Research and Development Laboratories

of the

Portland Cement Association

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SYNOPSIS

This is a study of the capillary structure of cement paste in terms of data on permeability to water. Capillaries in fresh paste are continuous but if the specific surface area of the cement is 1800 cm²/g or greater (Wagner), and if the water-cement ratio W/C is not higher than 0.7 by weight, production of cement gel during the curing period will eventually segment the capillaries, forming "capillary cavities." If the specific surface area is higher, the limiting water-cement ratio is higher, and presumably, vice versa. Some practical consequences of capillary continuity or lack of it are discussed.

INTRODUCTION

In a previously published paper[1] we presented data showing that results of permeability tests on hardened cement paste are consistent with other evidence that the hydration products of portland cement, principally a colloidal material, is composed of small particles having a characteristic specific surface area. The specific surface area is independent of the original ratio of water to cement, at least for the usual range of water cement ratios, and it is the same at one stage of hydration as another, with a probable exception for the products of early reactions involving gypsum. The specific surface of the parti-

cles composing this product is about 5.5×10^6, cm^{-1}, as indicated by water-vapor adsorption[2]. The hydration products, "cement gel" and calcium hydroxide, principally, are produced gradually, by chemical reactions between the components of portland cement and water, the original cement becoming replaced by the new products. The volume of cement gel and other products is about 2.1 times that of the cement from which it was derived**. Therefore, hydration products replace not only cement but also some of the water-filled space in the paste; i.e., about 1.1 cc of water-filled space becomes filled with hydrated material for each 1 cc of cement used up.

Composed of particles aggregated in random array, cement gel is itself a porous material. The porosity is about 26 per cent of the overall volume of the hydration products, including the non-colloidal components, about 33 per cent of gel proper.

At a given stage of hydration, the volume of the gel plus the volume of remaining unhydrated cement is usually less than the overall volume of the paste***. The difference is composed of residues of what

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**In earlier papers factors higher than 2.1 have been reported. The present figure is based on the best information now available.

***In this discussion, air bubbles if present, are not considered to be a component of paste.

was water-filled space in the fresh paste. Such residual spaces constitute discontinuities in gel structure. They are called *capillary pores* or capillaries, or, as we shall see, *capillary cavities*. Pores in the gel itself are called *gel pores*, and, being interstices in randomly arrayed particles, they are interconnected.

Powers and Brownyard[3] considered the permeability of paste in terms of physical structure, i.e., they considered it in terms of the permeability of the gel itself and discontinuities in gel structure, the capillaries. From the relatively small amount of data then available, they observed that the degree of permeability was controlled mainly by the capillary porosity, and concluded that capillary pores were an interconnected network of channels through the gel. In the present paper, we shall show that mature pastes usually do not contain an interconnected system of capillaries. The capillaries in such specimens apparently exist as isolated cavities. We shall show also that in other specimens there are continuous capillaries.

The data on which these conclusions are based were obtained from an experimental study of permeability, partly reported in previous papers[1],[4]. The conclusion about continuity or lack of continuity of capillaries rests on conformity or lack of conformity of the data to an equation for permeability based on the assumption that resistance to flow through a granular body is determined by viscous drags on the individual particles composing that body.

TEST DATA

The data used for this paper were obtained from tests of permeability of specimens of neat cement. Details pertaining to preparation of specimens and method of test have already been published[4]. Batches of cement paste were mixed in a vacuum so as to obtain specimens free from air bubbles. The fresh pastes were put in cylindrical glass molds, and after the curing period, the molds were removed and test specimens were obtained by means of a lathe and a diamond saw.

Some of the specimens were prepared from a commercial Type 1 cement having a specific surface of 1800 cm²/g (Wagner). Other specimens were made with what is referred to as an ultra-fine cement. This cement was made by passing some of the cement referred to above through an air-

separator, and discarding the coarsest two-thirds. Except for gypsum content, the ultra-fine cement had about the same chemical composition as the cement from which it was prepared. The SO_3 content was 2.81 per cent as compared with 1.94 per cent for the original cement.

With respect to the chemistry of reactions involving gypsum, the gypsum content of the ultra-fine cement may be considered to be practically equal to that of the cement from which it was prepared. Since gypsum is involved in initial reactions only, and since the coarser two-thirds of a cement do not contribute much to initial reactions, it is proper to consider the gypsum requirement as depending mostly on the finest part of the cement. Since ball-milling gypsum with clinker reduces most of it to sizes like the finest portions of portland cement, the method used for preparing the ultra-fine cement tends automatically to give about the correct gypsum content.

With the ultra-fine cement, it was possible to prepare cement pastes that would not lose water during the period before setting. The ratios of water to cement ranged from 0.4 to 1.5 by weight. In most cases, the cement was completely hydrated at the time of test. The specimens may be considered, therefore, to be composed entirely of cement gel and the crystalline products of hydration, principally calcium hydroxide*.

All specimens were cured at 24 C (76 F). The molds, which were glass test tubes, were filled with pastes to a level about two inches below the top. Then, about one inch of water was placed over the fresh paste, and the mold was closed with a rubber stopper. In the course of about two years, practically all the alkali leached from the specimen into the curing water, at least for a group of specimens for which the curing water was changed from time to time during the latter part of the curing period. Other specimens, cured for a shorter period, retained enough alkali to influence

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*The distinction between crystalline material on one hand and gel on the other is not quite correct. The gel particles may have various degrees of crystallinity ranging from almost completely amorphous to degrees of organization that will give six or seven diffraction lines out of a possible 23 or more. The distinguishing feature between gel and the rest is the specific surface; the specific surface of gel is at least 10 times that of the calcium hydroxide crystals found in cement paste.

the test results. Effects of alkali will be noted further on.

Most of the permeability tests were carried out at 27 C (80.6 F). Some tests were made at four different temperatures, ranging from just above the freezing point to 27 C.

Results, discussed below, are dealt with in two sections, one dealing with specimens containing capillary cavities but no continuous capillaries, and one dealing principally with specimens containing continuous capillaries.

SPECIMENS CONTAINING CAPILLARY CAVITIES BUT NO CONTINUOUS CAPILLARIES

From the theoretical considerations and experimental results discussed in reference 1, the following equation was found to represent permeability data from leached specimens, for the whole range of temperatures used:

$$\ln \frac{K_1 c}{(1-c)^2} = \ln B - \ln \eta(\theta) - \left(\frac{a}{T} + \gamma\right) \frac{c}{1-c} \quad (1)$$

where,

K_1 = coefficient of permeability cm/sec,

c = particle concentration, i.e., volume of solids per unit volume of specimen,

η = viscosity of fluid, poises,

θ = temperature, °C,

T = temperature, °Kelvin,

a = an empirical constant that appears when viscosity is a function of average size of interparticle space,

γ = a factor, determined empirically, that depends partly on particle shape. (It is related to the Einstein "shape factor"),

$\ln$ = logarithm to the base e.

The function $\frac{c}{1-c}$ is inversely proportional

to the hydraulic radius, which is the ratio of pore space to the boundary area of that space, and is thus a measure of average distance between surfaces of solid particles. B is a factor depending on, among other things, size and shape of particle, viz.:

$$B = \frac{\zeta(c) \rho_f g}{18} d_s^2 \quad (2)$$

Where $\zeta(c)$ is a factor, taken to be constant at $\frac{2}{3}$, that is required in systems in which the particles are in fixed, random positions, unable to rotate as would a free-falling isolated particle*; ρ_f is density of fluid; d_s is the Stokes' diameter of the particle. Assigning values, we have:

$$\zeta(c) = \frac{2}{3}$$
$$\rho_f = 1.0$$
$$g = 980$$

and

$$B = 36.3 \, d_s^2 \quad (3)$$

As reported in reference (1), it was found by the method of least squares, using an electronic computer, that the best values of the constants are as follows:

$$B = (1.36 \pm 0.1) \times 10^{-10}$$
$$a = 1242 \pm 133$$
$$\gamma = 0.7 \pm 0.5$$

When these values are inserted in eq. 1, and logarithms to the base 10 are used, the relationship becomes:

$$\log 10^{12} K_1 \frac{c}{(1-c)^2} =$$

$$2.13154 - \log \eta(\theta) - \left(\frac{539}{T} + 0.3\right) \frac{c}{1-c}$$

and for $\theta = 27$, $T = 300$, it becomes:

$$\log 10^{12} K_1 \frac{c}{(1-c)^2} = 4.2 - 2.097 \left(\frac{c}{1-c}\right) \quad (4)$$

which is the equation of the line in Fig. 1.

With the value of B given above, and eq. 2, the Stokes' diameter turns out to be:

$$d_s^2 = \frac{136 \times 10^{-12}}{36.3} = 3.75 \times 10^{-12} \, cm^2$$

$$d_s = 198 \times 10^{-8} \, cm = 198A.$$

It thus is apparent that resistance to flow is due to viscous drag on extremely small particles. However, the relationship between the Stokes' diameter and the actual particles is somewhat obscure, and requires further consideration.

As shown in reference (1), the Stokes' diameter is defined as

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*The basic equation, prototype of eq. 1, was derived by Steinour[5] from Stokes' law for free-falling, isolated particles.

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$$d_\mu^2 = \frac{\delta^2}{d_d} \qquad (5)$$

δ^3 being the diameter of a sphere having the same volume as the actual particle, and d_d being the diameter of a sphere having the same viscous drag as the actual particle. The two "equivalent spheres" are not identical unless the particle represented is a sphere. Whatever the shape, the relationship applies only to a system composed of equal-size particles, a monodisperse system. Although the particles in hardened cement paste have various sizes, and have various shapes far from spherical, spaces between the particles are so small, and effects of adsorption so dominant, that viscous drag seems to depend on specific surface area of the particles, regardless of size and shape. At least, such an assumption leads to plausible results[1]. On this basis, the drag diameter, d_d, may be made identical with the surface diameter, Δ, which is the diameter of a sphere having the same surface area as the actual "typical" particle. By definitions, and the assumption just stated,

$$\cdot\, d_a^2 = \frac{\delta^3}{\Delta} = \psi^{1/2}\delta^2 = \frac{d^2}{\psi^{3/2}} \qquad (6)$$

where

$$\psi = \frac{d}{\delta} \qquad (7)$$

d is the diameter of a sphere having the same specific surface (cm^{-1}) as the actual particle, and ψ is the sphericity factor defined by eq. 7.

$$\text{Since } d = \frac{6}{\sigma}, \qquad (8)$$

σ being the specific surface area, cm^{-1},

$$\frac{d^2}{\psi^{3/2}} = \frac{36}{\psi^{3/2}\sigma^2} = d_\mu^2 \qquad (9)$$

$$\sigma = \frac{6}{\psi^{3/4}d_\mu} \qquad (10)$$

Thus, the Stokes' diameter is related to the specific surface through a sphericity factor. Only when the particles are spheres of one size is it equal to the actual diameter, in which case $\psi = 1.0$.

The indicated specific surface can be obtained from the observed value of d_a if ψ is known. In this case, ψ was evaluated from the value of σ given by water vapor adsorption[2]. It was found that, for the whole hydration product,

$$\sigma = 5.5 \times 10^6 \text{ cm}^{-1}$$

which, by eq. 8, gives a specific-surface diameter of

$$d = 109A.$$

Using the above value for σ gave $\psi = 0.46$. After a correction for non-colloidal calcium hydroxide in the specimens, the value became $\psi = 0.36$. Such a low value is characteristic of sheets or fibers, and thus is in agreement with Grudemo's electron micrographs obtained in 1957[6].

The foregoing data on particle size and shape, derived from permeability tests and surface area measurements by water-vapor adsorption, could not have been obtained if flow in the permeability test had occurred in continuous capillaries that bypassed clusters or masses of the particles that are measured by water-vapor adsorption, namely, the gel particles. It is concluded, therefore, that flow through specimens represented by the points in Fig. 1 was resisted by the gel particles individually, even though the specimens contained considerable amounts of capillary space. It seems that such space must exist as isolated cavities, the cavities being separated by walls of porous gel.

As to the volume of capillary cavities in these specimens, it may be calculated from the following relationship, which holds only for completely hydrated specimens; it is based on data showing that the porosity of gel* is about 26 per cent[7].

$$p = (1 - c) - 0.26 \qquad (11)$$

where,

p = capillary porosity,
c = volume of solids in unit volume of fully hydrated specimen.

When $1 - c = 0.26$, capillary porosity is nil; hence, when $\frac{c}{1-c}$ is less than 0.74 / 0.26, or 2.85, the specimen contains capillary space. When, for example, $\frac{c}{1-c} = 1.0$, capillary porosity is 24 per cent.

SPECIMENS CONTAINING CONTINUOUS CAPILLARIES

The conclusions stated in the preceding section, to the effect that the specimens represented in Fig. 1 contained capillary

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*Gel as used here includes all the hydrated solids, including calcium hydroxide. The calculated porosity of gel proper is higher, perhaps 33 per cent, as pointed out in the introduction.

cavities but not continuous capillaries, is strengthened by the data to be presented in this section indicating that some other specimens do contain continuous capillaries. The data are given in Fig. 2.

Fig. 2 is like Fig. 1, but contains a wider range of data. The various points represent mature pastes, fresh pastes, and pastes at intermediate degrees of maturity. The cements were all made from the same commercial clinker. Three different grinds, made at the plant, are represented by the points on lines D, E, and F, the specific surface areas being indicated. The points on lines B and C, and the solid triangles near but below line A, represent specimens made of a blend of the medium and fine cements, the blend having a specific surface area of 1800 cm²/g (Wagner) or σ = 10,600 cm⁻¹. The circled points in the vicinity of line A represent specimens made with the same ultra-fine cement as that represented by the points in Fig. 1, but they represent a wider range of cement contents, and were tested at an earlier age than those for Fig. 1. The ultra-fine cement was prepared from the finest of the three grinds, the one represented by line F. Line H is an estimated function for fresh paste made with ultra-fine cement.

Fresh Paste

As already indicated, points on lines D, E, and F, were derived from experimental values of the permeabilities of fresh pastes. Water-cement ratios of the pastes may be

read from the scale of abscissas at the top. The coefficient of permeability was obtained from the initial rate of bleeding by means of the relationship shown in eq. 12:

$$K_1 = \frac{Q \quad V_p}{(d_c - d_f) \ C} \qquad (12)$$

where,

Q = rate of bleeding,[8] cm/sec,
d_c = density of cement g/cc,
d_f = density of aqueous solution g/cc,
C = weight of cement, g,
V_p = volume of paste cc.

The positions of the lines through the points was established by the data points, except that *relative* positions of the intercepts with the zero ordinate were made to conform to the theoretically correct relationship between intercept and specific surface, eqs. 3 and 10. The data are due to Steinour[9].

For fresh pastes, c represents the volume concentration of particles of cement. The volume of cement was computed from the specific volume *as measured in water.* That procedure effected a partial correction for the changes due to solubility and initial chemical reactions.

Conformity of data points to lines D, E, and F, has the same significance with respect to flow in fresh paste that conformity to the line in Fig. 1 has with respect to flow in hardened paste. That is, resistance to flow through the floc-structure is determined by the individual ce-
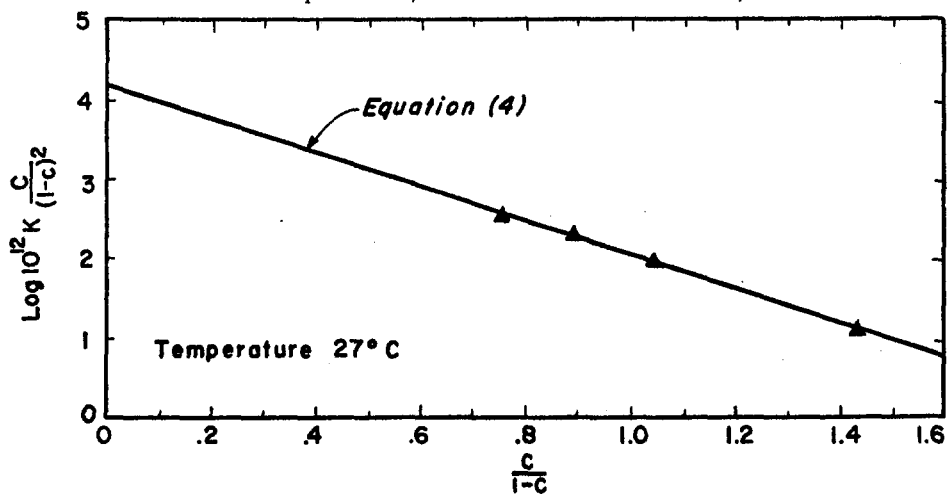

Fig. I — Relationship between Experimental Data and Semi-Theoretical Equation, Signifying Discontinuity of Capillaries.

ment particles and there are no continuous channels through which the flow can bypass groups of particles. It would be easy to demonstrate, however, that for each of the three cements there is a minimum value of $\frac{c}{1-c}$ below which the data points will not fall on the straight line but above it, describing a locus that diverges sharply upward, signifying the occurrence of "channelled bleeding"[8].

Transition From the Fresh to the Mature State

Curves B and C each represent one specimen for which permeability data are available at all stages of hydration. The points at the upper extremities represent fresh paste. They are experimental in that their positions are established by their respective water-cement ratios and by the general relationship established by experimental points on lines D, E, and F. The points are on a line parallel to and below E, as required by the slightly higher specific surface of the cement used for these specimens. The other points on B and C are from hardened specimens put under test two days after casting them. The first useful data were obtained on the fourth day, and the final points were established on the twenty-fourth day for B and the twenty-sixth for C, at which ages the process of hydration was almost complete, about 98 per cent*.

The top terminal point of curve B or C represents the state when virtually all the water in the specimen is capillary water, and of course, these capillaries are completely interconnected. Dimensions of the capillaries are determined by the spaces between the grains of cement. As the process of hydration begins to consume the original cement grains, and to lay down gel in the capillaries, the coefficient of permeability drops rapidly, about one magnitude a day for the first 4 days. The first experimental point below the beginning, representing the state of the specimen at about the 5th day, shows that the coefficient of permeability at this stage is far higher than the coefficient that would be indicated by the point directly below

*It is not usual for cement of this fineness (1800 cm²/g Wagner) to reach such an advanced stage of maturity in only 4 weeks. Possibly the fact that water was kept flowing through them (very slowly, to be sure) keeping them fully saturated and washing out alkali, accounts for the unusually high average rate of hydration.
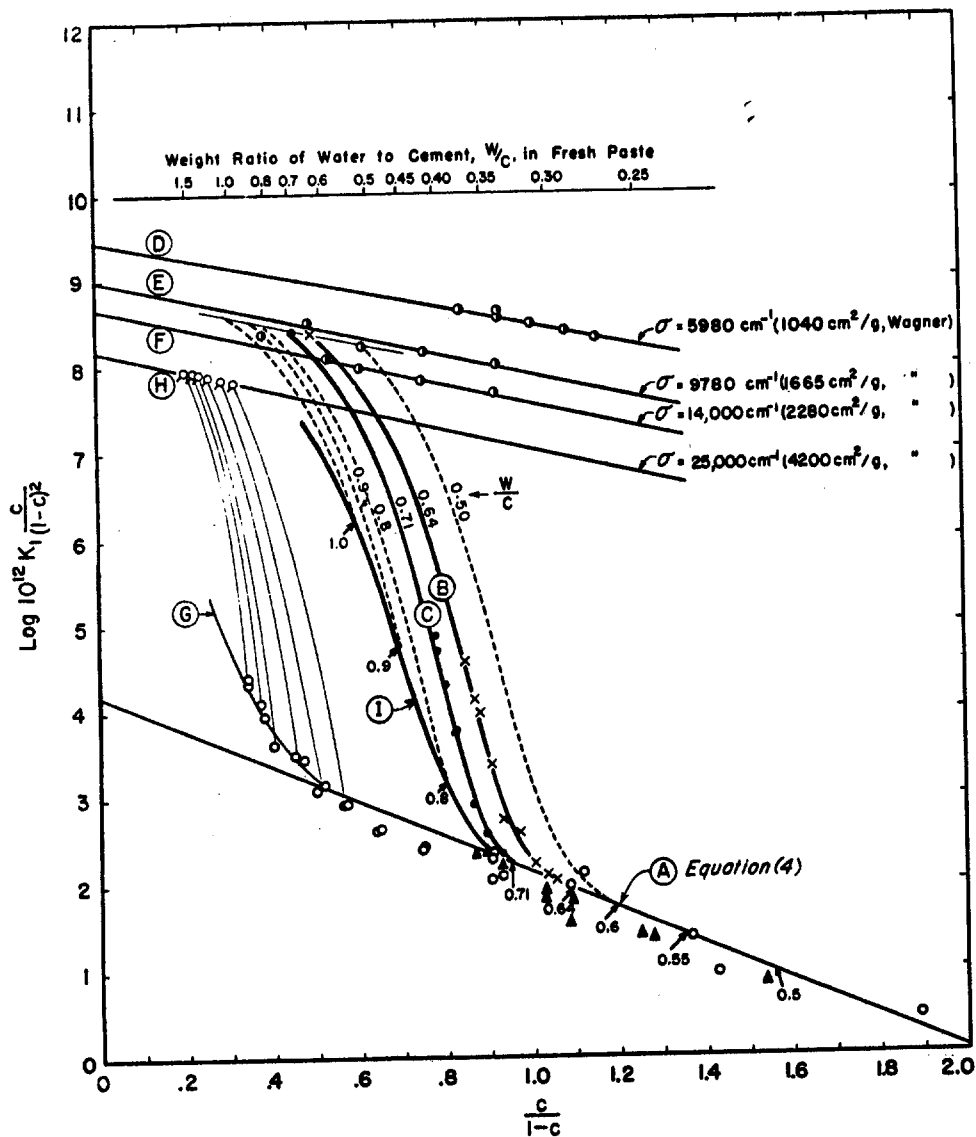
on line A. Since line A is the same as that appearing in Fig. 1 it represents, at any given point, the permeability of a specimen in which there are no continuous capillaries. Therefore, the points on B and C that are above line A represent specimens in which capillaries, certainly continuous at the start, are still continuous. Continuity of the capillary system apparently persists all the way along curves B and C. Not until the lower terminals are reached does it appear that continuity is lost. As already pointed out, loss of continuity does not signify disappearance of capillary space; all specimens in which the value of $\frac{c}{1-c}$ is lower than about 2.85 will contain capillaries or capillary cavities. Capillary space cannot be "cured out" unless the water-cement ratio was originally not over about 0.35 by weight.

The fact that line A, representing data from ultra-fine cement, is valid for a coarser cement of the same composition has not been established by the foregoing discussion. Data pertinent to this question will be considered next. The circled points near but mostly below line A represent specimens made with ultra-fine cement, but containing more residual alkali than the similar specimens represented in Fig. 1. When specimens made with ultra-fine cement were tested at various ages after they reached maturity, the coefficients of permeability showed a progressive increase; that is, the flow-rate at a given pressure increased with time. The relationship in Fig. 1 appeared after 600 days of leaching**. Completeness of leaching was verified by chemical analyses (flame photometer) on the specimens after tests.

The corresponding points in Fig. 2 represent specimens of an average age of 116 days, at which time they contained slightly more residual alkali than the specimens that were used to establish line A. Experiments by Verbeck[10] showed that small amounts of alkali have relatively large effects on rate of flow. Hence it is concluded that all these points would fall on line A if leaching of alkali had been complete, excepting the points along curve G, which will be discussed farther on.

The points enclosed in triangles represent specimens made with the same ce-

**The time required would have been much shorter, if conditions for leaching had been improved.

Weight Ratio of Water to Cement, W_C, in Fresh Paste

1.5 1.0 0.8 0.7 0.6   0.5 0.45 0.40 0.35   0.30   0.25

(D)
(E)
(F)
(H)

$\sigma = 5980\ cm^{-1}\ (1040\ cm^2/g,\ Wagner)$

$\sigma = 9780\ cm^{-1}\ (1665\ cm^2/g,\ $ " $)$

$\sigma = 14,000\ cm^{-1}\ (2280\ cm^2/g,\ $ " $)$

$\sigma = 25,000\ cm^{-1}\ (4200\ cm^2/g,\ $ " $)$

$\frac{W}{C}$

0.91 0.8 0.71 0.64 0.50

1.0

(B)

(C)

(G)

0.9

(I)

0.8

(A) Equation (4)

0.71

0.64

0.6

0.55

0.5

$Log\ 10^{12}\ K_1 \frac{c}{(1-c)^2}$

$\frac{c}{1-c}$

• - Various ages; normal cement; $\frac{W}{C} = 0.71$ by weight.

× - " " " " " = 0.64 " "

▲ - Mature; normal cement; leaching incomplete.

○ - " " ; ultra-fine cement; " "

◐ - Fresh paste.

↗ - Terminal points at complete hydration.

ρ - Estimated permeabilities of fresh pastes made with
        ultra-fine cements.

C = Solid content of specimen. K_1 = Coefficient of permeability cm/sec.

Fig. 2 — Permeability Functions for Fresh, Hardening and Mature Pastes.

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ment as that used for the specimens of curves B and C, 1800 cm²/g (Wagner). Nine of the ten points of this kind fall near but below line A. Collateral studies showed that they contained enough residual alkali to account for their relatively low positions. It is concluded, therefore, that the points representing pastes made with cements of ordinary fineness will conform to line A, eq. 4, after the alkali is leached from them. When specimens contain alkali, they are apt to take various more or less random positions below line A, according to their respective alkali contents, provided that all are free from continuous capillaries.

Fig. 2 thus provides a picture of the transition of portland cement from the virtually anhydrous state to complete hydration, in terms of changes of paste permeability. At the start, resistance to flow depends on size, shape and concentration of the original cement grains; at the end it depends on size, shape and concentration of gel particles and on whether or not original capillaries have become completely segmented. At each extreme, the particles composing the system function individually, but of course there are interaction effects.

Capillary Continuity with Ultra-Fine Cement

The paragraphs above pertain mostly to specimens made with ordinary cement, for which capillary continuity in mature pastes appears at W/C above about 0.7. With ultra-fine cement, capillary continuity does not appear until W/C exceeds about 1.0; at ratios above this, the points fell along curve G. In terms of the solid contents of mature pastes (these were completely hydrated) the break-away point is at about $\frac{c}{1-c} = 0.5$, as compared with 0.94 for the coarser cement.

The beginning points for specimens represented along curve G are shown on line H. No measurements of rate of bleeding were made on pastes containing ultrafine cement, but the position of the line could be estimated well enough from the relationship between intercept and specific surface area for lines D, E, and F. The connecting lines between the terminal points for each specimen have shapes suggested by curves B and C.

All the points plotted in Fig. 2 that represent mature specimens having values of $\frac{c}{1-c}$ not less than 0.5 fall on or below line A. It might be concluded, therefore, that this value of $\frac{c}{1-c}$ is a general limit defining the division point between mature pastes with and without continuous capillaries. However, if the data had covered a wider range of conditions, it would be clear that this is a wrong conclusion. To show this with data at hand, it is necessary to estimate what the missing data would show. The shapes of curves B and C, and the relationships between the terminal points for the specimens represented along curve G, show beyond reasonable doubt that other data obtained from specimens not greatly different from those represented by curves B and C would have similar shapes. Since the uppermost point of any curve can be established from the known relationship between permeabilities of fresh pastes and W/C, it is not difficult to estimate the probable locus of the rest of the curve. For example, the dash-line curve to the right of curve B begins at a point representing the permeability of a fresh paste having a water-cement ratio of 0.5 (top scale). To the left of curve C, another dash line is shown, starting at the point representing the permeability of a fresh paste having a water-cement ratio of 0.8. Thus the family of broken-line curves associated with B and C was established*.

The curve for water-cement ratio 0.5 appears to reach line A at a value of $\frac{c}{1-c} = 1.2$. This would not be its terminal point, however, for some of the cement would still be unhydrated at this stage. The bottom terminal point of any curve can be calculated from its water-cement ratio by means of eq. 13:

$$\frac{c}{1-c} = \frac{1+mk}{v_w d_c \frac{W}{C} - mk} \qquad (13)$$

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*At W/C much above 0.7, channelled bleeding would occur with this cement; hence, the starting points of the curves for 0.8, 0.9, and 1.0 would probably be higher than now shown, the curves might be closer together, and curve I (see further on) would rise more steeply. However, the discussion as it stands serves the purpose of showing that a curve such as I must exist, and that its low end starts about where shown.

where, as before, c is the volume of solid material in unit volume of paste; m is the fraction of cement hydrated, the maturity factor; v_w is the specific volume of the aqueous solution in the specimen; d_c is the density of the cement; W is the weight of water in the system; C is the weight of cement; $(1 + k)$ is the volume of hydration product from one cc of cement. For the cement used here,

$$v_w = 0.99 \text{ cc/g}$$
$$d_c = 3.18 \text{ g/cc (as measured in water)}$$
$$k = 0.568$$

At the terminal point, m = 1; hence for $\frac{W}{C} = 0.5$, $\frac{c}{1-c} = 1.56$. Therefore after curing had increased $\frac{c}{1-c}$ from the original value of 0.62 to about 1.2, describing some such locus as the dash line, further curing would produce points that would follow line A from 1.2 to 1.56. (Probably the points would fall a little below the line as long as some unhydrated cement remained, for the relatively large clinker particles reduce the effective area for flow. Certainly they would fall below if the specimen contained more than a trace of alkali.)

The maturity at which a curve intersects line A, hence at which capillary continuity is lost, depends on W C of the fresh paste. The maturity of a given paste can be computed from W/C and $\frac{c}{1-c}$ by means of eq. 14, which is eq. 13 solved for m, and constants as given above:

$$m = \frac{3.15 \frac{W}{C}\left(\frac{c}{1-c}\right) - 1}{0.568\left[1 + \left(\frac{c}{1-c}\right)\right]} \quad (14)$$

From the points of intersection with line A of curves B and C, and with the estimated point for $\frac{W}{C} = 0.5$, a smooth curve was drawn giving a relationship between the water-cement ratio of fresh paste and the value of $\frac{c}{1-c}$ at the intersection of line A. From this relationship, the points of intersection for other water-cement ratios were estimated and indicated in Fig. 2 by arrows and corresponding values of W C.

With the values of $\frac{c}{1-c}$ indicated at each

of the arrows, and eq. 14, the respective maturity factors at which capillaries lost continuity were estimated for each of the water-cement ratios. The results are shown by the solid part of the curve in Fig. 3. The broken-line part is what seems to be the most probable locus for the rest of the curve. It indicates, for example, that with the water-cement ratio at 0.4, capillary continuity is lost when only about 50 per cent of the cement has become hydrated. Under standard curing conditions this would require about 3 days.

If when W/C = 0.7, all the cement must be hydrated to obtain capillary discontinuity, it follows that capillary continuity cannot be "cured out" at any higher water-cement ratio. The arrow marked 0.8 indicates the maximum value of $\frac{c}{1-c}$ and the value of the permeability function for a paste having W/C = 0.8. Other arrows, higher on the graph, show the corresponding estimated points for water-cement ratios of 0.9 and 1.0. Curve I connects these points, and is thus an estimate of the lowest possible permeability for pastes having water-cement ratios too high to permit curing out of capillary continuity. Curve I corresponds to curve G, and the difference
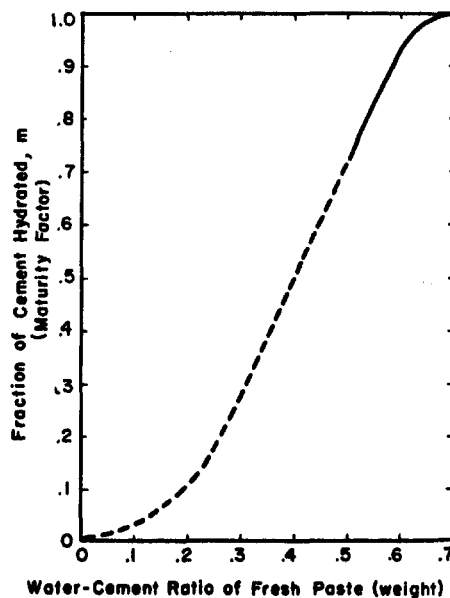

Fig. 3 — Estimated Relationship between Water-Cement Ratio of Fresh Paste and Maturity of Hardened Paste at which Capillary Continuity is Lost.

in positions of these curves may be attributed to the difference in specific surface area of the two cements. It may be assumed that for cements having specific surface areas below 1800 cm²/g, the limiting ratio would be below W/C = 0.7, and the curve corresponding to G and I, would be to the right of I.

SOME APPLICATIONS

Under various circumstances it is important to reduce the rate of penetration of concrete by water as much as is practically possible. For example, consider concrete subject to frost action. With the cement paste adequately protected with entrained air, the life of concrete is likely to be determined by the length of time required for the aggregate, or the most vulnerable part of it, to become critically saturated during periods before freezing occurs[11]. Since the aggregate particles are enveloped in paste, the permeability of paste is obviously an important factor determining the length of time required. It would thus be exceedingly unwise to use a cement paste containing continuous capillaries in concrete subject to frost action, even though such pastes can be protected with entrained air. Indeed, if practices recommended by recognized agencies are followed, continuous capillaries will be eliminated.

Other uses where pastes with continuous capillaries should be avoided include reinforced concrete in or near the sea. Although there are no specific data at hand, it seems safe to say that corrosion of reinforcement, and consequent spalling of the concrete cover, is much more liable to occur if the paste contains continuous capillaries than if it does not.

Concrete subject to attack by aggressive waters, or to the leaching of soft water, obviously should not contain a paste with continuous capillaries.

Preclusion of continuous capillaries in the paste is, as has already been seen, a matter of selection of water-cement ratio of the fresh paste and control of curing conditions. Fig. 3 is an estimate of the degree of maturity required for different water-cement ratios, when using a cement of ordinary fineness. The length of curing required to produce these degrees of maturity will of course depend mostly on prevailing temperatures and characteristics of the cement. Under standard laboratory conditions, the required time for an ordinary Type 1 cement might be about as shown in the following table:

W/C	Time Required
0.40	3 days
0.45	7 days
0.50	14 days
0.60	6 months
0.70	1 year
>0.70	Impossible

It may be noted parenthetically that the rate of hydration implied in this table is lower than that indicated by curves B and C, but the figures in the table are believed to be the more typical (see footnote on lower left of page 43).

Water-proofing agents, when present in the pores of a permeable body, are theoretically able to prevent or reduce the rate of ingress of water by capillary penetration. Such materials reduce surface tension of water, or increase the angle of contact between water and solid and the junction of the wet and dry parts of the body. They have not generally been effective in concrete, and the reason why is apparent. To penetrate concrete of good quality, water must penetrate cement gel. Such penetration is effected by surface-diffusion, which process does not involve surface tension of water, or contact angle. The motive force is derived from the free-energy of adsorption, not from the surface tension of water. Some tests show improvements due to "integral water proofers", but they usually involve specimens containing probably numerous continuous capillaries.

CONCLUSIONS

The foregoing study suggests the following conclusions:

Capillaries in fresh paste are defined by the cement particles and are continuous. Hydration of cement increases the solid content of the paste, and if it is increased sufficiently, the original capillaries become blocked by gel, and capillary cavities are thus created.

For any given cement, there is a maximum water-cement ratio above which complete hydration does not produce enough gel to block all the capillaries. For a Type 1 cement, the limiting W/C (by weight) was about 0.7; for an ultra-fine cement it was about 1.0; for cements coarser than average, it presumably would be below 0.7.

Recommended practice for producing good concrete is such as to eliminate continuous capillaries from the paste.

At water-cement ratios below the maximum at which discontinuity can be produced, capillaries become discontinuous before all of the cement has become hydrated. The stage of maturity at which this occurs depends on the difference between W/C and the maximum W/C for discontinuity. Likewise, the length of curing required depends on W/C, and on temperature. For standard laboratory conditions, and for a Type 1 cement, the estimated necessary curing times are as follows: W/C = 0.7, 1 year; 0.6, 6 months; 0.5, 14 days; 0.45, 7 days; 0.40, 3 days.

Pastes containing continuous capillaries should not be permitted in concrete used where the lowest possible rate of penetration of water is needed. Such uses include most structures subject to frost action, or subject to aggressive waters, or to leaching, and reinforced concrete used in or near the sea.

Water-proofing agents are generally ineffective because water does not penetrate concrete of good quality by the process that such agents are designed to control.

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