

Physical structure of hardened cement paste.

A classical approach

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It is explained how the classical model of the structure of hardened Portland cement paste was deduced by T.C. Powers and coworkers from data on water vapor adsorption isotherms. Moreover, it is shown how the fractional volumes of all major constituents in the physical structure of room temperature cured Portland cement paste can be estimated from information on water-cement ratio and degree of hydration of the cement.

A large element of Powers' model remains sound after almost forty years, and it remains the only model upon which quantitative calculations of the volumetric composition of hardened Portland cement pastes can be based.

The paper is written for civil engineers in order to promote a better understanding of some fundamental ideas upon which many later developments in concrete technology are based.

1. INTRODUCTION

In the freshly mixed state, Portland cement paste is composed of grains of cement in an aqueous solution. In the hardened, mature state, it is composed of solid reaction products and spaces that are penetrable by water.

The hydration products formed within a body of cement paste occur as dense masses that have a characteristic porosity (gel pores). The dense, though porous, substance is called cement gel, since it is composed of solid particles having a large specific internal surface area such as is characteristic of colloidal gels. From a chemical point of view cement gel consists primarily of calcium silicate hydrates (CSH) of various compositions.

The amount of cement gel is usually not sufficient to fill all the space within a specimen of cement paste originally occupied by mixing water. The space not filled with cement gel is called capillary pores. Hence, hardened cement paste is composed of cement gel, capillary pores, if any, and a residue of unreacted cement, if any. Total porosity comprises the capillary pores and the gel pores. Pores are generally submicroscopic, and the gel pores are much smaller than capillary pores.

Structural differences among pastes are mainly due to differences in capillary porosity. Chemical composition is not very important because it turns out that

physical characteristics of hardened cement gel are influenced to only a minor extent by such differences in chemical composition as are found among different types of Portland cement.

Knowledge of the structure of cement paste is essential to an understanding of almost all concrete properties of technical importance.

These concepts of the structure of cement paste were originally deduced by T.C. Powers and co-workers [1] and [2] from data on physical properties, more specifically from data on water vapor adsorption isotherms.

It is true that some workers now believe that water interacts so strongly with the solid phases through chemisorption that the pore structure of hardened cement paste is unstable in H_2O -vapor adsorption experiments. It is also true that there is a certain amount of overlap in the binding energy between different classes of water, which makes the distinction between capillary pores, gel pores, and interlayer spaces in gel particles somewhat arbitrary.

Lea [3], Hansen, Radjy, and Sellevold [4]; and Sereda, Feldman, and Ramachandran [5] have evaluated objections which have been raised against Powers' concepts of the physical structure of hardened Portland cement paste, many of which are valid.

However, in spite of its shortcomings a large element of Powers' model remains sound, and until now, Powers' model remains one of the few coherent models which are capable of explaining the physical properties

of hardened cement paste and the only model upon which quantitative calculations of the volumetric composition of hardened Portland cement pastes can be based.

It is well to remember that a model is merely a theoretical description proposed to explain observed experimental facts and to provide additional insight into the behavior of a material. A model cannot, and should not, be considered to be a correct description in any absolute sense. This explains why more than one model may adequately interpret the known facts. This is indeed the case for what concerns physical structure and properties of hardened Portland cement paste (see Appendix B). However, without a basic knowledge of Powers' classical work it is difficult to understand later developments in concrete technology and thus for laymen, and in this respect civil engineers are considered laymen, to understand relationships between structure and properties of hardened Portland cement pastes and concretes.

It is the purpose of this paper to explain how Powers derived his model. Based on the model it is then demonstrated how simple formulas can be derived which make it possible numerically to estimate the fractional volumes of all major constituents in the physical structure of Portland cement pastes which are cured at room temperature.

It is important to realize, however, that Powers' model and the conclusions which can be drawn from an analysis of this model may not be valid when pastes are cured above room temperature or when certain types of admixtures are used.

2. DEVELOPMENT OF A MODEL OF HARDENED PORTLAND CEMENT PASTE

2.1. Surfaces and surface forces

The surface region of any body is, in a thermodynamic sense, more reactive than the interior of the body. For most engineering systems, surface energies can be disregarded. But, when the system is composed of tiny particles such that the ratio of surface area to volume is very large, surface reactivity is extremely important.

In general we become aware of surfaces when dealing with colloidal systems. A colloidal system is defined as a system composed of colloidal particles, so-called colloids. Colloids are defined as bodies which have at least one dimension in the size range of 100 nm to 100 μm . The ratio of surface area to the volume or weight of the system is a way of indicating the relative importance of surfaces. This ratio is termed the specific surface and is usually expressed in units of cm^2 per cm^3 or cm^2 per gram. Surface forces become important when the specific surface ranges above a few hundred thousand.

Surface forces can be visualized by imagining a cube representing a crystal of sodium chloride as shown in figure 1. A sodium atom in the body of the crystal

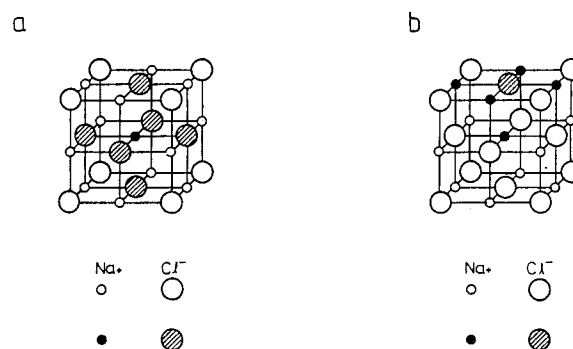


Fig. 1. — Crystal lattice of sodium chloride.

(represented by the black dot in figure 1 a) is surrounded by six chlorine atoms (represented by the larger hatched circular areas in figure 1 a), four on the sides, one above, and one below. Similarly each chlorine atom is surrounded by six sodium atoms.

However, a chlorine atom located at the surface of the crystal (represented by the hatched circular area in figure 1 b) is surrounded by only five sodium atoms (represented by the black dot in figure 1 b), four on the sides and one below. (Similarly each sodium atom is surrounded by six chlorine atoms.) To compensate for the missing sodium atom the chlorine atom may attach itself more firmly to its neighbors in the surface, which gives rise to a *surface tension*, or it may seize some other atom or molecule from its surroundings; for example, it may attract a water molecule from the atmosphere. A sodium atom at the surface of the crystal also exhibits a tendency to attract external substances. This property of atoms on the surface to attract substances outside the crystal is called *adsorption*.

When two surfaces are brought close together, they also attract each other. Therefore the particles of cement gel adhere to each other. They also adhere to small crystals in the hardened paste such as calcium hydroxide, to grains of sand, and to pieces of coarse aggregate, cementing everything together.

The cementing action depends on the extent and nature of the surface. There are substances such as silica gel (colloidal silicon dioxide) that have larger internal surface area than cement gel, but the latter is a better cementing material because it possesses much greater force per unit of surface. On the other hand, calcium hydroxide exerts a stronger attractive force per unit area than cement gel, but it is a poorer cementing material because even the most finely divided calcium hydroxide has only about one-tenth the internal surface area of cement gel.

Some simple geometric computations may give us a little insight into the range of dimensions of cement paste. We will consider a gram of unhydrated cement.

A gram of a typical cement clinker will occupy a solid volume of about 0.317 cm^3 . If this clinker could be molded somehow into a smooth, solid sphere, its diameter would be 0.848 cm. The surface area of this

sphere is 2.26 cm^2 . The specific surface, now expressed as cm^2 per gram, is then 2.26.

The same gram of cement clinker is now ground to the fineness of commercial cement and by measurement its specific surface is about $2,000 \text{ cm}^2$ per gram. If we assume that the ground cement consists of a great number of uniform spheres, it is computed that there must be about 700,000,000 particles at a diameter of 0.00095 cm each. If these 700,000,000 particles could be lined up like a row of bowling balls in a rack, the line would stretch some 6.7 km.

Now we hydrate the gram of cement. Again, assume uniform spherical particles. The specific surface is in the neighborhood of $2,000,000 \text{ cm}^2$ per gram. Each colloidal sphere is about 0.0000015 cm in diameter. The number of particles is about 220,000,000,000,000. Lined up, these particles would stretch some 3,300 km.

2.2. Preparation of granulated cement paste samples

Most of the following information was gathered from studies of granulated cement paste samples.

The cement to be tested is first mixed with a certain amount of water and the original water-cement ratio is recorded. It is cast in cylindrical molds and after about 2 hours the bleeding water is measured. The molds are then placed in a water bath for curing. After curing the hardened paste is crushed and sieved. The granules passing the ASTM No. 35 sieve and retained on the No. 100 sieve are dried at a vapor pressure of 0.0005 mm Hg and at a temperature of 25°C . These desiccated granules are now ready for testing.

2.3. State of water in hardened portland cement pastes

In general, water in a paste can be divided into three different states although the distinction between the three states is not absolute [5]. It can be chemically bound, physically adsorbed, or it can be free.

Chemically combined water is that part of the water which becomes an integral part of the cement gel. That is, it is the water which combines chemically with the cement to produce a new phase unlike either water or cement. In the later discussion, this is termed *non-evaporable water*.

Physically adsorbed water (or chemisorbed water [3], [4], [5]) is that part of the water which is adsorbed at surfaces of gel particles. Adsorption or chemisorption is a result of the surface reactivity of the gel. The physically adsorbed water occupies the gel pores.

Free water is the remainder of the water in the saturated paste. It occupies the capillary pores.

The sum of physically adsorbed water and free water is termed *evaporable water*. "Evaporable" is always a relative term, hence for cement pastes the evaporable water is defined as the weight lost when a saturated sample is brought to equilibrium at a vapor pressure of 0.0005 mm Hg at 25°C . This standard desiccating

procedure removes about the same amount of water as oven drying at 105°C .

2.3.1. Non-Evaporable water

As stated previously, the non-evaporable water is the hydration water. The quantity of non-evaporable water is determined by heating the granules to $1,000^\circ\text{C}$ and determining the weight loss. This heating is termed ignition.

Non-evaporable water is expressed in units of grams per gram of original cement.

2.3.2. Total evaporable water

Total evaporable water is that quantity of water held in the capillary- and gel pores of a saturated specimen. A quantity of the test granules is placed in a jar and slowly saturated by adding drops of water. The saturated granules are subjected to the same dehydrating atmosphere employed in producing the original desiccated material. The water lost during this second dehydration of the granules is the total evaporable water and is expressed in units of grams per gram of original cement. It is to be noted that the sample being tested must be ignited to determine the original weight of the cement.

A rather logical question arises. What is the effect of the original desiccation? Apparently the first drying is accompanied by some irreversible shrinkage and capacity to hold water. In essence, the material we are testing is not quite the same as the material which was taken from the crusher. The original desiccation is simply a method to standardize the paste and permit reproducible results to be obtained.

2.3.3. Gel water and capillary water

From the previous discussions we know that part of the evaporable water is held in the gel pores and part in the capillary pores. It is important to determine the quantities of each.

A study of the changes in the quantity of evaporable water held by a sample as the environmental vapor pressure is varied is helpful in this regard.

Recall that in determining the evaporable water capacity, a saturated sample of granules was simply dehydrated at a vapor pressure of 0.0005 mm Hg . The saturated sample, by convention, was in equilibrium with an environment vapor pressure of 23.8 mm Hg . All dehydrating tests are conducted at 25°C . We can now ask: How much evaporable water is lost if we dehydrate to 11.9 mm Hg ? or to 2.38 mm Hg ? Is there a simple proportional relationship between relative vapor pressure and evaporable water capacity? In other words, if we halve the saturation vapor pressure of 23.8 mm Hg , do we remove 50% of the evaporable water? The answer is no, and the reason for this answer provides a clue to a method for determining the relative proportions of gel and capillary pore water.

Figure 2 is a typical plot of the total water (evaporable and non-evaporable water) held in a paste as a

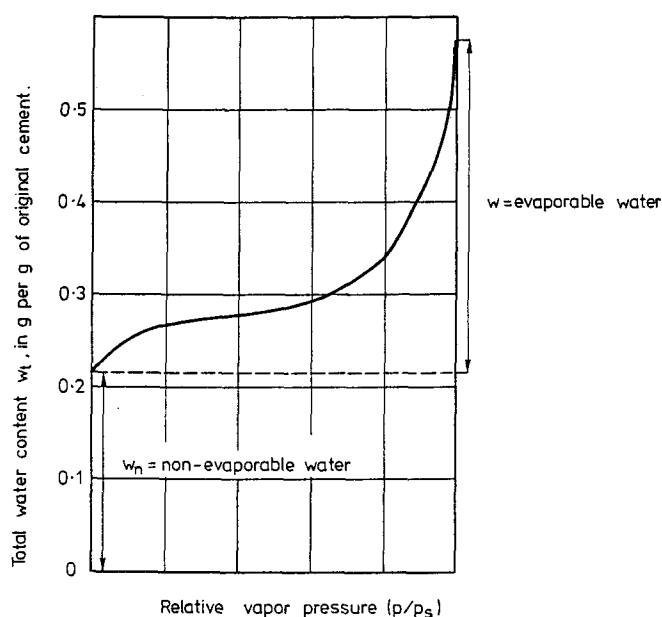


Fig. 2. — Typical adsorption isotherm for hardened Portland cement paste.

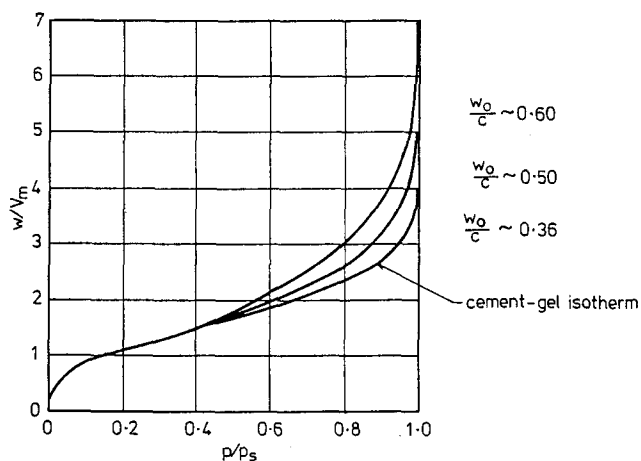


Fig. 3. — Effect of original water-cement ratio w_0/c on w/V_m curves.

function of the relative vapor pressure. The shape of the curve is typical of cement pastes. The ordinate at $p/p_s = 0$ represents the non-evaporable water content, w_n . The ordinate at $p/p_s = 1.0$ represents the total water content, w_t , and the difference between these ordinates represents the evaporable water, w . Curves of this sort are called adsorption isotherms.

Figure 3 is a variation of the plot where the ordinate is a ratio quantity w/V_m . w is the weight of evaporable water held by the sample. V_m is a constant for the sample; it is proportional to the surface area of the cement gel. Theoretically, V_m is the weight of water in grams which will cover the entire surface area of 1 g of the solid hydration products with a single layer of adsorbed water.

To fully appreciate the ratio, w/V_m , we must resort to the principles of surface chemistry. Two principles are involved. These are the theories of capillary-condensation and of multi-molecular-adsorption, or

BET adsorption. Both are briefly reviewed in Appendix A. It can be demonstrated through the application of these theories that capillary water cannot exist in a cement paste at relative vapor pressures less than about 0.40.

2.3.3.1. State of water at relative vapor pressures below 0.40

For relative vapor pressures below 0.40 the BET theory applies. The most widely used mathematical statement of the theory is the following expression relating w/V_m and p/p_s :

$$\frac{w}{V_m} = \frac{C(p/p_s)}{(1 - (p/p_s))(1 - (p/p_s) + C(p/p_s))} \quad (1)$$

in which:

w = quantity of vapor adsorbed at vapor pressure p ;

V_m = quantity of adsorbate required for a complete condensed layer on the solid, the layer being 1 molecule deep;

p = existing vapor pressure;

p_s = pressure of saturated vapor.

C is a constant related to the heat of adsorption as follows:

$$C = ke \left(\frac{(Q_1 - Q_L)}{RT} \right)$$

where

k = constant assumed to be 1.0 in computations;

Q_L = normal heat of condensation of the vapor per mole of vapor;

Q_1 = total heat of adsorption per mole of vapor;

$Q_1 - Q_L$ = net heat of adsorption per mole of vapor;

R = the gas constant;

T = absolute temperature;

e = base of natural logarithm.

Referring again to figure 3, we note the coincidence of all curves below $p = 0.40 p_s$. Data from many pastes of widely differing characteristics yield nearly the same curve. All evaporable water is gel water in this range of vapor pressure. This observation coupled with other information leads us to believe that *the physical structure and the physical properties of room temperature cured cement gel such as strength, elasticity, creep, shrinkage, permeability, and thermal properties are nearly the same in all pastes (see Verbeck and Helmuth [6]).* This is a very significant conclusion for it means that *the gel of any Portland cement paste is very nearly the same as the gel of any other Portland cement paste* ⁽¹⁾. The characteristics of the *paste structure*, however, depend on the extent and manner in which the cement gel occupies the available space.

⁽¹⁾ This may not be true when pastes are cured above room temperature or when certain types of admixtures are used.

All this is not very surprising, considering that both tricalcium silicate and dicalcium silicate in Portland cement clinker form approximately the same amounts of the same gel component, i. e. CSH. Moreover, only limited variations are allowed in the proportions between calcium silicates and calcium aluminates if a cement is to be characterized as a Portland cement. Therefore, it is limited how large variations can occur in the contents of CSH between different cements, and CSH is the primary component which determines the physical structure and properties of hardened Portland cement paste.

2.3.3.2. State of water at relative vapor pressures above 0.40

For relative vapor pressures exceeding about 0.40, there is capillary condensation of water in addition to molecular adsorption, and the data for individual pastes will plot as unique curves. However, no data will ever plot below the lowest curve shown. This limiting curve is termed the cement-gel isotherm and represents a condition wherein cement gel occupies all available space in the paste. Capillary pores do not exist.

The statement that the cement gel occupies all available space is not to be construed to imply that the paste is non-porous. The gel exists as a colloidal mass and as such it encompasses a certain volume of gel pores. It is evident that the gel pores contain an amount of evaporable water represented by the cement-gel isotherm and that any excess evaporable water is held in the capillary pores. At saturation the weight of gel water w_g is 3-4 V_m and the capillary water is the remainder of the evaporable water. Powers found as a good average that:

$$w_g = a V_m \quad (2)$$

where $a \approx 3.3$.

However, the ratio of colloidal to non-colloidal hydration products should be expected to differ among cements of different chemical composition.

Hence the ratio should be different for different cements. This has been expressed as follows:

$$V_m = k w_n \quad (3)$$

where

$$k = 0.230 (C_3S) + 0.320 (C_2S) + 0.317 (C_3A) + 0.368 (C_4AF);$$

C_3S = weight fraction of tricalcium silicate in the cement;

C_2S = weight fraction of dicalcium silicate in the cement;

C_3A = weight fraction of tricalcium aluminate in the cement;

C_4AF = weight fraction of tetracalcium aluminate ferrite in the cement.

As $k \approx 0.25$ is reported to be a fairly constant and reasonable average for all Portland cements at all sta-

ges of hydration, it may be inferred that *the different hydration products which make up any hardened cement paste are formed at approximately the same rate and therefore in approximately the same mutual proportions at all stages of hydration.*

V_m may be evaluated by an application of the BET adsorption theory (more specifically Equation (1)). V_m has been found to vary from about 0.03 to 0.07 g per gram of cement gel. In the following computations we shall assume with Powers that $V_m \sim 0.055$ g per gram of the solid hydration products.

As mentioned above, V_m is proportional to the gel surface area. The following equation applies:

$$S = a_1 \frac{N}{M} V_m$$

where

S = total surface area of sample in cm^2 per gram;

a_1 = average area covered by a single adsorbed water molecule taken as $(11.4) (10^{-16}) \text{ cm}^2$;

N = Avogadro's number = $(0.6024) (10^{24})$;

M = molecular weight of water = 18.

Then, $S = (38.2) (10^6) V_m \text{ cm}^2$ per gram.

Now if $V_m \sim 0.055$ grams per gram, we find $S = 210 \text{ m}^2$ per gram of dry hydrated cement. This is an average value for many real cement pastes containing about 25% by weight of non-colloidal solid components mainly calcium hydroxide, which only contributes a negligible amount to the internal surface. If correction is made for non-colloidal components, we find $S \sim 260 \text{ m}^2$ per gram of hydrated cement as an average value of pure cement gel.

Among commercial cements of different types, the specific surface area of the hydration products differ from the average by less than 10%. This is an important part of the evidence that *the physical characteristics of the hydration products which are formed at room temperature are only slightly influenced by differences in chemical composition and that most of the products are in the colloidal state.*

Since the specific surface of crystalline calcium hydroxide is negligible compared with that of colloidal material, V_m is also considered to be proportional to the amount of colloidal material in a paste. The quantity w_n represents the amount of non-evaporable water in both colloidal and non-colloidal material. Therefore, if a given cement produces the same kind of hydration products at all stages of its hydration, the ratio V_m/w_n should be constant for any given cement under fixed conditions.

2.4. Conclusions ⁽¹⁾

On the evidence presented we may conclude that the hydration products which are formed within a body of

⁽¹⁾ These conclusions may not be true when pastes are cured above room temperature or when certain types of admixtures are used.

cement paste primarily occur as dense masses that have a characteristic porosity (gel pores). The dense, though porous, substance is called cement gel, since it is composed of solid particles having a large specific internal surface area such as is characteristic of colloidal gels.

The amount of gel is usually not sufficient to fill all the space within a specimen of cement paste originally occupied by mixing water. The space not filled with cement gel is called capillary pores. Hence, hardened cement paste is composed of cement gel, capillary pores, if any, and a residue of unreacted cement, if any. Total porosity comprises the capillary pores and the gel pores. Pores are generally submicroscopic, and the gel pores are much smaller than capillary pores.

A simplified model of the structure of hardened Portland cement paste is shown in figure 4 according to Powers' concepts.



Fig. 4. — Simplified model of hardened Portland cement paste structure. Masses of randomly oriented groups of black lines represent cement gel. Spaces like those marked C represent mature paste. Upper drawing represents mature paste $w_0/c = 0.5$, capillary porosity 20%; lower drawing represents nearly mature paste $w_0/c = 0.3$, capillary porosity 7% [2].

We may also conclude that from the point of view of physical structure and physical properties all Portland cements form approximately the same hydration products at room temperature, and form them at approximately the same rate and therefore in the same mutual proportions at any stage of the hydration process, regardless of the chemical composition of the cements.

In other words, the physical properties of room temperature cured Portland cement paste do not to any

appreciable extent depend on the chemical composition of the Portland cement from which it is formed.

The physical properties of room temperature cured Portland cement paste largely depend on the original water-cement ratio, w_0/c , which determines the capillary porosity of the paste, and on the degree of hydration of the original cement, m , which determines the amount of hydration products which have been formed at any given stage of hydration. Except for differences in original water-cement ratio and degree of hydration, all hardened Portland cement pastes are largely equal in physical structure and physical properties.

It is possible to calculate both the amount of gel water and the amount of chemically bound water in hardened cement paste as functions of V_m , the weight of water in grams which will cover the entire surface area of 1 g of the solid hydration products with a single layer of adsorbed water, see equations (2) and (3).

This makes it feasible for us to estimate the fractional volumes of all major constituents in any room temperature cured Portland cement paste as functions of the original water-cement ratio, with which the paste was made, and the degree of hydration, m , which the paste has reached.

Such estimates are very important because knowledge of the volumetric composition of hardened Portland cement paste makes it possible on the basis of theories which have been developed for composite materials to analyze physical properties of hardened cement pastes and concretes such as strength, elasticity, creep, shrinkage, permeability, and thermal properties.

3. VOLUMETRIC COMPOSITION OF HARDENED PORTLAND CEMENT PASTE

3.1. The unit volume of hardened portland cement paste

The total volume of a cement paste which contains cg of originally unhydrated cement can be expressed as a sum of the volumes of the individual structural components, as shown in equation (4).

$$V_{\text{total}} = c V_c + w_n V_n + (w_g + w_c) V_d \quad (4)$$

where

c = weight of cement in volume considered, in g;

w_n = weight of non-evaporable water, in g;

w_c = weight of capillary water, in g;

w_g = weight of gel water, in g;

V_c = specific volume of cement in cm^3 per gram;

V_d = specific volume of capillary and gel water $\sim 1 \text{ cm}^3$ per gram;

V_n = specific volume of non-evaporable water, in cm^3 per gram,

w_n , w_c , and w_g all refer to a volume of cement paste which contains cg of originally unhydrated cement.

As the total volume of cement paste remains unchanged throughout the hydration process, V_{total} must also

equal the original volume of cement and mixing water, as shown in equation (5).

$$V_{\text{total}} = c V_c + w_0 V_d \quad (5)$$

where

w_0 = weight of original mixing water, in g;

V_d = specific volume of mixing water $\sim 1 \text{ cm}^3$ per gram,

w_0 refers to a volume of cement paste which contains c grams of originally unhydrated cement.

3.2. Fractional volume of cement gel

The total volume of cement gel can be expressed as the sum of that part of the volume of the original cement which has become hydrated plus the volumes of non-evaporable water and gel water as shown in equation (6).

$$V_B = mc V_c + w_n V_n + w_g V_d \quad (6)$$

where

V_B = volume of cement gel in cm^3 per gram cement;

m = weight fraction of cement that has become hydrated, also called degree of hydration (see Section 3.5).

Inserting equation (2) in equation (3), we obtain equation (7)

$$w_g = ak w_n \quad (7)$$

Inserting equation (7) in equation (6) gives equation (8)

$$V_B = mc V_c + (V_n + ak) w_n \quad (8)$$

Dividing equation (8) by equation (5) gives equation (9), the fractional volume of cement gel in cement paste

$$\begin{aligned} \frac{V_B}{V_{\text{total}}} &= \frac{mc V_c + (V_n + ak) w_n}{w_0 + c V_c} \\ &= \frac{m V_c + (V_n + ak) w_n / c}{(w_0 / c) + V_c} \end{aligned} \quad (9)$$

3.3. Fractional volume of gel water

The fractional volume of gel water is obtained when dividing equation (7) by equation (5)

$$\frac{w_g}{V_{\text{total}}} = \frac{ak w_n}{w_0 + c V_c} = \frac{ak w_n / c}{(w_0 / c) + V_c} \quad (10)$$

3.4. Fractional volume of capillary pores

Inserting equation (5) in equation (4) and solving for w_c , we find the volume of capillary water w_c in equation (11)

$$w_c = w_0 - (V_n + ak) w_n \quad (11)$$

The fractional volume of capillary pores is obtained when dividing equation (11) by equation (5)

$$\begin{aligned} \frac{w_c}{V_{\text{total}}} &= \frac{w_0 - (V_n + ak) w_n}{w_0 + c V_c} \\ &= \frac{(w_0 / c) - (V_n + ak) (w_n / c)}{(w_0 / c) + V_c} \end{aligned} \quad (12)$$

3.5. Degree of cement hydration

The extent to which the cement has hydrated is expressed by the degree of hydration, m , which is defined as the weight fraction of original cement which has become hydrated ($0 \leq m \leq 1$)

$$m = \frac{c_h}{c} \quad (13)$$

where

c_h = weight of hydrated cement, in g.

For all cements we have

$$m = \frac{c_h}{c} = \frac{w_n}{w_n^0} \quad (14)$$

where

w_n^0 = weight of non-evaporable water in completely hydrated paste, in g.

3.6. Fractional volume of unhydrated cement

The volume of unhydrated cement can be expressed in terms of volume of original cement and degree of hydration as shown in equation (15)

$$c_{uh} V_c = (1 - m) c V_c \quad (15)$$

where

c_{uh} = weight of unhydrated cement, in g.

The fractional volume of unhydrated cement is obtained when dividing equation (15) by equation (5)

$$\frac{c_{uh} V_c}{V_{\text{total}}} = \frac{(1 - m) c V_c}{w_0 + c V_c} = \frac{(1 - m) V_c}{(w_0 / c) + V_c} \quad (16)$$

Introducing $w_n = m w_n^0$ from equation (14) in equations (9), (10), (12), and (16), we obtain the following set of equations (17) to (21) from which the fractional volumes of all major structural components in a cement paste can be calculated as functions of the two main parameters, i.e. water-cement, ratio w_0 / c , and degree of hydration, m .

3.7. Formulas for the calculation of volumetric composition of hardened portland cement paste

Fractional volume of cement gel

$$\frac{m V_c + (V_n + ak) m (w_n^0 / c)}{(w_0 / c) + V_c} \quad (17)$$

Fractional volume of gel water (gel pores)

$$\frac{ak m (w_n^0/c)}{(w_0/c) + V_c} \quad (18)$$

Fractional volume of capillary pores

$$\frac{(w_0/c) - (V_n + ak) m (w_n^0/c)}{(w_0/c) + V_c} \quad (19)$$

Fractional volume of unhydrated cement

$$\frac{(1 - m) V_c}{(w_0/c) + V_c} \quad (20)$$

Fractional volume of total pores (equations (18) + (19))

$$\frac{(w_0/c) - V_n m (w_n^0/c)}{(w_0/c) + V_c} \quad (21)$$

where w_n^0/c can be calculated from equation (22).

$$\frac{w_n^0}{c} = 0.187(C_3S) + 0.158(C_2S) + 0.665(C_3A) + 0.213(C_4AF) \quad (22)$$

m in equations (17)-(21) can either be determined by means of X-ray diffractometry or indirectly by measuring the weight loss of cement paste on ignition at 1,000°C.

3.8. Restraints on the hydration process

The physical structure of hardened cement paste can only be calculated on the basis of equations (17) to (21) provided that the following two conditions are met:

1. Sufficient space is available for all hydration products.
2. Sufficient water is available for the hydration process to proceed.

Re 1. The original volume of the cement paste is not changed during hydration. During hydration the gel products gradually fill the voids initially occupied by the mixing water. When no more capillary space is available, hydration stops due to the fact that there is no longer room for the hydration products. If equation (19) is assumed to equal 0, this condition can be expressed in terms of the largest possible degree of hydration, m_{\max} , for a given cement paste

$$m_{\max} = \frac{w_0/c}{(V_n + ak) w_n^0/c} \leq 1 \quad (23)$$

Re 2. The non-evaporable (chemically bound) water only contributes to the volume of the hydration products by a fraction $V_n/1.0$ of its original volume, where $V_n < 1.0$. Therefore, capillary water is used up at a faster rate than the capillary pores are filled with gel. Excess water must therefore be available for the chemical process, beyond the water which is required in order to satisfy the requirement of sufficient space for the

hydration products. This water must either be available from exterior sources if hydration is to continue, or it must be present in the form of excess water when concrete is mixed. The volume of excess water required for hydration to proceed can be determined from equation (24).

$$w_{\text{excess}} = (1 - V_n) m w_n^0 \quad (24)$$

The fractional volume of excess water can be determined by dividing equation (24) by equation (5).

$$\frac{w_{\text{excess}}}{V_{\text{total}}} = \frac{(1 - V_n) m w_n^0}{w_0 + c V_c} = \frac{(1 - V_n) m (w_n^0/c)}{(w_0/c) + V_c} \quad (25)$$

If this excess water can enter the specimen from the outside, equation 23 will determine the maximum possible value of the maturity factor. However, this is only the case for small specimens, permanently stored in water. In larger specimens of cement paste and in most concretes this excess water must be present as mixing water when fresh paste is cast, or the process will stop before all cement has hydrated. Thus, in order for the process to proceed, we must require that

$$\frac{(w_0/c) - (V_n + ak) m (w_n^0/c)}{(w_0/c) + V_c} - \frac{(1 - V_n) m (w_n^0/c)}{(w_0/c) + V_c} \geq 0 \quad (26)$$

Thus the maximum possible degree of hydration which can be attained for a paste made with a given water-cement ratio when no water is available from external sources is achieved when equation (26) equals 0, and can be determined from equation (27).

$$m_{\max} = \frac{w_0/c}{(1 + ak) w_n^0/c} \leq 1 \quad (27)$$

For sealed specimens a capillary volume equal to w_{excess} will always be empty as shown in equation (28).

Fractional volume of empty capillaries

$$= \frac{(1 - V_n) m (w_n^0/c)}{(w_0/c) + V_c} \quad (28)$$

4. NUMERICAL EXAMPLE

For most Portland cements we may assume with Powers

$$V_c \cong 0.32 \text{ cm}^3 \text{ per gram;}$$

$$V_d \cong 1.00 \text{ cm}^3 \text{ per gram;}$$

$$V_n \cong 0.75 \text{ cm}^3 \text{ per gram;}$$

$$a \cong 3.3;$$

$$k \cong 0.25;$$

$$w_n^0/c \cong 0.23;$$

4.1. Increase in volume of cement by hydration

The volume of cement gel formed by complete hydration of 1 g cement can be determined from equation (8). When inserting values from above and $w_n = w_n^0$, we find

$$V_B = mc V_c + (V_n + ak) w_n^0 = 0.32 \\ + (0.75 + 3.3 \cdot 0.25) \cdot 0.23 = 0.682 \text{ cm}^3 \quad (29)$$

Considering that 1 g of unhydrated cement occupies 0.32 cm^3 , we find that $0.682/0.32 = 2.13 \text{ cm}^3$ is required in order to accommodate the hydration products formed by 1 cm^3 of unhydrated cement.

4.2. Minimum water-cement ratio required for complete hydration of cement paste when water is available from external sources

The minimum water-cement ratio required for complete hydration of cement paste when water is available from external sources can be determined by inserting numerical values from above and $m_{\max} = 1$ in equation (23).

$$\frac{w_0}{c} = (V_n + ak) w_n^0 / c \\ = (0.75 + 3.3 \cdot 0.25) 0.23 = 0.36. \quad (30)$$

4.3. Minimum water-cement ratio required for complete hydration of cement paste when water is not available from external sources

The minimum water-cement ratio required for complete hydration of cement paste when *no* water is available from external sources can be determined by inserting numerical values from above and $m_{\max} = 1$ in equation (27).

$$\frac{w_0}{c} = (1 + ak) \frac{w_n^0}{c} = (1 + 3.3 \cdot 0.25) 0.23 = 0.42. \quad (31)$$

4.4. Maximum degree of hydration when water is available from external sources

When water is available to the entire bulk of paste from external sources, the maximum degree of hydration, m_{\max} , which the hardened Portland cement paste can attain may be calculated from equation (23) as shown in equation (32).

$$m_{\max} = \frac{w_0/c}{(V_n + ak) w_n^0/c} \\ = \frac{w_0/c}{(0.75 + 3.3 \cdot 0.25) 0.23} = \frac{w_0/c}{0.36} \quad (32)$$

This means that under the above-mentioned conditions the maximum value of m ever to be used in equations (17) to (21) is m_{\max} from equation (32), when $0 < w_0 < 0.36$ and $m = 1$ when $w_0/c \geq 0.36$.

4.5. Maximum degree of hydration when no water is available from external sources

When water is not available to the entire bulk of paste from external sources, the maximum degree of hydration, m_{\max} , which the hardened Portland cement paste can attain may be calculated from equation (27) as shown in equation (33).

$$m_{\max} = \frac{w_0/c}{(1 + ak) w_n^0/c} = \frac{w_0/c}{(1 + 3.3 \cdot 0.25) 0.23} = \frac{w_0/c}{0.42} \quad (33)$$

This means that under the above-mentioned conditions the maximum value of m ever to be used in equations (17) to (21) is m_{\max} from equation (33) when $0 < w_0/c < 0.42$ and $m = 1$ when $w_0/c \geq 0.42$.

In practice, equation (33) will apply to the interior parts of most structural concrete members.

4.6. Porosity of cement gel

The quantity of gel water, w_g , which is bound when 1 g of cement hydrates can be determined by inserting numerical values of a , k , and $w_n = w_n^0 = 0.23$ in equation (7).

$$w_g = ak w_n = 3.3 \cdot 0.25 \cdot 0.23 = 0.19 \text{ g} = 0.19 \text{ cm}^3. \quad (34)$$

Considering that it was shown in equation (29) that 1 g of unhydrated cement occupies 0.68 cm^3 , the gel porosity, ε , which equals the fractional volume of gel that is occupied by gel water, can be determined from equation (33).

$$\varepsilon = \frac{0.19}{0.68} = 0.28. \quad (35)$$

4.7. Density of solid gel particles

By solid gel particles we understand solid matter including chemically bound water, but excluding gel pores and gel water. The volume, V_s , occupied by the solid hydration products formed by 1 g of cement can be determined from equation (34) by inserting numerical values from above and $w_n = w_n^0 = 0.23$.

$$V_s = V_c + V_n w_n = 0.32 + 0.75 \cdot 0.23 = 0.49 \text{ cm}^3. \quad (36)$$

Considering that 1 g of cement combines with 0.23 g of water, it may be concluded that 0.49 cm^3 of solid particles weigh 1.23 g . The density of solid gel particles is therefore $1.23/0.49 = 2.51 \text{ g/cm}^3$. The specific volume is $1/2.51 = 0.40 \text{ cm}^3/\text{g}$.

4.8. Size of gel pores

As the specific surface of hydrated cement gel particles is independent of the porosity of the paste, and as the pores are interstitial spaces among such particles,

it is a simple matter to compute the boundary area of the voids per unit volume of void space, which is a specific surface area.

Thus the specific surface area of the void space may be calculated from the following equation

$$\sigma_v \cdot \varepsilon = (1 - \varepsilon) \sigma_{hc} \quad (37)$$

where

σ_v = specific surface area of gel pores, in cm^2/cm^3 ;

σ_{hc} = specific surface area of hydrated cement particles, in cm^2/cm^3 ;

ε = porosity of paste.

However, it has been shown experimentally that the specific surface area of hydrated cement is approximately $210 \text{ m}^2/\text{g}$, and the specific volume of hydrated cement is $0.40 \text{ cm}^3/\text{g}$. Hence, the specific surface area of solid hydrated cement particles per cm^3 of solids is

$$\sigma_{hc} = \frac{210}{0.40} = 525 \text{ m}^2/\text{cm}^3. \quad (38)$$

Moreover, we have found the porosity of cement gel, ε , to be

$$\varepsilon = 0.28.$$

Therefore,

$$\begin{aligned} \sigma_v &= \frac{1 - \varepsilon}{\varepsilon} \sigma_{hc} \\ &= \frac{0.72}{0.28} \cdot 525 = 1,350 \text{ m}^2/\text{cm}^3. \end{aligned} \quad (39)$$

The hydraulic radius of a pore, r , is defined as the volume of the pore divided by the area of the pore. Therefore, the specific surface area of pores is the reciprocal value of the mean hydraulic radius of pores.

The average size of a gel pore having a given hydraulic radius can be estimated by assuming that the cross section of the pore resembles a rectangular slit. Let b , h , and l be the width, thickness, and length, respectively of the slit. Then, ignoring the end surfaces $2hb$, we obtain

$$r = \frac{hbl}{(2h + 2b)l} = \frac{hb}{2(h + b)} \quad (40)$$

or

$$\frac{1}{r} = 2(1/b + 1/h). \quad (41)$$

Solutions of this equation for various values of h and b are given below.

$$h = b, \quad r = b/4,$$

$$h = 2b, \quad r = b/3,$$

$$h = 4b, \quad r = 4b/10,$$

$$h = 10b, \quad r = 10b/22,$$

$$h = 100b, \quad r = 100b/202 \sim b/2.$$

Thus, as h/b is made larger, r approaches $b/2$ as a limit. This means that the width of the pores is at least twice and at most four times the hydraulic radius.

We can now estimate the mean distance between solid surfaces in gel pores on the basis of the specific surface area of the pores.

$$\frac{2-4}{0.135 \cdot 10^8} \text{ cm} = 150-300 \text{ nm}.$$

If we are correct in assuming that every gel particle is covered by a layer of water, $a = 3.3$ water molecules thick, and a water molecule has a diameter of 36 nm, then the mean distance between two solid gel surfaces must be $6.6 \cdot 36 = 240 \text{ nm}$, which is of the same order of magnitude as computed above.

4.9. Size of gel particles

If we consider all gel particles to be rectangular prisms, having dimensions b , l , and t for width, length, and thickness, we find

$$\sigma_{\text{gel}} = \frac{2(bt + lt + bl)}{blt} \quad (42)$$

and after rearranging

$$t = \frac{2(1 + t/b + t/l)}{\sigma_{\text{gel}}} \quad (43)$$

where σ_{gel} = specific surface area of gel particles per cm^3 .

As the specific surface area of hydrated cement per cm^3 is $\sim 525 \text{ m}^2/\text{cm}^3$ and as hydrated cement contains 20-25% of non-colloidal calcium hydroxide, which does not contribute significantly to the surface area, the specific surface area of hydrated gel must be about 25% larger than the specific surface area of the total hydrated cement, or

$$\sigma_{\text{gel}} = 525 \cdot 1.25 \sim 650 \text{ m}^2/\text{cm}^3. \quad (44)$$

Inserting this value of σ_{gel} and converting to nm, we find from equation (43)

$$t = 31(1 + t/b + t/l) \quad (45)$$

On the basis of electronmicrographs we can estimate the length of gel particles to be approximately 100,000 nm and the width to be approximately 5,000 nm, so we find

$$t \sim 330 \text{ nm}$$

As the thickness of a single layer of a tricalcium silicate hydrate crystal is about 100 nm, the gel particles must be from three to four molecule layers thick.

4.10. Formulas for estimating the overall physical composition of cement paste

Inserting $V_c=0.32$, $V_n=0.75$, $a=3.3$, $k=0.25$, and $w_n^0=0.23$ in equations (17) to (21) and (28), we obtain a set of formulas by means of which we can quantitatively calculate the volumetric composition of hardened cement paste as a function of original water-cement ratio and degree of hydration.

From equations (17) to (21) and (28) we obtain

Fractional volume of cement gel

$$\frac{0.68m}{(w_0/c) + 0.32} \quad (46)$$

Fractional volume of unhydrated cement

$$\frac{(1-m)0.32}{(w_0/c) + 0.32} \quad (47)$$

Fractional volume of gel pores

$$\frac{0.19m}{(w_0/c) + 0.32} \quad (48)$$

Fractional volume of capillary pores

$$\frac{(w_0/c) - 0.36m}{(w_0/c) + 0.32} \quad (49)$$

Fractional volume of total pores

$$\frac{(w_0/c) - 0.17m}{(w_0/c) + 0.32} \quad (50)$$

Fractional volume of empty capillary pores

$$\frac{0.0575m}{(w_0/c) + 0.32} \quad (51)$$

where

w_0/c = original water-cement ratio by weight;

m = fraction of original cement which has become hydrated = degree of hydration.

From equations (32) and (33) we find that:

1. When water is available to the entire bulk of paste from external sources, the maximum degree of hydration, m , to be used in equations (46) to (51) is

$$m = \frac{w_0/c}{0.36} \quad \text{when } 0 < \frac{w_0}{c} < 0.36 \quad (52)$$

or

$$m = 1 \quad \text{when } \frac{w_0}{c} \geq 0.36. \quad (53)$$

2. When water is not available to the entire bulk of paste from external sources, the maximum value of m to be used in equations (46) to (51) is

$$m = \frac{w_0}{0.42} \quad \text{when } 0 < \frac{w_0}{c} < 0.42 \quad (54)$$

or

$$m = 1 \quad \text{when } \frac{w_0}{c} \geq 0.42. \quad (55)$$

The restrictions under item 2 apply to the interior parts of most structural concrete members.

3. When no other information on the degree of hydration of a given Portland cement is known, the values of m in Table I are suggested for obtaining estimates.

TABLE I

APPROXIMATE DEGREES OF HYDRATION OF HARDENED PORTLAND CEMENT PASTES AS A FUNCTION OF AGE AFTER CONTINUOUS CURING IN WATER AT 20°C [7].

ASTM Type of Cement	Time of Curing in days	Approximate Value of m
I and II	1	0.30
	3	0.50
	7	0.60
	14	0.65
	28	0.70
	91	0.80
III	1	0.40
	3	0.60
	7	0.70
	14	0.80
	28	0.85
	91	0.90

For two different values of the degree of hydration, $m=0.5$ and $m=1.0$, volume fractions of the main structural components of hardened cement paste have been calculated from equations (46) to (51) as functions of water-cement ratio m from equations (52) and (54) have been used where applicable. The results are presented in figures 5, 6, and 7. The graph in figure 7 was obtained assuming that no water is available from external sources.

APPENDIX A

BET theory and theory of capillary condensation [1]

Various theories have been advanced to explain the taking up of gases and vapors by porous solid materials. Among the most useful is the theory of Brunauer, Emmett, and Teller, known as the *Multimolecular-Adsorption Theory, or the BET theory* for brevity.

It is beyond the scope of this paper to discuss the BET theory in full; reference should be made to Brunauer's treatment of the topic [8]. The following is a brief review of the main features of the theory.

The theory rests on the assumption that the taking up of a gas by a solid is the result of a physical attraction between the molecules of the gas and the surface molecules of the solid. The attraction forces are of lesser order of intensity than those involved in

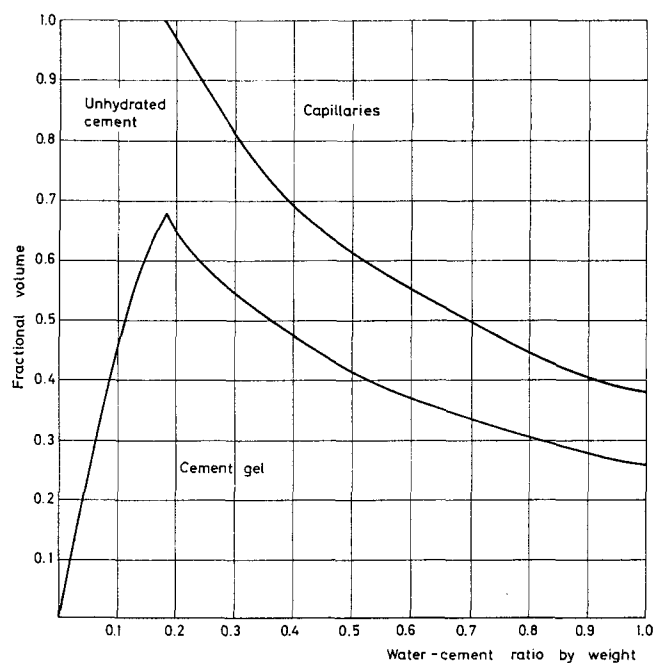


Fig. 5. — Physical composition of 50% hydrated Portland cement paste, continuously cured and stored in water. $m=0.5$ or calculated from Equation (52) where applicable.

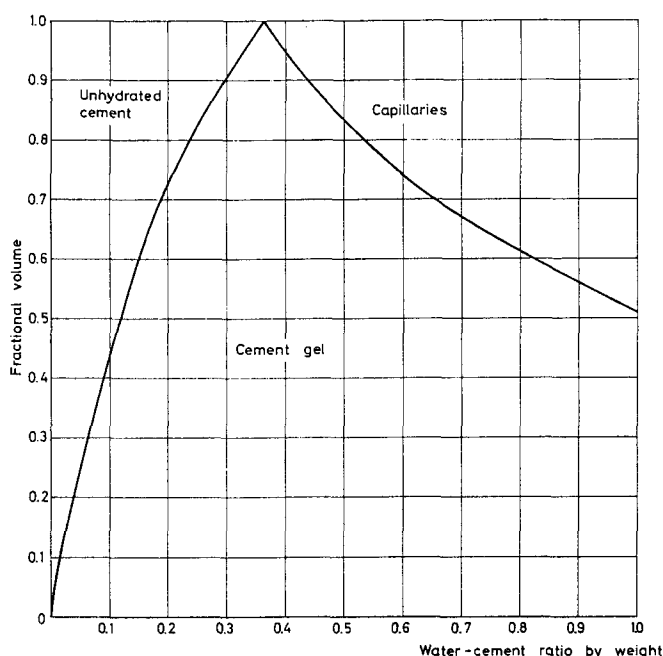


Fig. 6. — Physical composition of 100% hydrated Portland cement paste, continuously cured and stored in water. $m=1.0$ or calculated from Equation (52) where applicable.

most chemical reactions, but they may be effective over greater distances.

A solid surface exposed to a continuous bombardment of gas molecules catches and holds some of the gas molecules, at least momentarily. Moreover, when the gas is also a vapor such as water, the molecules caught on the surface are in a condensed state and may be considered as a separate phase.

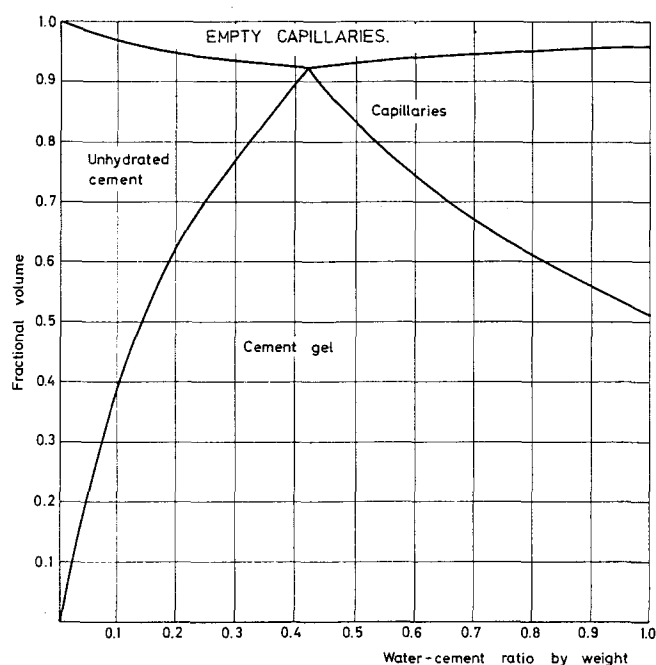


Fig. 7. — Physical composition of sealed and fully hydrated Portland cement paste. $m=1.0$ or calculated from Equation (54) where applicable.

Some of the adsorbed molecules acquire enough kinetic energy to escape from the force field of the solid surface. The overall result is a continuous interchange between the surface region and the interior of the gas phase, but the average molecular concentration at the solid surface remains higher than that of the interior of the vapor phase by virtue of the surface attraction.

The BET theory rests on the assumption that for any given vapor pressure the amount adsorbed is directly proportional to the surface of the solid. The most widely used mathematical statement of the theory is Equation 1 in Section 2.3.3 of the main text relating w/V_m and p/p_s .

Powers found that the BET theory applies to hardened Portland cement paste at relative vapor pressures between 0.05 and 0.40.

Condensation of vapor in a porous cement paste at relative vapor pressures above 0.40 seems to be most adequately explained by a combination of a theory based on the energy available at the solid surface, such as the BET theory, and a theory based on energy available at the surface of a liquid, such as the *capillary condensation theory*.

The capillary condensation theory rests on the fact that the surface of a liquid is the seat of available energy. The molecules at the surface of a liquid, not being completely surrounded by other molecules of like kind, are under an inwardly directed intermolecular force. Consequently, when left to itself, a small body of liquid tends to become spherical, since that is the form giving a minimum of surface.

This phenomenon has an effect on the vapor pressure of the liquid. How this comes about can be seen by

considering the behavior of water in a small glass cylinder, as shown in figure 8. The solid curve at the top represents the meniscus of the water surface. Owing to the surface tension which strives to straighten the meniscus, that is to reduce the surface area, the water in the vessel is under tension. Consequently, the vapor pressure of the water in the tube will be less than normal for the existing temperature. The smaller the tube, the greater the curvature of the meniscus, and therefore the lower the vapor pressure.

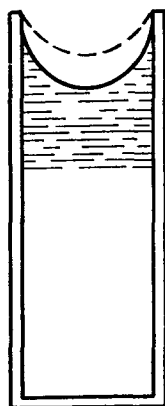


Fig. 8. — Model of capillary pore and meniscus.

The relationship between surface curvature and vapor pressure was worked out by Lord Kelvin. It may be written

$$\ln \frac{p}{p_s} = - \frac{2 \sigma M}{d_f R T} \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$

where

p_s = vapor pressure over plane surface at temperature T , the saturated vapor pressure;

p = the existing vapor pressure over a concave surface;

σ = surface tension of liquid;

d_f = density of liquid;

M = molecular weight of liquid;

R = the gas constant;

T = absolute temperature;

r_1 and r_2 = the principal radii of curvature.

It can be demonstrated that no appreciable capillary condensation can take place in porous solids at vapor pressures below about 0.40.

Many of Powers' interpretations of water vapor adsorption isotherms rest on the theories described above. The BET theory was applied to the range of relative vapor pressures $p/p_s = 0.05$ to $p/p_s = 0.40$, while a combination of the BET and the capillary condensation theory was applied to relative vapor pressures $p/p_s > 0.40$.

APPENDIX B

The Powers-Brunauer versus the Feldman-Sereda model of hardened portland cement paste

Many researchers now believe that an alternative model which was developed by Sereda and Feldman [9] in the sixties comes closer to reality than Powers' model [1]. However, the Feldman-Sereda model has not yet been developed to the same extent and cannot yet give the same quantitative answers as Powers' model. It is possible, however, that it may eventually replace Powers' model when it reaches maturity. Until then, Powers' model continues to give the right answers, although some critics say, for the wrong reasons.

Powers considers CSH, the main component of hardened Portland cement paste to be colloidal particles made up of two or three layers bonded together as in a clay. There is not sufficient long-range order to consider the material crystalline. CSH is made up of a random arrangement of these particles bonded together by surface forces with occasional strong, ionic-covalent bonds linking adjacent particles. Water-vapor can penetrate all the spaces between the particles and can move reversibly in and out of the space between particles to provide a measure of their surface area. On the other hand, the water between the layers is held until strong drying occurs, when it is lost irreversibly.

Feldman and Sereda [9] visualize the structure of CSH as developing a complete irregular array of single layers which may come together randomly to create interlayer space but in no ordered way. In contrast to Powers, they consider that water can move reversibly in and out of the interlayer space and that adsorption of water molecules within the interlayer region distorts the measurements with water vapour. Bonding between layers is considered to be through solid-solid contacts which are visualized as bonds intermediate in character between weak Van der Waal's and strong ionic-covalent bonds. The solid-solid contacts form on drying but are disrupted on wetting. According to Feldman and Sereda bonding is a special kind of chemical bonding and cannot be considered as interaction between surfaces.

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RÉSUMÉ

Structure physique de la pâte de ciment Portland durci. — On expose comment Powers et ses collaborateurs ont déduit le modèle classique de la structure de la pâte de ciment Portland durci à partir de données sur les isothermes d'absorption de la vapeur d'eau. On montre, en outre, comment on peut obtenir une évaluation numérique du pourcentage en volume de tous les composants essentiels formant la structure physique de n'importe quelle pâte de ciment Portland conservée à tempé-

rature ambiante à partir d'informations sur le rapport eau/ciment et le degré d'hydratation du ciment.

Une grande partie du modèle de Powers reste valable après 40 ans ou presque, et c'est le seul modèle sur lequel on puisse établir des calculs quantitatifs de la composition volumétrique de pâtes de ciment Portland durci.

Cet article, écrit à l'intention des ingénieurs en génie civil, a pour but d'améliorer la compréhension de certaines idées fondamentales sur lesquelles s'appuient de nombreux développements ultérieurs de la technologie du béton.