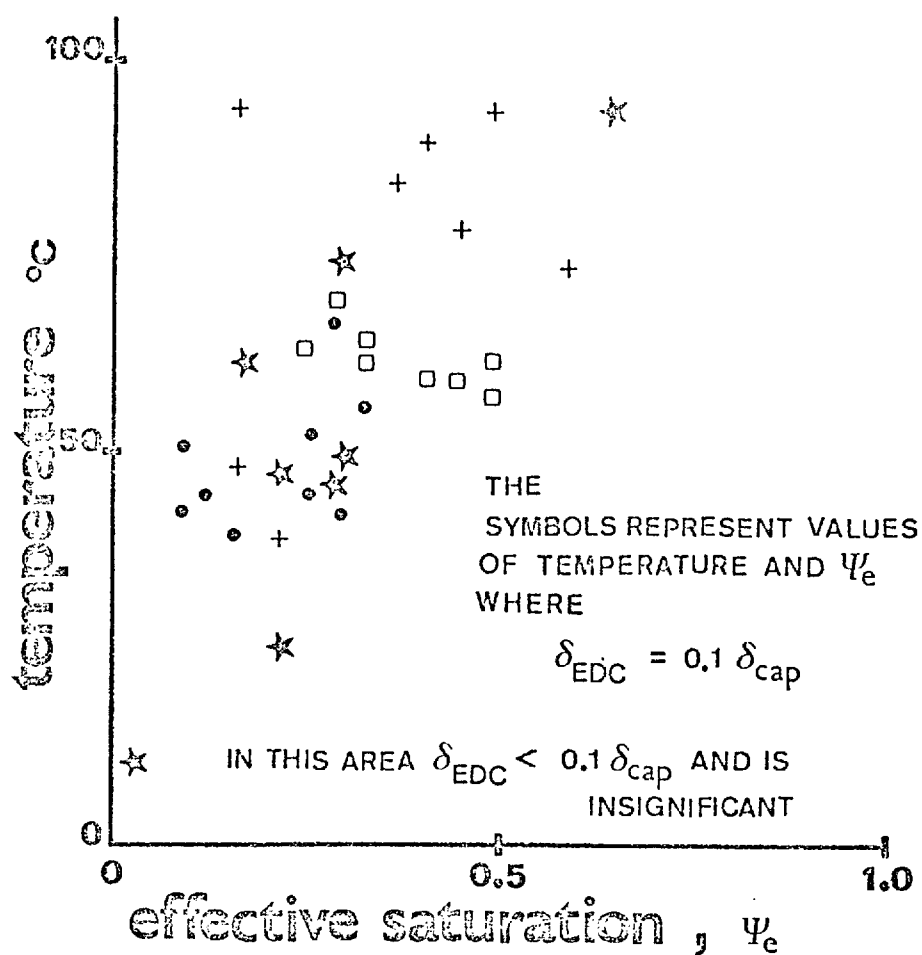


Fig. 7.8. Comparison between the magnitudes of δ_{EDC} and δ_{cap} in quartz sand at various local values of moisture content and temperature.

symbol	surface temperatures of the bed (thickness 10 cm)	direction of the heat flow
★	0°C and 95°C	upwards
+	0°C and 95°C	downwards
•	40°C and 70°C	upwards
□	40°C and 70°C	downwards

liquid flux is very strongly dependent on the moisture content and it decreases with decreasing moisture content. On the other hand, the vapour flux is at its maximum in an unrestricted vapour phase. Therefore, the maximum attainable heat flux would be attained if the material were fully wetted except for separate channels provided for the transport of vapour.

This discussion may be brought to its conclusion with some general remarks about the prediction of the steady state effective thermal conductivity of a wetted closed porous system. From what has been said above it is clear that this quantity is a function of a number of variables so that its prediction is a result of a comprehensive study of the behaviour of a wetted porous material under the influence of a temperature gradient. No simple approximate method of predicting the effective thermal conductivity of a wetted porous system is likely to be reliable because the basic transport equations (2.41) and (2.42) contain terms which are very strongly dependent upon a number of parameters which describe the material being studied.

CHAPTER 8

CONCLUSIONS

The following conclusions and extensions to the knowledge of the overall effective thermal conductivity of wetted porous systems in the steady state can be drawn from the work presented in this thesis.

A method has been developed for the prediction of the effective thermal conductivity of a slab of wetted porous material which is isolated from the environment with respect to mass transfer but which has prescribed surface temperatures. For the prediction process, basic transport equations which describe the moisture content and temperature fields have been formulated in terms of the evaporation thermal gradient coefficient, the capillary thermal gradient coefficient, the local effective thermal conductivity, and the capillary rise and drain properties of the material.

The evaporation thermal gradient coefficient has been introduced in the present work, and it has been found to be useful for the estimation of the contribution of the evaporation, diffusion, condensation, and return liquid flow cycle to the moisture content gradient. For the prediction of the evaporation thermal gradient coefficient a new form of the capillary coefficient has been introduced, and a simple method has been developed for the experimental determination of this latter quantity. This capillary coefficient has been defined so that it describes the capacity of a porous material to transport liquid by capillary forces.

Of the other quantities appearing in the basic transport equations an easily applicable expression has been developed for the estimation of the capillary thermal gradient coefficient. In this expression the information required about the material is given by the capillary rise or drain curves.

The local value of the effective thermal conductivity of a wetted porous material can at present be calculated only by the use of approximate expressions. An improved approximate expression has been developed and it has been found to give acceptable agreement between predicted and experimentally determined values. In this expression some experimental values of the effective thermal conductivity must be known at various moisture contents and at two different temperatures.

An expression has been developed which enables the entire capillary rise and drain curves to be predicted from a small number of experimentally measured moisture content versus height values. A simple expression has been developed which enables the drain curve to be predicted from the rise curve or vice versa if only one moisture content versus height value of the unknown curve is available.

The basic transport equations have been solved numerically by the use of the quantities described above for a bed of quartz sand. For solutions to be obtained, the following information about the material must be known: the capillary coefficient; local values of the effective thermal conductivities at various moisture contents and at two different temperatures; the residual moisture content; at least four values of the capillary drain curve and at least one value of the rise curve; the maximum attainable saturation in the material; and the density of the solid matrix. All the other quantities needed in the solution procedure can be calculated from the above information by the methods given in the present work. If the local effective thermal conductivity of the material is not known at various moisture contents and at two different temperatures then these data can be

predicted by an approximate method from the thermal conductivities of the completely dry and fully wetted material.

The validity of the solutions of the basic transport equations has been verified by a comparison of predicted and experimental moisture content fields. An acceptably good agreement between the predicted and the measured moisture content fields was obtained. From the solution of the basic transport equations, mean values of the effective thermal conductivities of a wetted porous bed of quartz sand have been calculated at different imposed surface temperatures as functions of moisture content.

It has been found that the steady state effective thermal conductivity of a wetted closed porous system is dependent on the direction of the heat flow. At low moisture contents the conductivity of the layer has been found to be greater in the case of heat flowing upwards. It has also been found that with surface temperatures not far from the boiling point of the liquid the conductivity of the layer is at a maximum at intermediate moisture contents.

Although no attempt was made to tie the results of this work to a particular practical application the results should nevertheless be of value to research workers who need to predict the steady state effective thermal conductivity of wetted porous materials. The results should also be of value to those who study the flows of heat, vapour, and liquid in wetted porous media subjected to temperature gradients.

APPENDICES

APPENDIX 1

Calculation of the Steady State Moisture and Temperature Fields in a Wetted Porous Slab and Prediction of the Heat Flux.

In this appendix the solution procedure of equations (2.41) and (2.42) is discussed. The method of solution is briefly stated at the end of chapter 2. For the solution, the following data about the material must be known: the capillary coefficient; local values of the effective thermal conductivities at various moisture contents, including the completely dry and the fully wetted states, and at two different temperatures; the residual moisture content; at least four values of the capillary drain curve and at least one value of the rise curve; the maximum attainable saturation in the material; and the density of the solid matrix. From this information were calculated the following quantities which were used in the programme: the four parameters of the capillary curve, m , σ^2 , κ_3 , and κ_4 ; the coefficient which is needed in order to predict the rise curve from the drain curve, C_h ; the tortuosity of the material at fully wetted state, $T_{\psi=1}$; and the coefficients for the polynomial expression for the b-function and the value of the coefficient E, for the estimation of the local value of the effective thermal conductivity, see equations (4.12) and (4.13).

The surface temperatures of the slab were specified. The solution was obtained by Runge-Kutta integration from one of the surfaces at which the moisture content was specified. The calculations were made in the temperature versus moisture

content co-ordinate system. In the first iteration loop only the capillary thermal gradient coefficient, δ_{cap} , was taken into account. From this first loop the moisture profile in terms of distance was calculated as was the heat flux through the slab which was expressed in terms of a mean value of the effective thermal conductivity. The iteration was continued until this mean effective thermal conductivity changed by less than a predetermined amount. Because both the effective thermal conductivity and the evaporation thermal gradient coefficient are strongly dependent upon moisture content and temperature as many as 50 integration steps were required. This non-linearity was particularly notable at some intermediate mean moisture contents, and resulted to the difficulty of obtaining convergence. For example when the surface temperatures were 40°C and 70°C and the thickness of the layer was 10 cm, the solution was not convergent in a narrow range of mean moisture contents as shown in figs. 7.1 and 7.2. However, the solutions provided sufficient information about the behaviour of the system despite this difficulty.

The prediction of the moisture content field c_{iso} , which appears in equation (2.42) and which is discussed after equation (2.39), was performed by a minimization of the difference between the actual mean moisture content of the layer and the mean moisture content calculated as though the same amount of liquid were distributed as determined by the appropriate capillary curve. The parameter which was varied was the moisture content of the bottom surface. The mean moisture content of the layer was estimated by numerical integration of the capillary curve. The ten-point closed Newton-Cotes formula was used. This minimization procedure proved to be

difficult but it was achieved successfully by a cubic minimization method developed by Sebastian (S2).

The derivative of the capillary curve, dh/dc , which appears in equation (2.42), was obtained by taking the analytical derivative of the expression for the height in equation (6.15).

In the course of the solution procedure the values of moisture content had to be solved when the heights were known, i.e. the inverse of equation (6.15) was needed. The problem was solved by using a standard quadratic minimization method in which the moisture content was the variable. The objective function was the absolute value of the difference between the known capillary height and the height calculated by the use of equation (6.15).

Although the method of solution of equations (2.41) and (2.42) was time consuming, no particular features worthy of further discussion were encountered. All essential information about the behaviour of the system studied was discussed in chapter 7.

APPENDIX 2

Properties of Water.

A2.1 The Surface Tension of Water.

Values of the surface tension of water at different temperatures were taken from the International Critical Tables (II, Vol.IV, p. 447). These data were fitted to a polynomial equation by the standard method of least squares polynomial fit. It was found that in the 4th power fit the smoothed values deviated from the experimental values by less than the error of measurement. Consequently the 4th power fit was accepted. The expression found is as follows:

$$\sigma = C_0 + C_1 T + C_2 T^2 + C_3 T^3 + C_4 T^4$$

where

σ surface tension of water, dynes/cm (10^{-3} N/m)

T temperature, $^{\circ}\text{C}$,

and

C0	75.6349
C1	-0.13723
C2	-4.0666×10^{-4}
C3	1.3617×10^{-6}
C4	-3.5533×10^{-9}

Values of the surface tension at different temperatures, calculated, by the use of the above expression:

T °C	σ dynes/cm (10 ⁻³ N/m)
0	75.6
10	74.2
20	72.7
30	71.2
40	69.6
50	67.9
60	66.2
70	64.4
80	62.6
90	60.7
100	58.9

A2.2 The Derivative of the Surface Tension of Water with Respect to Temperature.

The equation for the derivative of the surface tension with respect to temperature was obtained by taking the derivative of the polynomial equation given in the previous section.

The resulting expression is as follows:

$$\frac{d\sigma}{dT} = C_0 + C_1 T + C_2 T^2 + C_3 T^3$$

where

- σ surface tension of water, dynes/cm (10⁻³ N/m)
- T temperature, degrees Centigrade
- C₀ -0.13723
- C₁ -8.1332 x 10⁻⁴
- C₂ 4.0851 x 10⁻⁶
- C₃ -1.42132 x 10⁻⁹

The expression above gives following values:

T °C	$\frac{d\sigma}{dT}$ (dyne/cm)/ °C
0	-0.137
10	-0.145
20	-0.152
30	-0.158
40	-0.163
50	-0.168
60	-0.171
70	-0.175
80	-0.177
90	-0.178
100	-0.179

A2.3 The Thermal Conductivity of Water.

An equation for the thermal conductivity of water as a function of temperature has been presented by Haywood (H4). Haywood's expression is as follows:

$$k_w = C_0 + C_1 T_r + C_2 T_r^2 + C_3 T_r^3 + C_4 T_r^4 + \text{terms}$$

which are dependent on pressure and which become practically zero at pressures near to atmospheric pressure.

where

k_w the thermal conductivity of water, W/m°C

T_r (273.15+T)/273.15

T temperature, °C

C0 -922.47
C1 2839.5
C2 -1800.7
C3 525.77
C4 -73.44

It was calculated that the contribution of the terms that are dependent on pressure is of the order of 0.01 per cent of the approximated conductivity if the pressure is changed by less than one atmosphere from the standard atmospheric pressure.

Values calculated by the use of the above equation are as follows:

T deg C	k_w W/m °C
0	0.569
10	0.587
20	0.603
30	0.618
40	0.632
50	0.643
60	0.653
70	0.662
80	0.670
90	0.676
100	0.681

A2.4 The Viscosity of Water.

A series of measurements of the viscosity of water at different temperatures between 0°C and 100°C were taken

from the International Critical Tables (II, Vol. V, p. 10).

The accuracy of the measurements was stated to be better than one per cent. A polynomial was fitted to the measured values and the degree of the polynomial was increased until the maximum difference between the measured values and the values smoothed by the polynomial was less than one per cent. The polynomial obtained was:

$$\mu = C_0 + C_1 T + C_2 T^2 + C_3 T^3 + C_4 T^4 + C_5 T^5$$

where

- μ viscosity of water, cP ($=10^{-3}$ Ns/m²)
- T temperature, °C
- C₀ 1.78673
- C₁ -0.58209×10^{-1}
- C₂ 0.12414×10^{-2}
- C₃ -0.16586×10^{-4}
- C₄ 0.12122×10^{-6}
- C₅ -0.36360×10^{-9}

Values of viscosity calculated by the use of the above expression are as follows:

T °C	μ centipoises
0	1.787
10	1.313
20	1.005
30	0.799
40	0.656
50	0.551
60	0.469

cont...

70	0.405
80	0.357
90	0.318
100	0.280

The values of viscosity of water given in the International Critical Tables differ slightly from the more recent values given by Haywood (H4). The standard deviation of Haywood's values from the expression above is, however, only 1.4 per cent which is of the same order of magnitude as is obtainable by a direct polynomial fit of Haywood's values.

A2.5 The Partial Pressure of Water Vapour.

Both the partial pressure of water vapour and its derivative with respect to the temperature are required for the calculation of the equivalent thermal conductivity of water vapour by the use of equation (4.3). The following three empirical expressions for the partial pressure of water vapour seem to be in common use:

1. The equation of Gerry (G1), quoted in Steam Tables (S4):

$$\log_{10} p_{H_2O} = A + B \log_{10} T(K) + C T(K) + D/T(K) \quad (A2.1)$$

where p_{H_2O} is in bars

$$\begin{aligned} A &= 28.59051 & B &= -8.2 & C &= 0.0024804 \\ D &= -3142.31 \end{aligned}$$

2. The equation of Osborne and Meyers (01) whose experiments show that their equation is more accurate than that of Gerry.

$$\log_{10} p_{H_2O} = A + \frac{B}{T(K)} + \frac{C \cdot x}{T(K)} (10^{Dx^2} - 1) + E 10^{Fy}^{(5/4)} \quad (A2.2)$$

where p_{H_2O} is in international atmospheres and

$$A = 5.4266514 \quad B = -2005.1 \quad C = 1.3869 \times 10^{-4}$$

$$D = 1.1965 \times 10^{-11} \quad E = -0.0044 \quad F = -0.0057148$$

$$x = (T(K))^2 - 293700 \quad y = 374.11 - T(^{\circ}C)$$

3. The equation of Goff (G3) is of more recent date than those quoted above.

$$\log p_{H_2O} = A(1-T_r) + B \log_{10}(1/T_r) + C(1-10^{D((1/T_r)-1)}) \quad (A2.3)$$

where p_{H_2O} is in international atmospheres and

$$A = 10.79574 \quad B = 5.028 \quad C = 1.50475 \times 10^{-4}$$

$$D = -8.2969 \quad E = 4.76955 \quad F = 2.2195768$$

$$H = 4.2873 \quad T_r = 273.16/T(K)$$

All these expressions were used for the calculation of the equivalent thermal conductivity of water vapour and the results will be compared in the following section.

A2.6 Predicted Values of the Equivalent Thermal Conductivity of Air Caused by Evaporation, Diffusion, and Condensation of Water.

Temperature °C	Equivalent thermal conductivity, k_d W/m°C			
	Column 1	Column 2	Column 3	Column 4
0	0.0200	0.0204	0.0203	0.0191
20	0.0710	0.0727	0.0726	0.0662
40	0.219	0.222	0.222	0.197
60	0.632	0.639	0.638	0.551
80	2.10	2.12	2.12	1.78
90	5.19	5.22	5.21	4.34
95	11.4	11.5	11.4	9.48

Table A2.1. Values of the equivalent thermal conductivity of air caused by evaporation, diffusion, and condensation of water.

Vapour pressure.

Column 1 - vapour pressure data by Gerry (G1), equation (A2.1).

Column 2 - vapour pressure data by Osborne and Meyers (O1),
equation (A2.2).

Column 3 - vapour pressure data by Goff (G3), equation (A2.3).

Column 4 - vapour pressure data as in column 3.

Diffusivity.

Columns 1 - 3 - diffusivity calculated by the use of equation
(4.5).

Column 4 - diffusivity calculated by the use of
equation (4.4).

APPENDIX 3

The Thermal Conductivity of Particles of Quartz.

In chapter 4 an expression for the prediction of the thermal conductivity of a porous material was developed. In order to use such an expression the thermal conductivity of the solid phase must be known. In this work quartz sand was studied. It was assumed that the thermal conductivity of the quartz sand particles is the same as that of pure quartz. The following values of the thermal conductivity of quartz were found in the literature:

Temperature		Thermal conductivity			
°C	°F	10 ³ joule/cm s °C		Btu/hr ft °F	
		Direction of heat flow to principal axis			
		normal	parallel	normal	parallel
0		71	134		
50		62	107		
100		55	88		
	100			3.40	6.40
	200			3.00	5.40
	300			2.60	5.02

The first three pairs of values in the table above were taken from the Handbook of Chemistry and Physics (H1, p. E5) and the last three pairs of values from the International Critical Tables (I1, Vol.V, p. 106).

The following polynomial expressions for the conductivities in the directions normal and parallel to the main axis, k_n and

k_p , respectively, were obtained from the above data by the use of the least squares method:

$$\begin{aligned} k_n &= (0.167 + 608 V) \times 1.163 \\ k_p &= (13.9 - 6644 V + 1.641 \times 10^6 V^2) \times 1.163 \end{aligned} \quad (A3.1)$$

where

$$V = 1 / (273.16 + T(^{\circ}\text{C})), \text{ and}$$

$$k_n \text{ and } k_p \text{ are in W/m}^{\circ}\text{C}.$$

If it is assumed that particles of quartz in a sand are thin plates oriented in random directions then, according to Carslaw and Jaeger (C3, p.46), the resulting mean value of the thermal conductivities of the plates can be calculated as follows:

$$k_{\text{plate}} = \frac{2}{3} k_n + \frac{1}{3} k_p \quad (A3.2)$$

The analogous expression when the particles are thin rods is, according to Carslaw and Jaeger (C3, p.47), as follows:

$$k_{\text{rod}} = \frac{1}{\frac{2}{3} \frac{1}{k_n} + \frac{1}{3} \frac{1}{k_p}} \quad (A3.3)$$

As the actual particles have a form which is between that of a rod and that of a plate it may be assumed that the mean value of the thermal conductivity of the particles can be approximated as follows:

$$k_s = (k_{rod} + k_{plate}) / 2 \quad (A3.4)$$

It is not important to calculate the value of the thermal conductivity of the solid phase very accurately if the solid phase is discontinuous and if the thermal conductivity of the solid is much greater than that of the other phases.

The use of the expressions given above yielded the following values for the conductivities k_s , k_n , and k_p :

Temperature °C	k_s W/m°C	k_n W/m°C	k_p W/m°C
0	8.77	7.04	13.4
10	8.40	6.80	12.7
20	8.06	6.57	12.0
30	7.76	6.36	11.4
40	7.49	6.17	10.9
50	7.24	5.98	10.5
60	7.02	5.81	10.2
70	6.81	5.65	9.84
80	6.63	5.49	9.57
90	6.46	5.35	9.34
100	6.30	5.21	9.15

APPENDIX 4

Estimation of the Reynolds Number of the Capillary Flow.

The Reynolds number is defined as follows:

$$N_{Re} = \frac{W \rho_1 d}{\mu}$$

where the diameter of the flow channel can be calculated by the use of equation (6.1) as follows:

$$d = \frac{4\sigma}{h \rho_1 g}$$

As shown in fig. A5.1, in appendix 5, the maximum experimentally determined linear velocity of the capillary rise was about 0.25 cm/s and the resulting Reynolds number was about 0.4. In most cases the liquid velocities and the Reynolds numbers are much lower. Hence it may be assumed that capillary flow is laminar.

APPENDIX 5

The Determination of the Velocity of the Capillary Flow in a Porous Medium.

A5.1. Introduction

According to equation (5.42) the capillary coefficient can be calculated as follows:

$$C_{cap} = \left[W / \left(\frac{h_{ext}}{h} - 1 \right) \right] \frac{(h_{ext})^2}{(\Psi_{e \ ext})^2} \quad (A5.1)$$

The basic experimental data required are the velocities of the capillary rise into an initially dry layer of material as a function of height from the free liquid surface. The material to be studied was put into a transparent plastic tube equipped with a metal wire mesh in its lower end. The internal diameter of the tube was about 10 cm and the wall was marked at one centimetre distances along the length. The tube was immersed vertically into the liquid, which was water in these experiments, so that the free water surface was just above the wire mesh. The water started to rise into the materials, and the velocity of the rise was determined by four different methods.

A5.2. Method 1.

The Determination of the Velocity of the Capillary Rise
by Observing Visually the Movement of a Wet Boundary.

The water rose into the material as a clearly distinguishable dark boundary. However, the boundary was not level which may have been caused by uneven packing. The rise profile was studied by allowing the water to rise to various heights and then the looser dry material was poured off. From these experiments it was seen that generally the highest point reached by the boundary around the edge of the tube was nearly the same as the highest point of all reached by the boundary. The highest point was usually close to the centre of the tube. This shows that following the velocity of the fastest peak of rise through the wall of the tube gives a good approximation of the velocity of rise in the centre of the tube where the interference caused by the walls of the tube is a minimum, and the reliability of the values is a maximum.

The times required for the liquid to rise to various heights were measured, and the data so obtained were used to calculate the velocity versus height relationship given in table A5.1. The summary of the results obtained is in table A5.2. It was estimated that these results allowed the capillary coefficient, C_{cap} , to be calculated with an accuracy of ± 20 per cent.

Height above free water surface, cm	Time for water to reach specified height, s	Mean velocity over interval, cm/s
1.5	2	0.250
2.5	6	0.166
3.5	12	0.100
4.5	22	0.067
5.5	37	0.044
6.5	60	0.050
7.5	80	0.045
8.5	102	

Table A5.1. A typical set of results obtained by visual observation of the rise of a wet boundary into a layer of quartz sand.

Height cm	Velocities in different experiments, cm/s							Mean velocity, cm/s
2.0	0.143	0.250	0.250	0.200	0.288	0.250	0.333	0.25
3.0	0.100	0.166	0.154	0.111	0.111	0.125	0.125	0.125
4.0	0.083	0.100	0.080	0.072	0.100	0.077	0.125	0.088
5.0	0.083	0.067	0.063	0.083	0.059	0.083	0.058	0.062
6.0	0.048	0.044	0.033	0.035	0.039	0.035	0.048	0.040
7.0	0.039	0.050	0.016	0.019	0.031	0.017	0.023	0.024
8.0	0.029	0.045	0.005	0.013	0.016	0.013	0.018	0.015

Table 5.2. Summary of the rise velocities of a wet boundary into the dry layer of quartz sand, obtained by visual observation.

A5.3. Method 2.

The Determination of the Velocity of the Capillary Rise
by Observation of the Movement of a Wet Boundary by
Photography.

The photographic technique is a refinement of the previous method in that a stopclock was incorporated in the photographs. The results are shown in fig. A5.1. It was found that this method did not provide a real improvement in accuracy.

A5.4. Method 3.

The Determination of the Velocity of the Capillary Rise
by Observation of the Time Required for the Liquid to
Attain the Top of a Layer of Material.

For this method a number of columns were filled with the quartz sand to various heights. The purpose of the arrangement was to facilitate the observation of the actual velocity of rise in the centre of the column. However, the accuracy was unsatisfactory for two reasons. It was noted that the level of the sand fell during the course of the liquid rising probably because the sand became more closely packed in the wetted state. Errors were also caused because each pair of height versus time values was obtained from a different column. The results are shown in fig. A5.1. This method was found to be unsatisfactory.

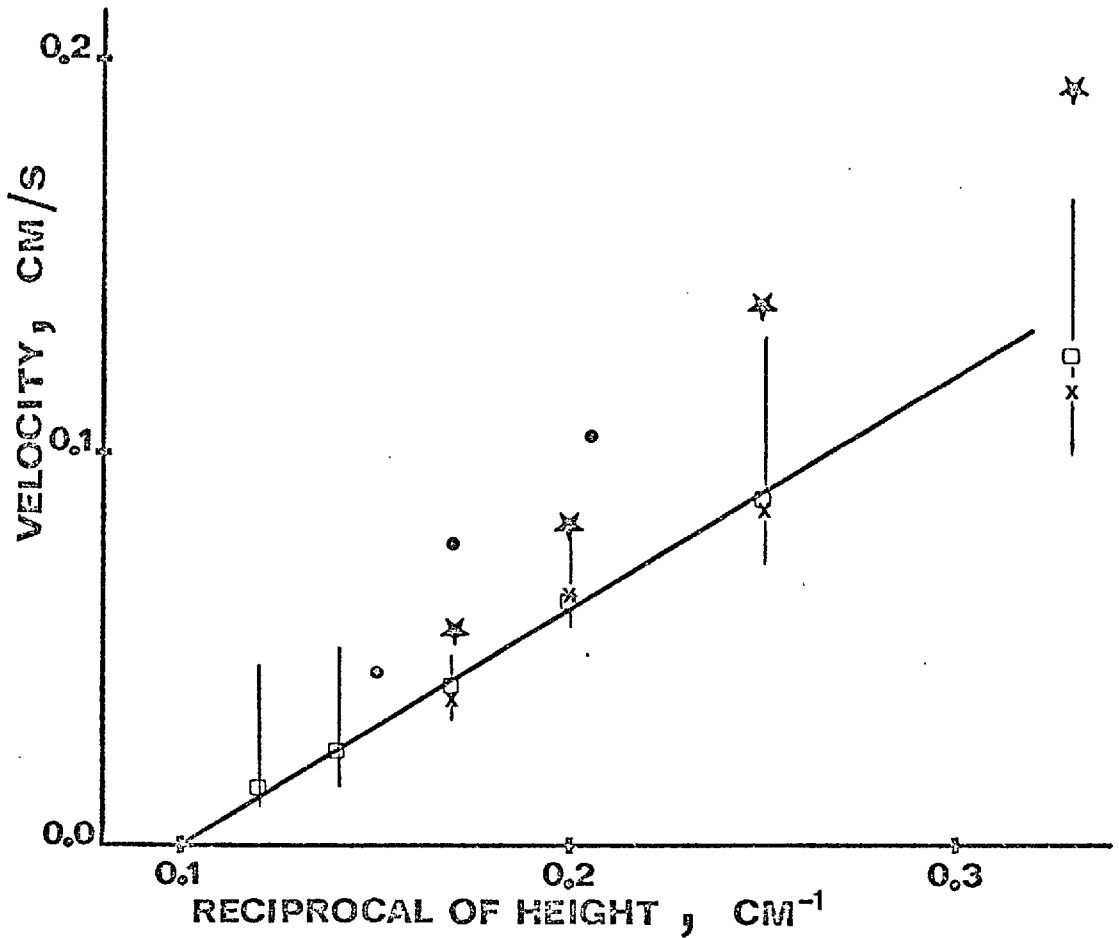


Fig. A5.1. Velocity of the capillary rise of water into quartz sand as a function of the reciprocal of height by the methods described in sections 2 to 5 in appendix 5.

- Values obtained by method 1. These are mean values of four to seven experiments. The vertical lines show the range of the obtained velocities including the stray values which were not taken into account in calculation of the mean values.
- Values obtained by method 2 (individual experiments).
- ★ Values obtained by method 3 (individual experiments).
- x Values obtained by method 4 (individual experiments).

A5.5. Method 4.

The Determination of the Velocity of the Capillary Rise
by Observation of the Time Required to Attain a Certain
Height by Hot Film Anemometer Probe.

The hot film anemometer probe was positioned consecutively at various heights in the column. Sand was poured in to a level well above the probe. The output from the probe was connected to a high speed recorder. This instrument was started simultaneously with the water beginning to rise into the material. The arrival of water at the probe caused a rapid voltage change which was registered, and the time of rise could be determined more accurately than by the other methods. The results are shown in fig. A5.1. This method gave values very close to those measured by the visual method.

A5.6. Conclusion.

Of the four methods described above the simplest one, the visual observation of rise of the wet boundary through a transparent wall of the column proved to be sufficiently accurate and did not require complicated equipment.

APPENDIX 6

Relationship between Tortuosity and the Capillary Coefficient.

The tortuosity can be calculated for the fully wetted state by the use of equation (5.42) as follows:

$$T_{\Psi=1} = \frac{\sigma \cos \Theta}{\Psi_{e \text{ ext}} \sqrt{2 \rho_l g \mu C_{\text{cap}}}} \quad (\text{A6.1})$$

The contact angle cannot be measured easily. For sand Luikov (L5) used the value of 0.8 for $\cos \Theta$, whereas Adamson (A2) gave the value of unity for $\cos \Theta$ when water is wetting silica. The purity of the surface influences the contact angle. In this work it was assumed that the value of $\cos \Theta$ for water wetting quartz sand is unity. Values of the tortuosity, $T_{\Psi=1}$, calculated for various materials by the use of equation (A6.1) are given in table 5.1 on p. 120. The calculated values for various granular materials are slightly higher than the values given by Krischer (K2, p. 168) whose values range between two and five. No conclusions can be drawn from this difference because the capillary coefficient, which appears in equation (A6.1), has very different values in different materials as shown in table 5.1.

APPENDIX 7

Relationship between Permeability and Capillary Coefficient.

Substitution of equation (5.34) into equation (5.2) gives the following expression:

$$K_w = \frac{\epsilon_{wnb} \mu W_{mean}}{(dp_c/dx)} \quad (A7.1)$$

The expression in the square brackets in equation (5.44) becomes, by application of equation (6.2), as follows:

$$\left[\frac{h_{mean}}{h} + 1 \right] = \frac{h_{mean} - h}{h} = \frac{1}{\rho_l g} \frac{\Delta p_c}{h} = \frac{1}{\rho_l g} \frac{dp_c}{dx} \quad (A7.2)$$

When equations (A7.2) and (5.44) are substituted into equation (A7.1) the following expression is obtained:

$$K_w = \epsilon_{wnb} C_{cap,T} (h^{-2})_{mean} \frac{\mu \psi_e}{\rho_l g} \quad (A7.3)$$

Values of permeabilities for various materials were calculated by the use of the above equation. The results were shown in table 5.1 on p. 120.

Farran and Starner (Fl) used a similar "rising wet frontier" experiment as was used in this work in order to determine permeabilities for an estimation of the wick properties of porous materials for heat pipe applications. Their method, however, does not include any correction which relates the

measured values to full liquid saturation. Therefore the permeability values measured by their method depend on the moisture content which occurs in the wet region of the material.

Application of equation (A7.3) together with the definition of the relative permeability, equation (5.3), gives the following expression for the relative permeability:

$$K_{rw} = \Psi_e^3 \frac{(h^{-2})_{\text{mean}}}{(h^{-2})_{\text{mean}, \Psi=1}} \quad (\text{A7.4})$$

The above equation was discussed in chapter 5 and was applied to a quartz sand.

APPENDIX 8

Experimental Determination of the Capillary Rise and Drain Curves of a Quartz Sand.

A8.1. Introduction.

A series of experiments for the determination of the capillary rise and drain curves in quartz sand were made. The main aims of these experiments were

1. to study the reproducibility of the capillary rise and drain curves,
2. to provide information for the study of the difference between the capillary rise and drain curves,
3. to test the validity of equation (6.15), and
4. to test the applicability of the expression derived for the capillary thermal gradient coefficient, equation (3.14), which presumes the capillary curve to be known.

The sand used was obtained from BDH Chemicals Ltd, Poole, England. The particle size was mentioned to be "about 40 to 100 mesh". According to the manufacturer the sand was purified by acid. The experiments showed that the maximum attainable moisture content was 0.270 kg water / kg dry material. According to the Handbook of Chemistry and Physics (H1, p. F1) the relative density of pure crystalline quartz is 2.65. In a real quartz sand this value may be slightly different. However, when the relative density of the sand particles used in this work was measured a value of 2.62 ± 0.02 was obtained. It was decided to adopt the value of 2.6.

Using this density the volume fraction of non-solids of 0.412 was obtained. It was found that the density of the packing varied between the values of $\epsilon = 0.37$ and $\epsilon = 0.43$ depending on the degree of shaking.

A8.2. The Measurements and the Results.

A column of height of about 50 cm was constructed of separate plastic rings of internal diameter of 10 cm and of height of one centimetre. The column was made water tight by fitting soft rubber gasket between each pair of adjacent rings. The sand was supported in the column by means of a wire mesh fitted in the bottom ring. The whole column was set in a tray so that the free water surface was just above the bottom of the column. The water level was maintained constant by means of a continuous feed and overflow. The experiment was carried out at 20°C, and distilled water was used. A loose-fitting cover was placed on top of the column to prevent evaporation without creating a pressure difference between the interior of the column and the environment. For the rise curves the sand was initially dry and the columns were left for 2, 4, and 6 days in order to determine when the steady state had been reached. In the case of the drain curves the sand was initially wet and the steady state was reached slowly and periods of 9, 10, and 13 days were used. For each time period the experiments were repeated to check the reproducibility of the results. The moisture content at each height was determined by weighing, drying at 110°C, and reweighing the contents of each ring. The results are shown in tables A8.1 and A8.2.

These tables show that the measured curves are not identical although they belong to the same material. The reproducibility of the measurements of the capillary curves was discussed in chapter 3, and fig. 3.2 was presented in order to demonstrate the effect of reproducibility of the predicted values of the capillary thermal gradient coefficient.

From the drain curve data it is seen that it is difficult to determine accurately the residual moisture content from a drain curve. From the rise curve data it seems that moisture is unable to rise higher than the height which corresponds to the height attained at the residual moisture content. This is in accordance with the explanation given for the existence of the residual saturation, namely the breaking down of the continuous liquid film.

Height cm	Duration of run (h)						
	94	94	47	46	96	144	119
	Moisture content, kg water/kg dry material, per cent						
	A	B	C	D	E	F	G
32				0.2		0.0	
31				0.2	0.2	0.2	
30				0.1	0.0	0.0	
29				0.1	0.0	0.0	
28				0.1	0.1	0.0	0.0
27				1.2	0.0	0.0	0.0
26	2.68	3.2	0.5	2.7	0.0	0.0	0.9
25	3.5	3.6	2.4	3.9	1.8	1.4	3.3
24	4.4	4.7	3.9	4.6	3.7	2.9	4.8
23	5.3	4.9	5.3	5.6	4.2	4.3	5.5
22	5.4	5.9	6.3	6.7	5.6	5.8	6.2
21	8.7	7.0	7.5	7.1	6.3	5.7	7.5
20	10.5	8.6	7.5	8.6	7.3	7.2	8.6
19	11.0	8.7	8.3	-	7.9	9.2	9.9
18	11.9	10.9	10.5	11.3	9.0	9.0	11.5
17	13.7	13.8	12.5	12.9	10.7	10.8	13.9
16	17.5	14.5	15.7	14.7	13.6	13.9	16.3
15	19.1	17.9	16.6	17.5	17.3	15.6	18.4
14	21.5	19.8	18.8	19.2	19.4	18.8	20.3
13	22.5	23.7	20.8	20.9	21.2	20.9	21.7
12	23.8	23.6	22.4	22.1	22.8	22.8	23.5
11	23.9	24.2	23.8	23.8	24.0	23.9	24.8
10	24.4	24.7	24.4	24.7	24.8	25.2	25.3
9	24.7	24.4	24.8	25.4	25.3	25.9	26.2
8	25.4	26.2	25.5	26.1	25.6	25.2	26.7
7	-	26.6	26.0	26.3	24.3	26.7	26.8
6	24.8	26.4	26.4	26.6	23.0	27.0	
5	27.0	27.2	26.6				
4	28.0	27.2	26.5				
3	27.4	26.7	26.7				
2	25.0	27.0	26.8				
1	26.5	25.8					

Table A8.1. Capillary rise data for quartz sand at 20°C.

Duration of runs A,B, and C was 241, 216, and 311 h, respectively.							
Height cm	Moisture content, <u>kg water</u> kg dry material, per cent			Height cm	Moisture content, <u>kg water</u> kg dry material per cent		
	A	B	C		A	B	C
57	0	0	0	28	10.2	12.1	13.8
56	0	0.3	0	27	10.9	15.8	13.6
55	0	1.0	0	26	14.1	17.0	14.1
54	0	1.5	0.2	25	18.1	20.6	18.4
53	0.3	1.7	0.4	24	19.0	20.7	22.9
52	1.4	2.1	1.1	23	19.9	22.4	23.9
51	2.3	2.6	1.5	22	23.0	23.6	23.6
50	2.1	3.1	2.0	21	24.2	24.2	23.7
49	2.3	3.0	2.2	20	24.4	24.4	23.8
48	2.3	3.3	2.4	19	24.9	24.2	25.1
47	2.4	3.3	2.7	18	24.8	23.7	25.3
46	2.4	3.1	3.0	17	24.8	25.8	25.7
45	2.4	3.7	3.0	16	25.6	25.6	25.4
44	2.7	3.6	3.0	15	25.8	-	25.8
43	2.9	4.6	3.3	14	25.6	-	26.2
42	3.5	4.0	3.4	13	25.6	25.9	25.5
41	4.8	4.3	3.7	12	25.6	-	26.1
40	4.4	5.4	4.1	11	25.9	-	24.5
39	5.1	4.8	4.3	10	-	-	-
38	4.6	4.9	4.8	9	-	-	-
37	4.6	5.6	6.4	8	-	26.2	26.1
36	5.9	5.9	5.1	7	-	-	-
35	6.1	6.4	5.5	6			
34	5.7	6.5	5.6	5			
33	6.3	6.4	5.9	4			
32	6.8	7.6	7.3	3			
31	8.4	8.5	8.4	2			
30	8.3	9.8	9.4	1	-	-	-
29	9.3	10.9	12.2				

Table A8.2. Capillary drain data for quartz sand at 20°C.

APPENDIX 9

Application of an Analytical Expression for the Capillary Curves.

A9.1.The Computer Programme.

The four parameters, m , σ^2 , κ_3 , and κ_4 , of the capillary curve in equation (6.15) must be determined from a capillary curve. The computer programme used for this task was based on a standard several variable minimization programme, VAO4A, developed by Powell (P7).

The objective function to be minimized was chosen to be the sum of squares of the distances between the experimentally determined heights and the heights calculated by the use of equation (6.15) for the same moisture content.

Minimization of the objective function proved to be difficult and the programme sometimes found false minima. This difficulty was overcome by the use of a series of short minimizations starting from different sets of assumed parameter values. The set which resulted in the lowest value of the objective function was chosen for the actual minimization.

A9.2.Discussion of the Results.

The results obtained by the procedure described above are given in chapter 6 in tables 6.1 - 6.3. In the beginning of table 6.1 the parameters of the rise curve A were determined in three different ways. In two cases, seven experimental values of the heights were used but different step lengths were used. In the third case, 16 experimental values of the heights were used. The results show that the way in which the minimization programme is used influences slightly the magnitude of the parameters obtained and that an increase

in the amount of experimental information provided did not, in the case studied, improve the goodness of the fit. These conclusions were supported by a number of other similar computer experiments which are not included in table 6.1.

The choice of the experimentally determined heights to be used was found to be difficult. Only values which corresponded to moisture contents which were neither very near to the residual moisture content nor very near to full saturation could be used because a minor error in the measurement of the moisture content at those extreme moisture contents corresponds to a large error in height. On the other hand, however, the influence of skewness and excess becomes more marked in these extreme moisture content ranges. Thus it became difficult to determine the optimum value of the parameters κ_3 and κ_4 . This problem resulted in an attempt to use another objective function in which the function was taken to be the sum of the shortest distances from the experimentally determined points to the curve described by equation (6.15). Each of the shortest distances was found by a single variable minimization programme. It was found, however, that this method did not improve the results but required much more computer time.

In some materials, especially in those studied by Brooks and Corey (B2), table 6.3, the values of the parameters κ_3 and κ_4 attain the limiting values allowed, i.e. ± 0.75 . The reason for imposing these limits was described in chapter 6, and was the result of poor convergence of the series on which equation (6.15) is based when the parameters κ_3 and κ_4 approach unity. However, even in these cases the predicted values were not very far from the experimentally measured values.

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