

PORES IN MATERIALS

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ABSTRACT

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Many common materials currently used in construction are porous. The presence of pores can significantly affect the mechanical, physical, and chemical properties of materials. The fundamental characteristics of pores are important in determining the properties of highly porous materials, and their suitability for particular applications. Of equal importance is the water that is held in the pores. This water can lead to the deterioration of a material and to the material's inability to meet its performance requirements. The types and amount of water present in a material will depend on the properties of the pores that are present in a material.

In this paper we will identify the pore properties which are fundamental to highly porous materials, and their influence on the behaviour of such materials. It will also be shown that there is a lack of knowledge and understanding of the pore properties, and that there is a need to develop new test methods in measuring these properties since the ones currently used are inadequate.

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LIST OF SYMBOLS

C	degrees Celsius
p	porosity
d_1	apparent density
d	true density
V	volume without pores
m	meter
kg	kilogram
MN	mega-newton
r	radius
Vp	total pore volume
S	specific surface
μm	micrometer
cm	centimeter
s	second
Sc	compressive strength
w_o	volume of mixing water
V_m	surface area of gel
lb	pounds
θ	contact angle

INTRODUCTION

INTRODUCTION.

All building materials are porous, whether they are natural or synthetic, mineral or organic. However, the term 'porous materials' has been adopted to represent hydrophilic solids,^{1,2} such as soils, masonry materials, glass and cellulose materials. The term 'non-porous' is used to represent hydrophobic solids,^{1,2} such as silicones, teflon, most polymers, most paint surfaces, asphaltic surfaces, etc. Non-porous is also used to describe materials such as metals, which when subjected to water, as vapour, liquid, or solid, will quickly reach equilibrium with the environment, because the amount of water that they can hold is very small.¹ Solids that are wetted by water, (hydrophilic), have an attraction for water molecules because of the high surface energy of a solid,¹ and because the contact angles are less than 90° .³ The amount of surface energy of a solid depends on the interaction of surface atoms with their surrounding atoms.¹

The presence of pores can significantly affect the properties of materials. By using the term 'non-porous' to describe certain solids, we tend to ignore the effect of any pores that may be present in it. For example, the compressive strength of various materials decreases with an increase in porosity, as illustrated in Figure 1.

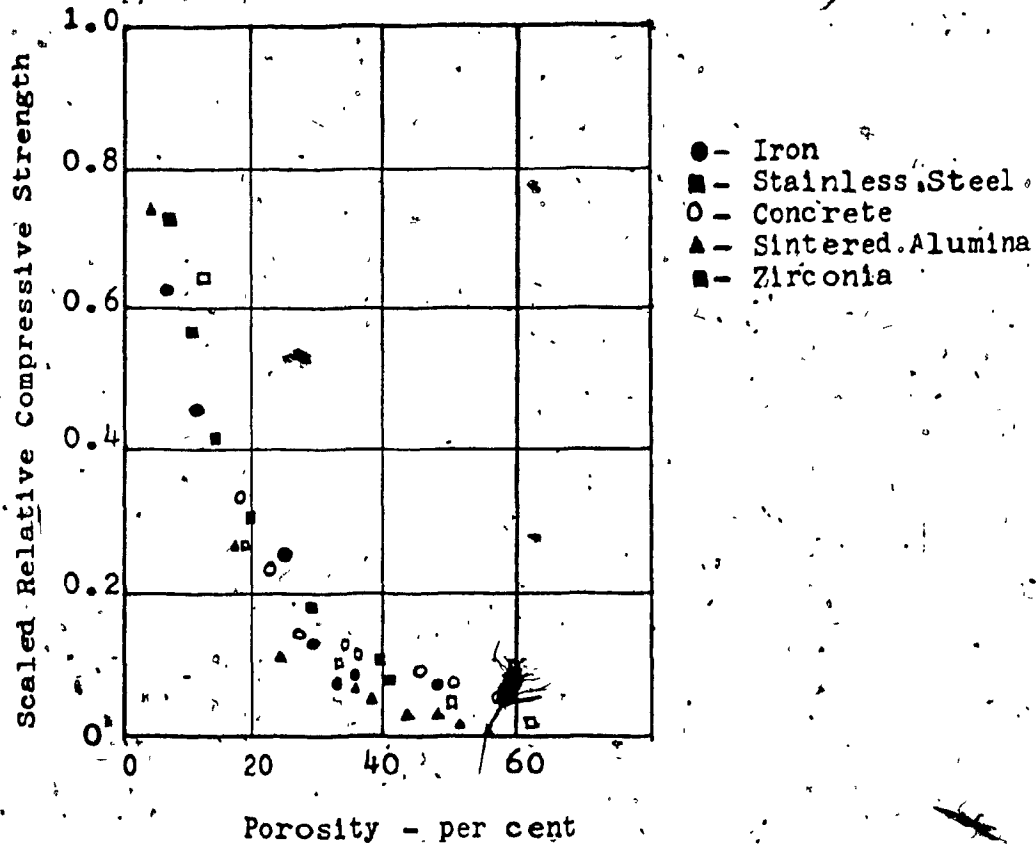


Fig. 1 Influence of porosity on scaled relative compressive strength of various material.¹⁰

The amount of decrease in compressive strength is relatively the same whether the material is hydrophilic, (concrete), or hydrophobic, (iron).

The term 'porous material' is used to describe a solid which differs in its catalytic behaviour and has different chemical reactions at the surface, from that of the same material in bulk. This is because of the increased surface area and the curvature of the solid

surface in the pore.⁴ The increased surface area is a result of a significantly larger amount of pores present in a material. Thus, the term 'highly porous material' may be more suitable than 'porous material' to describe such a solid.

It is not only necessary to know the number of pores, (porosity), in a material, but also their size, shape and distribution.⁵ These are important factors in determining the properties of such highly porous materials. For example, the fatigue limit of concrete with a given porosity, increases as the pore size decreases,⁶ as long as the pores are spherical in geometry, since flat pores will depress the fatigue limit.⁶

Properties such as pore size distribution and pore shape can not yet be determined accurately by reliable test methods.⁵ There is a need to develop non-destructive methods of analysis and measurements of such properties. Once we are able to measure them, we will be able to determine the specific characteristics of such highly porous materials.

A very important characteristic of a material is its resistance to deterioration in quality during its period of use.⁷ The resistance to deterioration is the durability of a material.⁷ The British Code of Practice for Durabi-

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lity, defines durability as "the quality of maintaining... satisfactory appearance and.. performance of required functions".

One of the most common agents that leads to the deterioration of a material is water. It is a vital and an abundant component of our environment, possessing unique qualities which account for its usefulness and desirability, as well as its damaging and hazardous effects.⁹ Water is a constituent of many building materials, i.e. concrete, and its presence or absence may be responsible for properties such as flexibility, strength, thermal and electrical conductivity, shrinkage and swelling and many others. Water can be present in its various phases of state; solid, liquid, and gas. It has the ability to dissolve many other substances. The anomalous decrease in density on freezing, and the presence of various foreign molecules in water, are believed to be responsible for the damage of highly porous materials. However, not all water present in a material will cause damage. For example, in the small pores, i.e. gel pores in the cement paste, water will not freeze at temperatures above -78°C ,¹⁰ whereas in some large capillary cavities, it may freeze at 0°C , and cause frost damage to the material.

Thus, most damage occurring in many building materials is due to the presence of water. This water is found in

the ambient conditions of the environment and in the pores of the material. The type and amount of moisture found in a material is greatly influenced by the character of the pores, i.e. their size, shape, and distribution. If we do not understand the fundamental properties of pores, then how can we reliably analyze their influence and the influence of water present in them on the behaviour of materials. The purpose of this paper is to stress the fact that not much is known about the properties of the pores, and that we need more reliable non-destructive test methods to determine the properties of pores, for current methods based on direct observations and on secondary or derived properties are not adequate.

In Chapter I, Fundamental Characteristics of Highly Porous Materials, we identify the properties which are fundamental in the description of highly porous solids. Chapter II, Moisture in a Highly Porous Material, describes the various forms of moisture present in a porous solid. The type and amount of water present in such a material will depend on its fundamental properties such as, porosity, pore shape, size and distribution. The type and amount of water in the pores, the number of pores and their properties will influence the behaviour of the material. The extent of these influences is discussed in Chapter III, Influence of Pores on Material Properties.

CHAPTER 1

FUNDAMENTAL

CHARACTERISTICS

OF

HIGHLY POROUS

MATERIALS

FUNDAMENTAL CHARACTERISTICS OF HIGHLY POROUS MATERIALS.

Mechanical, physical and chemical properties of porous materials are influenced by the pores and their distribution. There are two types of pores; ¹¹ open pores, (inter-connecting channels), which can permit the passage of fluids and can retain wetting liquids by capillary action, and closed pores, (those which have no inter-connections, and which usually do not contribute to the permeability of a material).

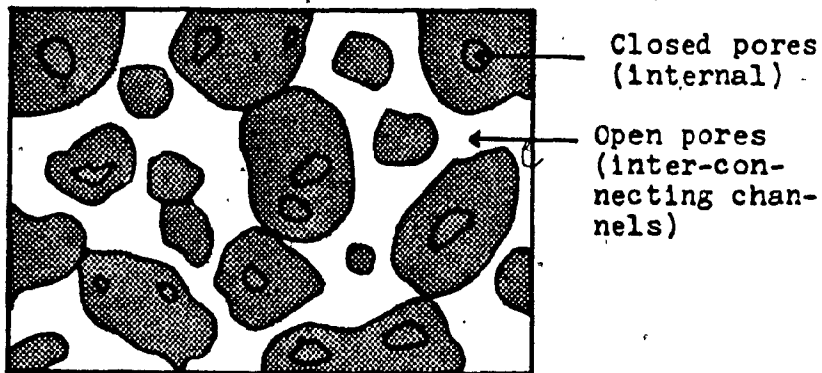


Fig. 2. Open and closed pores in a material.

Pores or voids may arise out of the process of natural growth, as in wood; they may be deliberately introduced into a material by processing, as in fire-brick or air-entrained concrete; or they may occur accidentally in some metals because of imperfect casting techniques. ¹²

Chemical reactions occur at the surface and the catalytic behaviour of a porous solid differs from that of the same material in bulk because of the increased surface area and the curvature of the solid surface in the pore.⁴ The size and distribution of the pores, their extent, and their shape are important factors in determining the properties of porous materials and their suitability for particular applications.

When a porous material is formed, its properties will be influenced by the character of the raw material, the size and shape of the constituent particles, and the area of boundaries formed by the interface of growing surfaces.¹³ However, there are four properties which are fundamental in the description of highly porous materials:⁵ porosity, specific surface, pore size distribution, and pore shape.

The porosity of a sample is the volume of pores or voids present in the material.¹² This is usually expressed as a percentage of unit volume. These pores, (voids), are considered as 'a phase of zero composition'.¹¹ Porosity, p , is usually defined by the ratio of the apparent density, d_1 , to the true density, d ,¹³ of the material with no pores.

$$p = 1 - V,$$

and

$$V = d_1/d,$$

where V is the ratio of volume

thus, porosity, in percentage, is:

$$p = (1 - d_1/d) 100$$

The apparent density of a material is the weight of one unit volume of the material in its native porous state.¹¹ Where possible, the true density of a material is determined by the ratio of the weight of an equal volume of compacted hard particles of the material without pores.¹³ For materials like concrete, where the final constituents are chemically different from the initial ones, the porosity may be determined by using the procedures of ASTM C 30 through to 37 (1970) for aggregates, and ASTM C 185 (1975) for cement paste.¹⁴

The terms apparent or true density are often used, depending upon whether open pores, or both open and closed pores are considered. Apparent porosity is open pore volume divided by total, (bulk), volume, and true porosity is open and closed pore volume divided by the total volume.¹¹

The term specific surface, (S), designates a particular quantity, the surface area of open pores contained in a unit volume of the solid.⁵ Haynes states that the specific surface area can be derived from porosity and pore size distribution. Specific surface

area is an important factor when dealing with the strength of concrete in its early stages¹⁰. For example, 7 day old concrete has twice the specific surface area and 50% more compressive strength than fresh concrete.

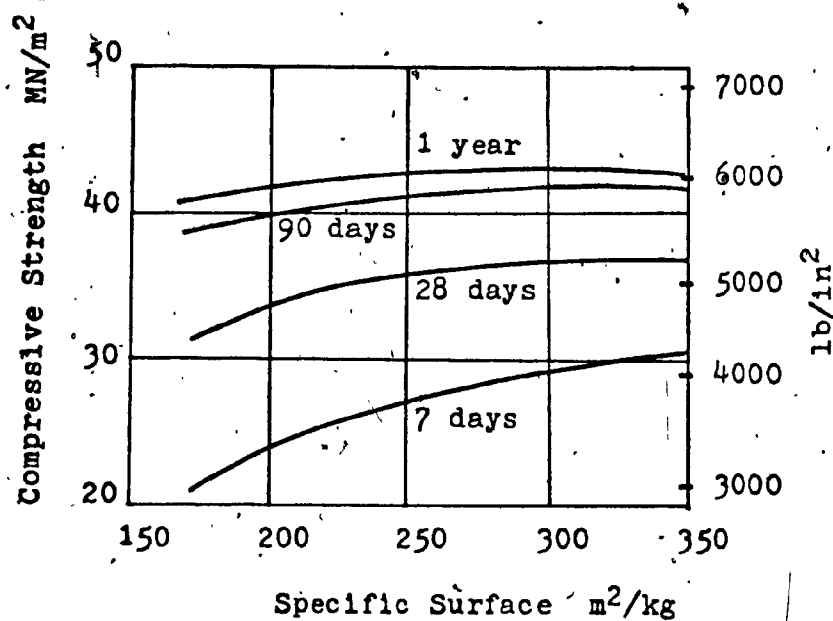
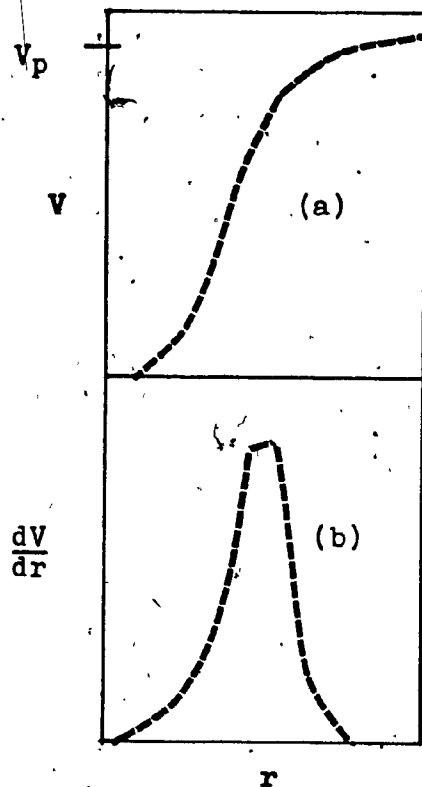


Fig. 3 Relation between strength of concrete at different ages and the specific surface area of cement.¹⁰

The differential pore size distribution is a curve showing the fraction of the total open pore volume for which the pores lie within various size ranges; it is a complex function of the shape of pores and the way in which they are inter-connected.



(a) Integral pore size distribution. V is the volume of pores having radii less than r . V_p is the total pore volume.

(b) Differential pore size distribution. The maximum occurs at the value of r where the slope of the curve in Fig. 4(a) is greatest. The area under the curve is V_p , and the curve can be normalized by plotting $(1/V)(dV/dr)$ instead of (dV/dr) .

Fig. 4 Pores Size Distribution in integral and differential form.⁵

The pore size distribution is difficult to calculate because of the variety of pore sizes. An overall analysis of the pore size distribution can be achieved if a simple pore shape is assumed. However, this does not give a proper indication because the pore shape and combinations vary considerably from sample to sample of the same material. The reason for this is that the

pores are the result of a chance arrangement of particles of a variety of sizes, shapes and surface characteristics. ¹³ Thus, this property can only be derived through direct observation.

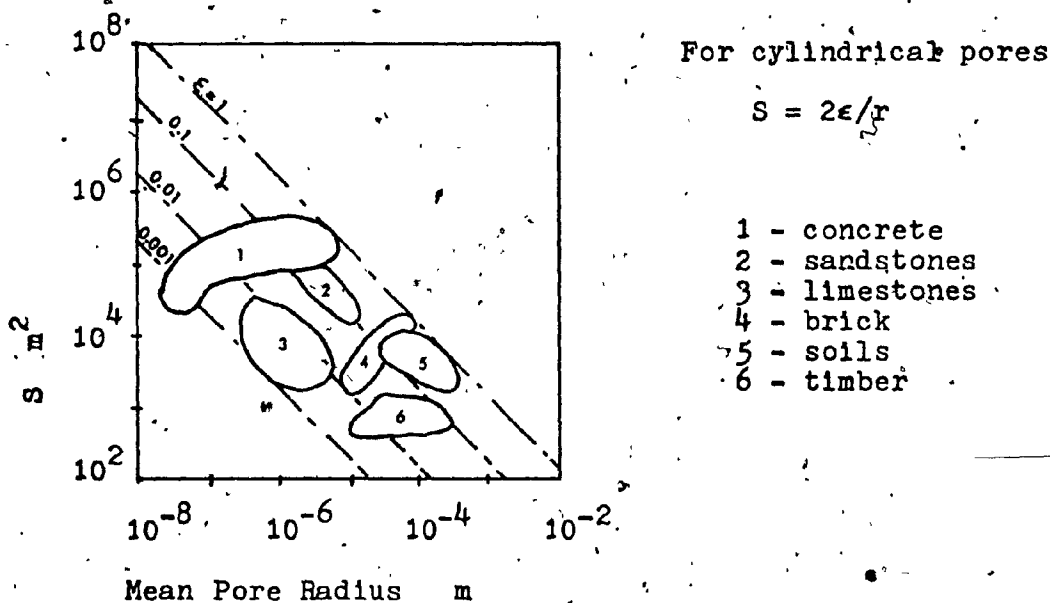


Fig. 5 Pore properties of common constructional materials. (Specific surface and mean pore radius are plotted on logarithmic axes. For any given pore geometry these quantities are related via the porosity. Contours of constant porosity, calculated on the assumption of cylindrical pores, are also shown.)

The fourth geometrical property, pore shape, also can only be evaluated by direct observation. ⁵

Indirect means of estimation, those based on secondary or derived properties, cannot be used because every analysis is based on an assumed pore shape, (spherical or cylindrical shapes are usually assumed).⁵

Many of the pores join to form oddly shaped, curved elongated labyrinths or interstices between particles of the material. In time, these interstices undergo considerable changes in shape and size, because of the physio-mechanical processes taking place.¹³ This can even result in partial or complete blocking of some capillaries, creating new pores.

After identifying the four properties which are fundamental to highly porous materials; porosity, specific surface, pore size distribution, and pore shape, we may proceed to an evaluation of their influence on the mechanical, physical, and chemical properties of porous materials. But first we must discuss the water present in the pores, for this water can lead to the deterioration of the material and cause the material's inability to meet its performance requirements.

CHAPTER II

**MOISTURE
IN A
HIGHLY POROUS
MATERIAL**

MOISTURE IN A HIGHLY POROUS MATERIAL..

Water is an abundant and vital constituent of our environment. Its presence and unique qualities account for its usefulness and desirability as well as its damaging and hazardous effects. Water is a constituent of many building materials, i.e. concrete, and its presence or absence may be responsible for properties such as flexibility, strength, thermal and electrical conductivity, shrinkage and swelling, and others.

As mentioned previously, water has unique properties, which at times add to the difficulty in understanding its behaviour and influence on materials. It has high heats of fusion and evaporation, and its electronic structure gives it the ability to dissolve many other substances. Maximum density occurs at 4°C . It has eleven phases of state: nine solids, a liquid, and a gas.

Water is found in various forms in a highly porous material. These forms are present simultaneously and exhibit a complex relationship. The water found in a material can be in the following forms:

- a) chemically combined water,
- b) physically bound water,

- c) bulk water,
- d) ice,
- e) water vapour.

Chemically combined water is a component of the hydrated substances contained in a material. In highly porous materials the amount of chemically combined water is generally small, usually up to 12%.¹³ This

type of water can be further subdivided into water of constitution and water of crystallization. Water of constitution is a chemical component of minerals and it is liberated in the process of destruction of the chemical composition of minerals at high temperatures.¹³

The water of crystallization is a constituent part of crystallohydrates and zeolites, such as water in gypsum, kaolinite, goethite, etc.¹³ The number of hydrated water molecules varies with the crystal structure, and depends on the ambient conditions when the crystal is formed. The water of crystallization is less strongly held than the water of constitution, and it is set free at lower temperatures.¹⁰

Physically bound water can be present in a material in its various phases of state, i.e. liquid, solid, and amount varies with ambient conditions and the properties of the pores. Physically bound water which is more strongly held, is referred to as hygroscopic moisture,

and loosely bound water is referred to as molecular or film water.¹³

Every porous material adsorbs vapour and water molecules that are held on the surface of its particles. The capacity to adsorb water vapour from the air is called hygroscopicity, and the moisture adsorbed by the surface is called hygroscopic water. The degree of hygroscopicity depends on the surface area of the material, the surface energy of the solid, and on the amount of relative vapour pressure in the air with which the material is in contact with. Hygroscopicity of a material increases with relative humidity, and it decreases with a rise in temperature due to the increased vibrations at the particle surfaces. The maximum amount of water adsorbed by a material from a space saturated with water vapour is called the maximum hygroscopic moisture.¹⁴ Water can enter almost all connecting pores to form films in them or it can even fill them completely as the film thickness becomes greater than the pore radius.² Dipolar water molecules are attracted and become fixed on the surface of particles by hydrogen bonds. Hygroscopicity is more dependent on molecular rather than thermal condensation.¹³

The moisture held by molecular forces around solid particles is called film water. When particles, satu-

rated with moisture up to the maximum hygroscopic level come into contact with liquid water, the adsorbed film thickness increases until the molecular forces of attraction reach complete equilibrium (molecular condensation).¹³ This water on the surface of particles forms a film which is held with less force than the original hygroscopic water. The dividing line between maximum hygroscopic water and film water is not clearly defined. The attraction of film water and its fixation on the surface of soil particles is mostly due to the forces caused by the electric charges of soil cations and anions.²⁶

The inner layer of water molecules corresponding to the hygroscopic moisture are tightly held by the particles. The loosely held outside layers of film water may move downwards under the influence of gravity, or be displaced in any direction under the effect of molecular forces upon drying out of the material.²⁷ The less physically bound water remaining in the material,¹³ the more firmly it is held by the surface particles. As the water film grows thicker, the molecular attraction of the material particles has less effect on the outer layer of water due to the shielding by the inner layer, and there is no net attraction beyond a certain limit.^{26, 27} This process of adsorption, (and the reverse effect known as desorption), involves a readjust-

ment in the balance of molecular forces, and thus, there are small accompanying dimensional changes.

Curves of moisture content in highly porous materials versus relative humidity at a given temperature are known as sorption isotherms. These are shown in Fig. 6 for both wetting and drying situations for common building materials. The difference between wetting and drying is known as hysteresis and this arises from the absence of bonding forces in the vapour.

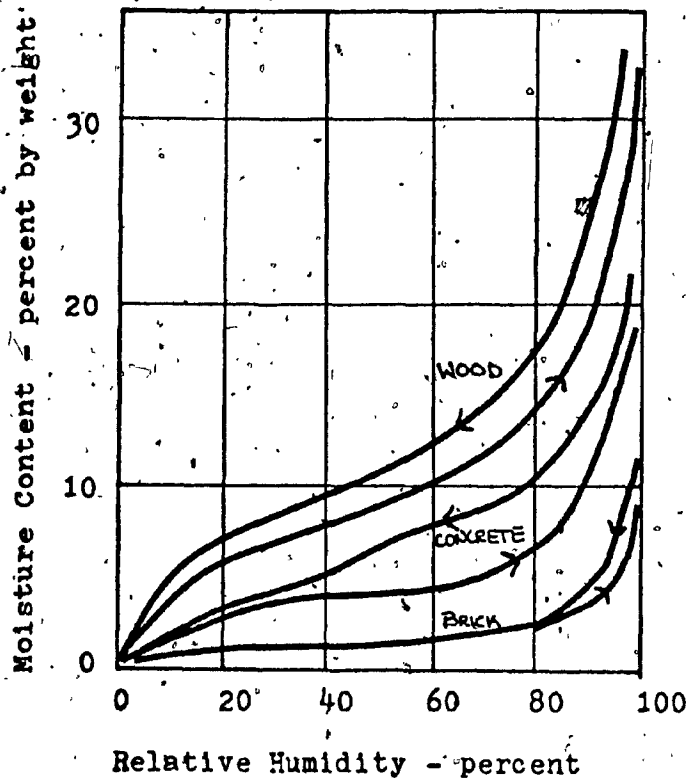


Fig. 6 Water held in some common porous materials at various relative humidities.

Capillary water is a transition between the molecular film water and the bulk water.¹³ It is held by the interfacial forces between the air, water and solid particles. These meniscus forces may be of attraction as in the case of wettable, hydrophilic solids, (soils, masonry materials, and cellular materials), with contact angles less than 90° , or of repulsion as for non-wettable, hydrophobic solids, (most polymers, teflons, silicones, etc.), with contact angles greater than 90° . The force of attraction or repulsion will depend on the character of the material, the moisture history of the material and its contact angle at that time, as well as the value of the surface tension of the water which increases with reducing temperature.

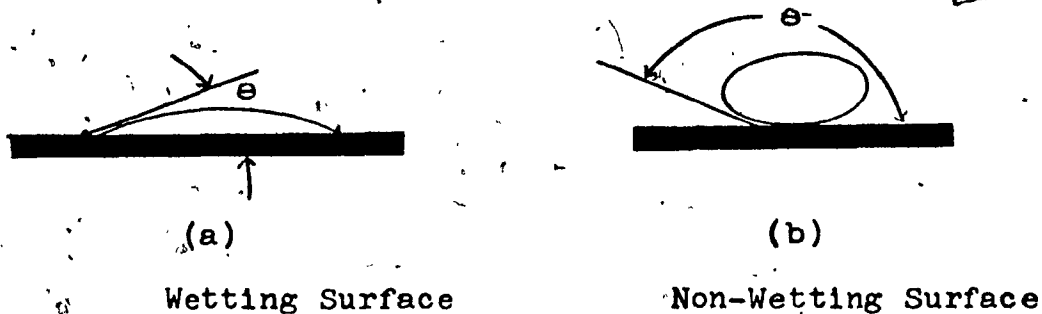


Fig. 7. Contact Angle for Wetting and Non-Wetting Surfaces.

Hence, capillary water may be defined as liquid water held by the cohesive forces of attraction or association that water molecules have between them. In smaller capillaries, water is held by intermolecular forces of attraction between it and either the solid or the hygroscopically held water. These forces can extend outwards from the solid about one hundred molecules and are sufficient to increase both the density and viscosity of the water so held, and cause a depression in the freezing point to less than that of bulk water.

Capillary water can be further subdivided into pendular, (angular), water, funicular water, capillary sorptively locked water, and capillary mobile water.

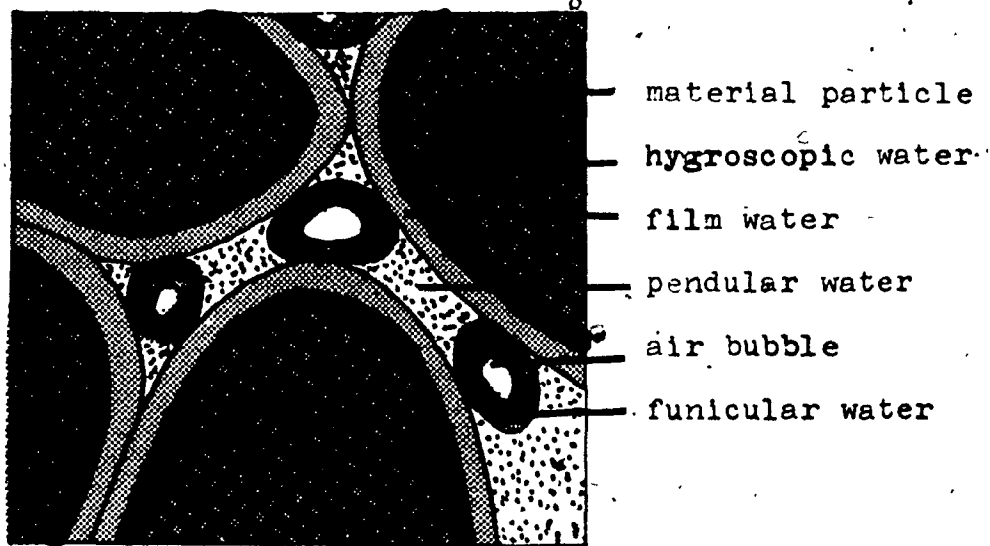


Fig. 8 Forms of water in a porous material.

Pendular or angular water is not continuous nor is it mobile. This water appears in the corners of the boundaries between material particles. The boundary which separates pendular water from the pores is the surface tension meniscus. This water may appear as a result of capillary condensation.¹³ The accumulation of pendular water increases progressively, the menisci widen, and finally, come into contact and merge with each other, forming funicular water with remaining gaps or bubbles of trapped air.¹³ Sections of capillary water, with menisci at the ends are obtained when the trapped air bubbles are ousted out because of resulting pressure differences. This water, which is now surrounded by hygroscopic and film water, is called capillary sorptively locked water.¹³ When the capillary pores are filled completely we get capillary mobile water.

Capillary water is subject to the capillary, (meniscus), forces, and to a smaller extent, to gravity. 'Capillary forces', or 'capillary potential', is used to designate a certain resultant of forces; surface tension, osmotic, and sorptive forces.

When all capillary pores are filled with water and the capillary potential is reduced to zero, water begins to move along the pores under the action of gravity.

This is known as bulk or gravitational water, which appears after rain, watering, or thawing and melting of ice.

Water vapour can be present in the pores of the material. It is a gas which occupies all the space that the air does. Water vapour can act independently of the air, since in general its properties do not depend on the presence of air. It exerts its own vapour pressure, and can move about through materials under differences in its own vapour pressure.

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As a result of changes in moisture content in highly porous materials, some forms of water pass into other forms. As the moisture content increases, water vapour is fixed as hygroscopic water, which increases in thickness and reaches the value of maximum hygroscopic moisture. It then passes into film water, and then into maximum film water and finally into capillary water. Pendular to begin with, then funicular, then locked capillary, and finally reaching maximum capillary readily mobile water. Finally, we get bulk or gravitational water when the pores are full.

CHAPTER III

INFLUENCE

OF

PORES

ON

MATERIAL PROPERTIES

INFLUENCE OF PORES ON MATERIAL PROPERTIES.

Pores influence the properties of materials, whether they are empty or whether they contain a liquid. In discussing pores and their influence on the properties of porous materials, we will limit ourselves to the material most commonly used in construction, namely concrete.

Concrete is a heterogeneous porous material in which there is more than one solid phase and more than one porous phase. ⁶ The presence of pores in both the cement paste and the aggregate contribute to the porosity of the concrete, and they have a great influence on properties such as strength, absorption, permeability, creep, durability, and others. We will first discuss the effect of pores on the cement paste, then on the aggregate, and finally on concrete.

Many of the mechanical properties of hardened cement and concrete depend on the physical products of hydration. Portland cement, the most commonly used hydraulic cement, consists of argillaceous and calcareous raw materials. The argillaceous materials, which may be clay, shale, or slate, provide alumina and silica. ¹⁵ The calcareous materials, which may be limestone, marl, or oyster shell, provide lime. ¹⁵

Thus the major constituents of portland cement are lime, silica and alumina.

When water is introduced, it attacks and decomposes all the compounds present in portland cement and forms a variety of products, which undergo complex reactions in a short time, later to be converted into other products in the process of hydration.¹⁵

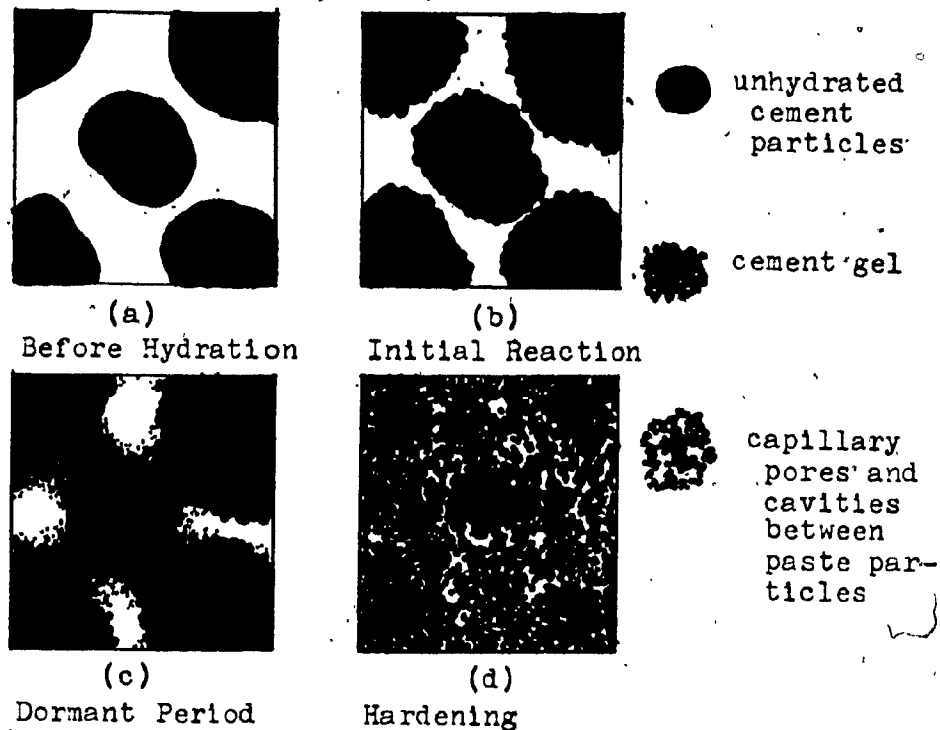


Fig. 9 Schematic representation of hydration and gel formation.¹⁵

These products form first at the boundaries of the

grains of cement, and as their development continues,
the cement paste 'sets' and later 'hardens'.¹⁵ Cement
hydration can be classified into various stages, based
on major changes in the reaction rate and the physical
structure of the cement paste. These are given in the
following table.

Hydration Stage	Typical Duration	Principal Chemical or Physical Changes
Initial reaction	5-10 min.	Initial solution and hydration.
Dormant period	1 hr.	Growth of reaction product membranes around cement particles.
Setting	6 hrs.	Membrane rupture, renewed hydration of particles.
Hardening	6 hrs. to 1 year	Hydration proceeds slowly and products exude into and fill capillary space.
Destructive hydration.	1-5 years	Disruption of surrounding hardened paste by expansion due to late hydration.

Table I. Stages of Hydration of Cement Paste.¹⁵

Many of the mechanical properties of hardened cement depend on the physical structure of the products of hydration. The fresh cement is a plastic network of cement particles in water, but once the paste has set, the gross volume remains approximately constant.¹⁰ During hydration, the hardened cement paste consists of hydrates of various compounds such as calcium aluminum hydrates, calcium silicates, etc., collectively referred to as gel, of crystals of $\text{Ca}(\text{OH})_2$, of some minor components of unhydrated cement, and of the space vacated by the water used up in hydration in the fresh paste.¹⁰ These spaces are called capillary pores. However, there are also interstitial voids in the gel referred to as gel pores.¹⁰

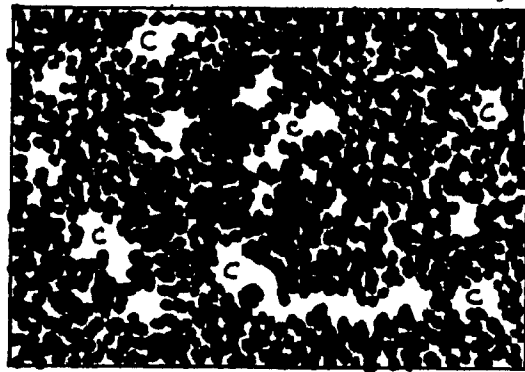


Fig.10 Simplified model of paste structure. (Solid dots represent gel particles; interstitial spaces are gel pores; spaces marked C are capillary cavities. Gel pore size is exaggerated.)¹⁰

At any stage of hydration the capillary pores are that part of the gross volume which has not been filled by the products of hydration. Since these products occupy more than twice the volume of the original solid phase, the volume of the capillary system is reduced as hydration progresses.¹⁰ Thus, the capillary porosity of the cement paste depends on both the water/cement ratio of the original mix and on the degree of hydration. The diameter of the capillary pores has been estimated to be of the order of $1.3 \mu\text{m}$, (5×10^{-5} in.).¹⁰ They vary in shape and form an inter-connected system randomly distributed throughout the cement paste.¹⁶ These inter-connected capillary pores are thought to be responsible for the permeability of hardened cement paste and its vulnerability to frost damage.

The gel pores are inter-connected interstitial spaces between the gel particles. They are much smaller than the capillary pores; between 1.5×10^{-3} and $2.0 \times 10^{-3} \mu\text{m}$ in diameter.¹⁰ This is only one order of magnitude greater than the size of a water molecules,¹⁰ and for this reason, the vapour pressure and the mobility of adsorbed water in the gel are different from the corresponding properties of free water¹⁰ and from that of capillary water. The amount of water which can move into and out of the gel di-

rectly indicates its porosity.¹⁷ The gel pores occupy about 28%¹⁸ of the total volume of the gel. As hydration progresses, the total volume of the gel increases and so does the total volume of gel pores, whereas the volume of capillary pores decreases.

The porosity of cement is a function of the water/cement ratio. The lower the water/cement ratio of the mix, the lower the porosity.¹⁰ Wischer¹⁹ found experimentally that for many cement pastes,

$$S_c = (1 - V_p)^{2.7} \times 3,100 \quad \text{kg/sq cm}$$

where S_c is the compressive strength and V_p is the volume of pores.

As the volume of pores increases, the compressive strength decreases. It follows that the compressive strength decreases with the use of a higher water/cement ratio.

The permeability of cement is not just a simple function of its porosity, but also depends on the size, distribution, and continuity of the pores.¹⁰ Although the cement gel has a porosity of 28%, its permeability is only 7×10^{-13} m/s.¹⁰ This is due to the extremely fine texture of hardened cement paste, for the pores and the solid particles are very small and numerous.

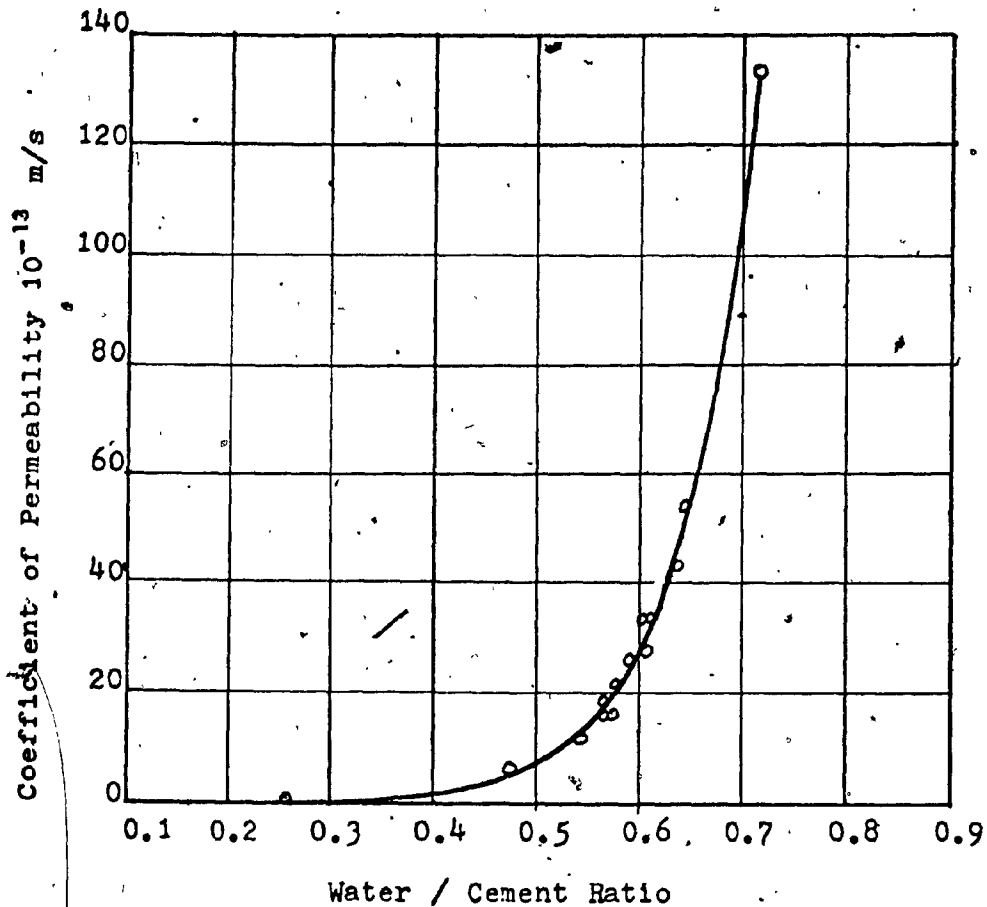


Fig. 11 Relationship between permeability and water/cement ratio for mature cement pastes.¹⁰

In aggregates, the pores, though fewer in number are much larger in size, lead to a higher permeability.¹⁰
 For the same reason, water can flow more easily through the capillary pores rather than through the smaller gel pores. The cement paste as a whole is 20 to 100 times more permeable than the gel itself.¹⁷ Thus it

follows that the permeability of the cement paste is controlled by the capillary porosity of the cement paste. The permeability of cement paste varies with the progress of hydration. In fresh paste, the flow of water is controlled by the size, shape and concentration of the original cement grains.¹⁰ With the progress of hydration the permeability decreases be-

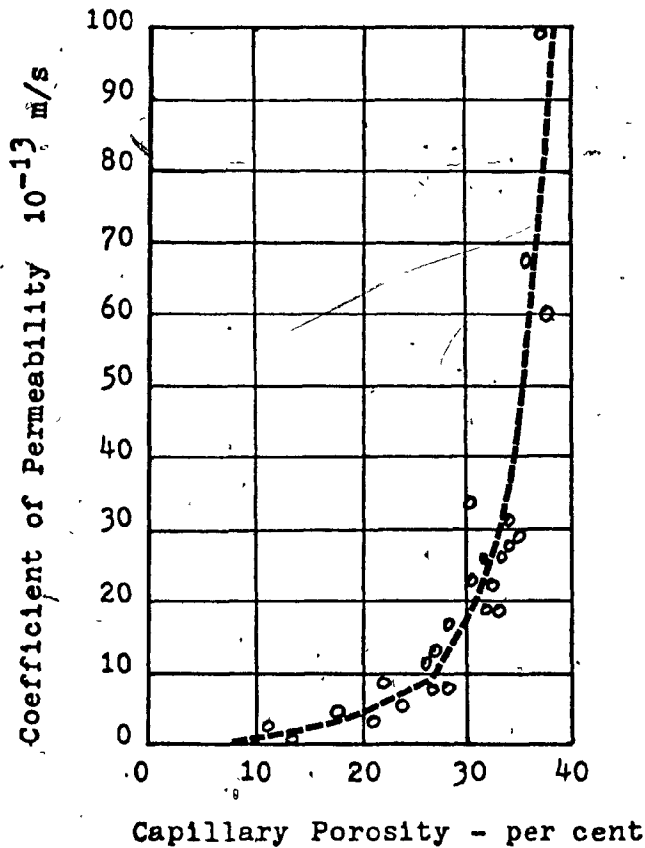


Fig.12 Relation between permeability and capillary porosity of mature cement paste.¹⁰

cause the gross volume of the gel is approximately twice the volume of the unhydrated cement, so that the gel gradually fills some of the original water-filled spaces. In a mature paste the permeability depends on the size, shape and concentration of the gel particles, and on whether or not the capillaries have become discontinuous. The permeability is also affected by the properties of the cement. For the same water/cement ratio, coarse cement tends to produce a paste with a higher porosity than a finer cement. Thus, it is possible to state, that the higher the strength of the paste the lower its permeability, since strength is a function of the relative volume of gel in the space available to it. However, in the case of severe drying, the cement paste increases its permeability, probably because the gel between the capillaries ruptures, opening new passages for the water.

The surface structure and the specific surface area of cement paste are important factors in the development of strength. It is assumed that the forces responsible for adhesion between the cement particles are greater for materials having irregular co-ordination of surface atoms, for example high surface energy. The surface energy arises because one half of the surrounding particles are not present to balance

out the forces exerted by the remaining half. With an increase in the surface area the amount of surface adhesion will increase. Powers¹⁶ states that the compressive strength of paste depends primarily on the physical structure of the gel.

$$S_c = 120,000 V_m/w_0 - 3,600 \quad \text{lb/in}^2$$

where V_m is the surface area of the gel, w_0 is the volume of mixing water, and S_c is the compressive strength of paste.

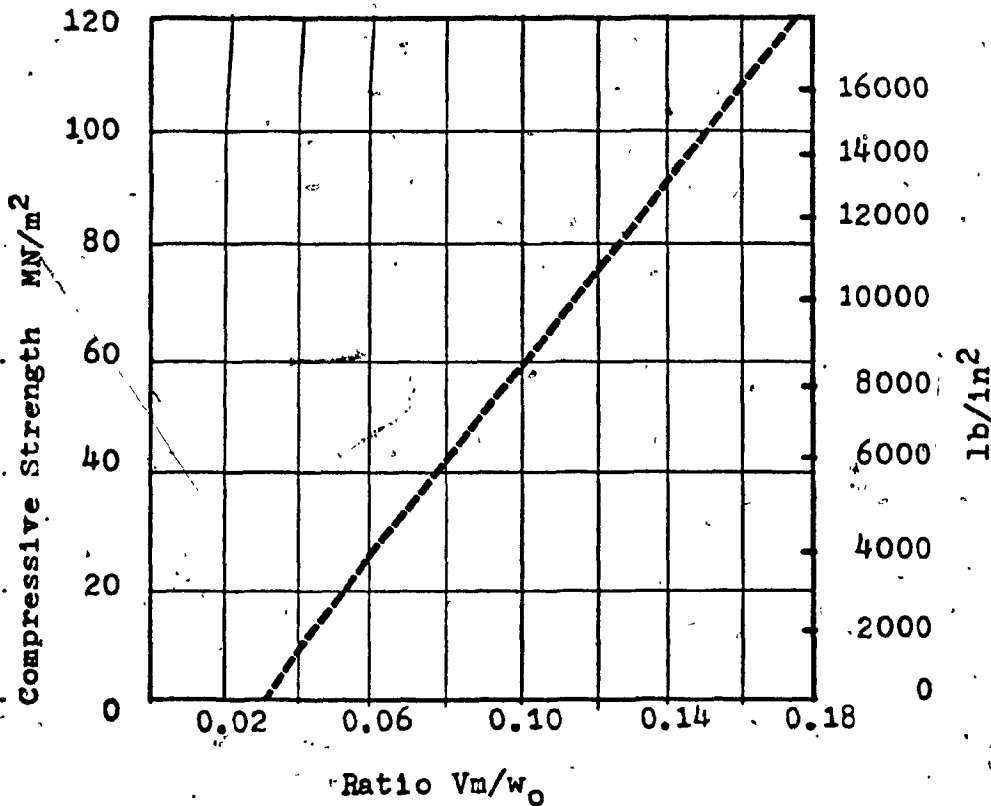


Fig.13 Relation between the strength of mature cement paste and the ratio of surface area of gel V_m to the volume of mixing water w_0 .

During the progress of hydration, the specific surface area may increase by a factor of 1,000.¹⁵

Another property of the cement paste that is influenced by pores is creep. Creep is a delayed elastic phenomenon in which full recovery is impeded by the progress of hydration.¹⁰ It occurs in the cement paste and it is related to the internal movement of the water of hydration.¹⁰ Glucklich's tests²⁵ have shown that concrete from which all evaporable water has been removed exhibits practically no creep at room temperatures. However, at high temperatures, when water does not play a role, the gel itself becomes subject to creep-deformation.¹⁰ This suggests a viscous flow or a sliding between gel particles, and it accounts for the influence of temperature, and the irreversible character of long-term creep.

It is suggested that creep and shrinkage of concrete are of a similar nature, and that they are based on the migration of water from the cement gel. This is supported by a number of well established experimental results:²¹

- a) A high ambient humidity discourages the removal of water held in pores and results in small values of creep and shrinkage.

b) A large specimen shrinks and creeps less than a small one because the movement of water from the interior is impeded by the distance through which it can travel before it can reach the surface and evaporate.

Porosity of aggregates has been found to influence the creep of concrete. Aggregates with a higher porosity generally have a lower modulus of elasticity which offers a lower restraint to those types of cement paste susceptible to creep. ¹⁰ Also the porosity and the absorption capacity of the aggregate influence the movement of moisture, and this migration of moisture, as previously stated, may cause creep and shrinkage in concrete.

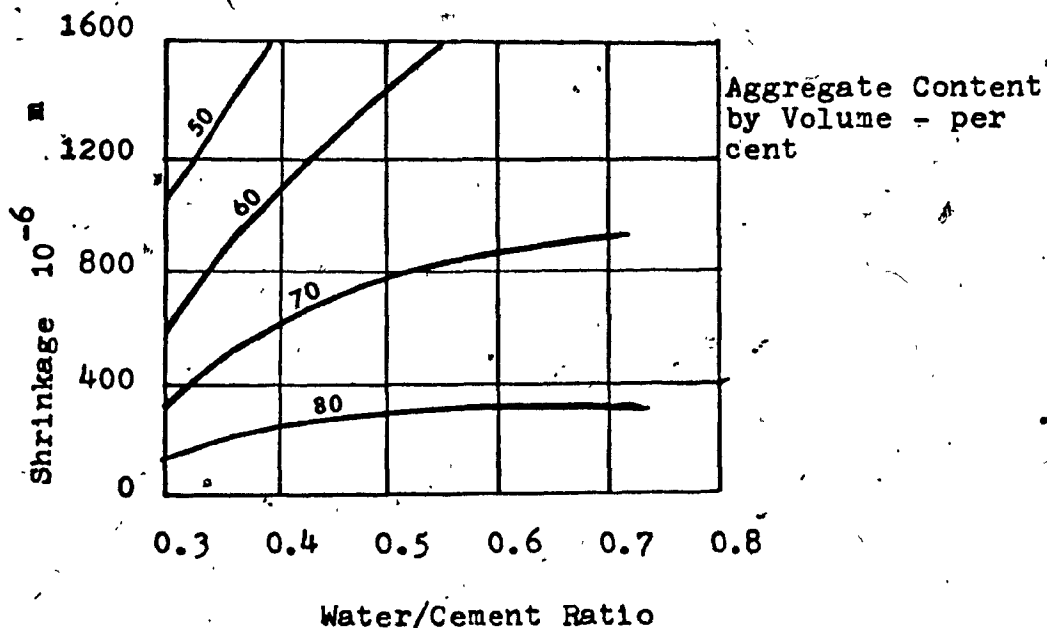


Fig.14 Influence of water/cement ratio and aggregate content on shrinkage.¹⁰

Soundness is the ability of aggregate to maintain dimensional stability despite changes in physical conditions.¹⁰ Unsoundness is exhibited by porous aggregates. The shape, size, and continuity of the pores in the aggregate control the rate and amount of water absorption, and the rate at which water can escape from the aggregate particles.¹⁰ Pores that are smaller than 4 to 5 μm are critical for they allow water to enter, but they are not large enough to allow for the expulsion of water under the pressure of ice.¹⁰ Aggregates may be tested for soundness by the procedure outlined in ASTM C 33.¹⁴

The resistance of concrete to freezing and thawing, its chemical stability, its resistance to abrasion, and the bond between the aggregate and the cement paste is influenced by the porosity, permeability and absorption of the aggregate.¹⁰ The pores in the aggregate vary in size from those slightly larger than the gel pores, (1.5×10^{-5} to 2.0×10^{-5} μm) to those being large enough to be seen by the naked eye.

The specific gravity of aggregate also depends on its porosity and thus the yield of concrete for a given weight of aggregate varies with porosity.¹⁰ Some of the aggregate pores are wholly within the solid, while the

others open to the surface of the particles. The cement paste can only penetrate the largest of the aggregate pores, so it is the gross volume that is considered in calculating the aggregate content of the concrete.¹⁰ However, water can enter the pores. The amount and rate of water penetration depends on the pore size, and continuity, and the total volume of the pore space. The aggregates usually represent about $3/4$ of the volume of the concrete,¹⁰ and so make the major contribution to the porosity of the concrete.

Susceptibility to creep, strength of paste and elastic extensibility are properties which govern the resistance of concrete to damage. The most common type of damage is the frost damage of concrete. The main factors that govern this are the degree of saturation with water and the pore structure of cement paste. The usually theory states that as temperature decreases the water held in the capillary pores freezes,^{22,23} first in the large cavities and finally in the smaller ones. Freezing is a gradual process because the freezing point varies with the size of cavity, the rate of heat transfer through the concrete, and because of the dissolved substances in the water. Since the surface tension of the water in the capillaries is lower than that

in the smaller pores, the freezing starts in the larger cavities and gradually progresses to the smaller ones. Gel pores are too small to permit the formation of ice nuclei above -78°C .¹⁰ With a fall in temperature and because of the difference in the chemical potential of the gel water and ice, the gel water acquires an excess potential which drives some water into the capillary cavities containing ice. This diffusion of gel water leads to a growth of an ice body and its expansion,^{10,22,23} (Powers' Model). The separation of frozen, (relatively pure), water from the solution increases the concentration of various solutes in the remaining water. The resulting osmotic pressures drive some solute molecules into the gel. These are partly replaced by water molecules in the capillaries, so more freezing can take place.²⁴

Another theory states that the volume of the ice is approximately 9% greater than the volume of the parent water, so that any excess water in the cavity is expelled.²³ When there is no place for the water to go, and the cavity is more than 91% full of water, the ice will exert pressure on the capillary walls.²³ Such a dilating pressure damages the concrete when its tensile strength is exceeded. The extent of damage varies from surface scaling to complete disintegration, starting

at the exposed surface of the concrete and progressing through its depth.

The relationship between porosity and the mechanical properties of concrete are concisely summarized by Fagerlund.⁶ He concluded that the greater the porosity of concrete, the lower its compressive strength and bending strength. The reason for this is that a pore in a material reduces the loadbearing area of the cross section and the pore often gives rise to stress concentrations. The elastic moduli of concrete changes with the degree of hydration, which in turn determines the type and size of pores in the cement paste. Young's modulus is equal to nought when the concrete is green.⁶ Ultimate strain decreases as porosity increases. Fagerlund also states that the fatigue limit for a certain porosity should increase for specimens with smaller pore sizes, as long as the voids are spherical in geometry, and that flat pores considerably depress the fatigue limit. The rate of creep increases if the pores are larger than the grain size of gel crystals. There must be few pores at the grain boundaries if creep is to be small, while pores inside individual grains have a lesser influence. Shrinkage and swelling are due to the compressive stresses in the porous materials caused by the changes in the tensile stresses in the pores due to the

movement of the moisture. The highest surface tension
is found in the smaller capillaries that contain water
24
mixed with solutes.

It can be concluded from the above discussion that
the presence of pores has a large influence on the be-
haviour of a material. These pores, or voids, whether
they are empty or contain water, influence the perfor-
mance of many building materials.

CONCLUSION

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CONCLUSION.

The presence of pores can significantly affect the properties and the performance of many building materials. It is not only necessary to know the number of pores, (porosity), in a material, but also their size, shape, and distribution. Currently, these four fundamental properties which are characteristic of highly porous materials are most easily evaluated by direct observation.

Direct measurements of these four properties involve the observations of the plane sections of the sample, either by photoelectric phase integration methods, or by areal, lineal, or point-counting analyses based on scanning techniques. Through these methods, the porosity of a sample can be easily determined. These methods of measurement are also used to determine the pore shape, size, and distribution, however, they are time consuming and often do not give a proper indication since these properties vary from sample to sample of the same material. There are also some features that can never be revealed by the examination of plane sections, such as the mode of interconnection of the pore shapes.

Indirect methods of measurement are those in which the presence of pores is inferred, and their properties deduced, from the measurements of secondary properties, such as density, permeability to fluids, adsorptive capacity, liquid imbibition rates, and so on. ⁵ Additional assumptions are often necessary in the interpretation of such measurements, which may concern either the mechanism of the process taking place, or the geometry of the pores; or even both. To the extent that different assumptions are involved, the various indirect methods may produce conflicting results. The measurement of pore shape, size, and distribution attained by these indirect methods are not reliable.

Thus, the current methods of assessment are not practical nor are they adequate, and there is a need to develop new methods of assessment. Perhaps one of the new diagnostic tools currently used in medical cardiology assessments, namely, two dimensional ultrasonic imaging, could be adapted to study pores and their properties in a material.

The two-dimensional ultrasonic imager has been developed within the last few years, and it utilizes three different approaches; (1) mechanical sector scanner, (2) multi-element linear array, (multiscan), and

(3) electronic sector scanner or phased-array system.

The mechanical scanner consists of a single crystal transducer that is made to oscillate rapidly by means of an electric motor through an arc of 30° to 60° .

This system is relatively inexpensive, it is non-destructive, it is portable, and it provides good-quality images. The disadvantages are that it has a narrow angle, it is noisy, and its resolution for minute particles is not very good. Images are recorded on 1-inch video tape, and hard copies or still frames can be obtained by utilizing a Polaroid or a 90-mm x-ray camera attachment or even a 35-mm camera assembly.

The principles involved in two-dimensional ultrasonic imaging are similar to those of sonar or depth sounding. A transducer is placed on the anterior wall of a sample, and it serves as the source of the sound beam and as the receiver to detect the returning echo signals. This transducer is a piezoelectric crystal that can 'transduce' electrical energy into mechanical energy, and vice versa. The ultrasonic pulse travels in a straight line through the sample, and a portion of the sound energy is reflected back towards the transducer whenever the pulse encounters a particle of different acoustic impedance. Thus a reflection or an echo could be produced by the interface

between a pore and a solid particle, between the water and the empty space within a pore, between the water in the pore and a solid particles of the material, and so on. The various states of water, as well as particles that settle in the water could be detected using this method. Since only a portion of the sound is reflected at each interface, and the remainder of the pulse continues to propagate through the sample in a straight line, it is possible to record echoes from targets deeper in the sample.

With modification to the two-dimensional ultrasonic imager used in cardiology, such as the use of higher frequencies and the use of wide-angle (80° to 90°) mechanical sector scanners which utilize multiple rotating crystals that have been recently developed, the two-dimensional ultrasonic imager could be adapted and used in the study of pores in highly porous materials. Once we gain knowledge and understanding of the pores and their properties, we will be able to study the influence of pores and the influence of water present in the pores on the behaviour of various materials. Many questions, such as, is it the volumetric expansion of water on freezing, or is it the growth of an ice body and its expansion, etc.,

that causes frost damage to many materials. When many such questions have been answered, we will then be able to improve the performance of various materials. This will be of both economic and scientific interest.

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