

# Flow of Water in Hardened Portland Cement Paste

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Permeability of hydrated portland cement pastes was measured at four temperatures. A theory based on viscous drag of fluid on particles, taking into account the effect of adsorption on viscosity, was applied. Particle size was estimated as  $\phi^{1/3} \delta = 194\text{\AA}$  or  $201\text{\AA}$ , first and second approximations, where  $\phi$  is the sphericity factor and  $\delta$  the volume diameter. The specific surface diameter, obtained from specific surface of the solid phase as measured by water vapor adsorption, was  $109\text{\AA}$  or  $95\text{\AA}$ . This gave  $\phi = 0.46$  or  $0.36$ , indicating sheets or fibers, in agreement with electron-micrographs obtained in 1957.

● STUDIES of the permeability of hardened cement paste to liquid water were carried on as one of several means of studying the colloidal structure of hydrated cement paste. Carman's (1) successful adaptation of the Kozeny (2) analysis of fluid flow in granular material indicated the possibility of the same kind of application to cement paste, which was known to be composed principally of colloidal particles. First attempts to apply the Carman-Kozeny approach were encouraging, but certain discrepancies were noted. The discrepancies between theory and experimental results prove to be fundamentally significant, and finally the Carman-Kozeny approach was set aside in favor of an analysis based on the Stokes concept of viscous drag as developed by Steinour (3). After modification as required by the extreme smallness of the water-filled spaces in hardened cement paste, this analysis led to a measure of particle size in terms of "surface diameter," and "sphericity factor." This value agreed with other information, particularly specific surface as determined by water vapor adsorption and the Brunauer-Emmett-Teller equation (4) and electron-micrographs obtained in 1957. The present paper describes the experimental methods and results, gives the theoretical basis of analysis, and shows the degree of fit between theory and experiment.

## METHODS AND RESULTS

### Preparation of Test Specimens

This paper is based on many experiments carried out over a period of about ten years. Although precision of measurement was adequate, data obtained were generally difficult to deal with because of differences between flow rates for supposedly identical samples. Early attempts at theoretical analysis were only partly successful because the data points were too scattered to settle crucial questions. Finally, it was discovered that the principal cause of variations among similar samples was small differences in alkali content of the solution in the pores of the specimens. Only the final experiments were used directly in this paper. They were made on specimens prepared as follows:

A group of specimens was prepared from which nearly all the alkali was removed by allowing it to diffuse into the curing water. Conditions were such that this required more than 600 days. The permeability coefficients were measured from time to time during the 600-day period, on companion samples. Gradual removal of alkali was shown by a slow increase in coefficient of permeability, the final coefficient exceeding the lowest by a factor of 5 or 6, and by chemical analysis at the end of the test. (Verbeck, in unpublished work, had previously shown that soluble materials reduced rate of flow through specimens of paste much more than could be accounted for by the ordinary effects of solutes on viscosity of water.)

These special specimens were made from an ultra-fine cement to obtain a final product practically free from unhydrated cement, and so that a wide range of water-

cement ratios could be used without appreciable bleeding during the plastic stage. The special cement was prepared by passing 30 lb of a commercial type I product through a small air separator and discarding the coarser two-thirds. The resulting ultra-fine product had a specific surface of about 8,000 g per sq cm as measured by the Blaine meter. The hydration products from the ultra-fine cement showed about the same physical characteristics as those from a cement of ordinary fineness prepared from the same clinker.

Neat cement pastes were prepared and cast in glass tubes in the way described in a previous publication (5). Four different ratios of water to cement were used: 0.5, 0.6, 0.7 and 0.8. Specimens having still higher water cement ratios were prepared and tested, but results are not reported here because not all the alkali was removed from them before and during the test.

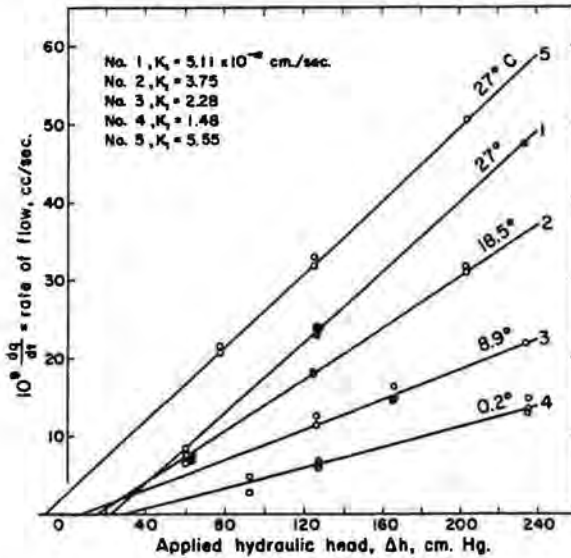


Figure 1. Rate of flow vs hydraulic head  
—W/C = 0.5, Specimen 4-13<sub>b</sub>-B.

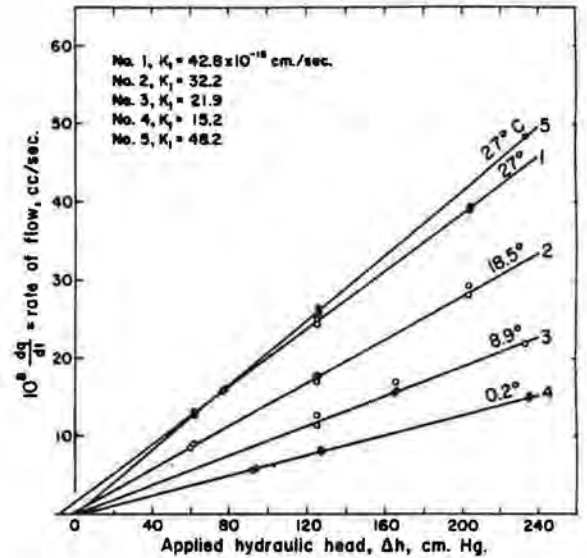


Figure 2. Rate of flow vs hydraulic head  
—W/C = 0.5, Specimen 4-14<sub>a</sub>-A.

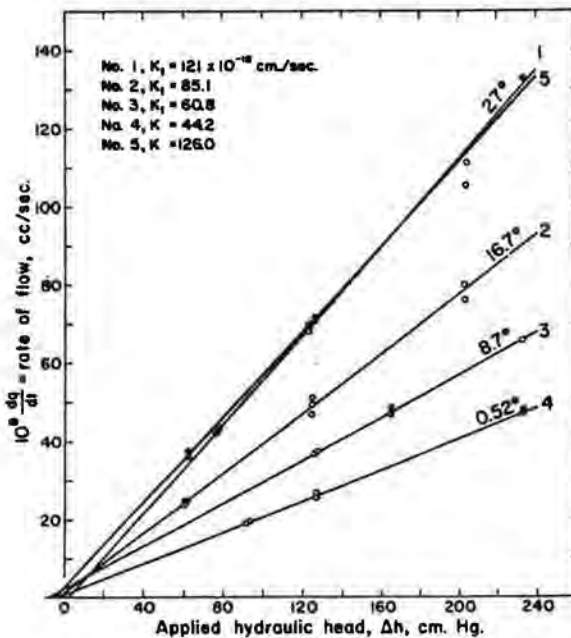


Figure 3. Rate of flow vs hydraulic head  
—W/C = 0.7, Specimen 4-20<sub>a</sub>-C.

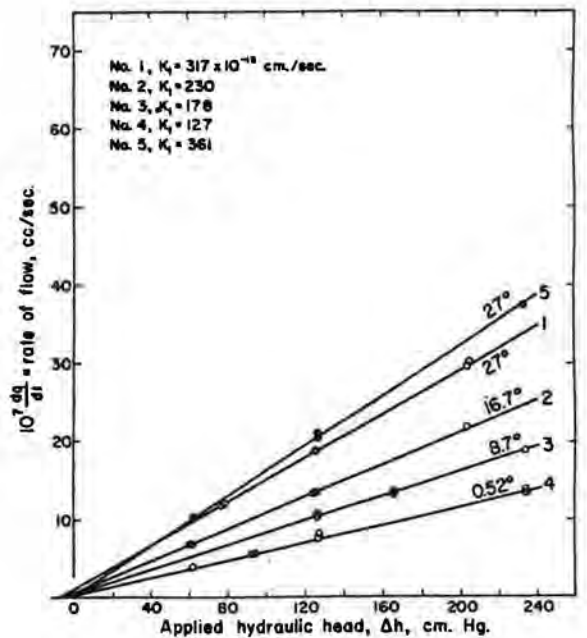


Figure 4. Rate of flow vs hydraulic head  
—W/C = 0.8, Specimen 4-28<sub>b</sub>-C.

The molds were not quite filled with paste, and immediately after placing the paste in the mold, 15 to 20 cc of water was added, and the mold was stoppered. The mold was then stored in a constant-temperature room (23 C) for about 20 months. During this time most of the alkali in the specimens diffused into the water at the top of the specimen (the "curing water"). Practically all the rest of it was removed while the specimen was under test, and before final rates of flow were established.

The mold was removed from the hardened cylinder of paste and one or more truncated cones for permeability tests were obtained by means of a lathe and a diamond saw, as previously described (5). After the permeability test was completed, each test specimen was analyzed for non-evaporable water content, evaporable water content, solid content, and alkali content. Cement and water were mixed under reduced pressure to obtain paste without air bubbles.

### Permeability Tests

Coefficients of permeability were determined by means of the apparatus described before (5), with a modification. The modification consisted of equipping each of the two water baths with a cooling coil. This made it possible to measure the coefficient of permeability of each specimen at four different temperatures. At each temperature, rates of flow were measured at three different pressures, approximately 1, 1½ and 3 atmospheres above ambient pressure. Sixty rates of flow were established, four at a time; two to five days being required to establish a rate at a given pressure.

The relationships between applied pressure and measured rate of flow are shown in Figures 1, 2, 3 and 4. Where two or three points for a given pressure are shown, they represent rates observed on successive days. A plot of such readings vs time shows that the differences are partly due to inaccuracy in measuring the exceedingly low rates of flow and partly due to small changes toward the final steady rate. The positions of the straight lines were established usually by the average of the last two or three readings at each pressure. Although some deviations may be seen, in general an increase in applied pressure produced a proportionate increase in rate of flow.

In most cases the best straight line for a given specimen and temperature does not pass through the origin. This is due to osmotic pressure, which in some cases aids the applied pressure and in other cases opposes it. During the course of an experiment it may vary in magnitude, and even may reverse direction, before final rates of flow are established. The development of osmotic pressure may be ascribed to electrolytes in the paste. The electrolytes tend to diffuse out of the specimen during a test and, because the volume of fluid exposed to the upstream face per unit of specimen area is not the same as that at the downstream face, and because of flow itself, small differences develop in concentrations of electrolyte. The test specimen functions as a semi-permeable membrane, thus osmotic pressure may be manifested. The principal electrolytes are sodium hydroxide, potassium hydroxide, and calcium hydroxide.

The specimens dealt with here were so nearly free from alkali that osmotic pressures were small, and in some cases nil. After the permeability tests were completed the specimens were tested for alkali content by means of the flame photometer (ASTM Designation C114). In each case the Na<sub>2</sub>O content was too low to be detected and the K<sub>2</sub>O was found to be, in order of ascending water cement ratios, 0.003, 0.003, 0.005 and 0.00 percent of cement weight. Osmotic pressure tends to change in the course of an experiment, but for this group of specimens the change was so slow under final conditions that the three flow-rates for a given temperature could be established before an appreciable change in osmotic pressure occurred.

The coefficient of permeability is directly proportional to the slope of a line such as one of those in Figure 1. The coefficient corresponding to each point in Figure 1 is tabulated in Table 1 along with other data to be discussed later. The method of calculation was the same as described before (5).

### DISCUSSION OF DATA

Hardened cement paste is predominantly a gel; that is, an aggregation of colloidal particles. It has high capacity for evaporable water; upwards of 30 percent by volume

TABLE I  
OBSERVED COEFFICIENTS OF PERMEABILITY  
c = solid content of specimen, cc per cc

Chronological Order	Temp., $\theta$ (deg C)	Temp., Abs., T	Permeability, $10^{13}K_i$ (cm/sec)	Log $10^{13}K_i$	$\frac{1,000}{T}$
Specimen 13 <sub>b</sub> -B; c = 0.586; $\frac{c}{1-c} = 1.415$					
1	27.16	300.34	5.11	0.708	3.330
2	18.54	291.72	3.75	0.574	3.428
3	8.92	282.10	2.28	0.358	3.545
4	0.20	273.38	1.48	0.170	3.658
5	26.97	300.15	5.55	0.744	3.332
Specimen 14 <sub>a</sub> -A; c = 0.511; $\frac{c}{1-c} = 1.045$					
1	27.16	300.34	42.8	1.631	3.330
2	18.54	291.72	32.2	1.509	3.428
3	8.92	282.10	21.9	1.340	3.545
4	0.20	273.38	15.1	1.179	3.658
5	26.97	300.15	48.2	1.683	3.332
Specimen 20 <sub>a</sub> -C; c = 0.471; $\frac{c}{1-c} = 0.890$					
1	26.86	300.04	126	2.100	3.333
2	16.67	289.85	85.1	1.930	3.450
3	8.70	281.88	60.8	1.784	3.548
4	0.52	273.70	44.2	1.645	3.654
5	26.87	300.05	121	2.082	3.333
Specimen 28 <sub>b</sub> -C; c = 0.428; $\frac{c}{1-c} = 0.748$					
1	26.86	300.04	317	2.501	3.333
2	16.67	289.85	230	2.362	3.450
3	8.70	281.88	178	2.250	3.548
4	0.52	273.70	127	2.104	3.654
5	26.87	300.05	361	2.558	3.333

particles would function as if they were larger than they are, and the total porosity would seem smaller than the total space occupied by evaporable water. There is also the possibility that water may enter the lattice of layered crystals, but not take part in flow.

Indications of the data to be presented hereafter are that flow through cement paste is not fundamentally different from flow through other porous bodies, even though flow is undoubtedly influenced by adsorption. As already mentioned, the data plotted in Figure 1 show conformity to Darcy's law. Many other data not included here confirm this aspect of the results. It may be concluded from that observation that if any of the water was immobile, it was immobile at all the pressures used in the experiments. Further analysis developed later herein leads to the conclusion that none of the water is immobile. There is no evidence that particles giving rise to viscous drag in the permeability test are larger than the particles of the solid phase; that is, there is no evidence supporting the supposition previously stated that some of the water held in the densest portions of the structure is immobile.

#### THEORY OF PERMEABILITY

Previous investigators have developed theories of flow through porous materials and granular beds. The subject has been dealt with mainly from two points of view. One view leads to considering the conduits in a granular bed to be analogous to a bundle of parallel capillaries, and applying the Poiseuille-Hagen law of capillary flow, using hydraulic radius (volume of water-filled space divided by the wetted boundary area of that space) as a measure of size of capillary. The Kozeny equation as used by Carman is the principal expression of this idea. The other point of view leads to considering the viscous drag of moving fluid on a particle. The drag may be developed by a particle falling through a fluid, or by flow through a granular bed where the particles are in fixed positions. This approach to the problem leads to a more general law than does the former.

The theory of permeability based on the concept of viscous drag can be approached by considering the drag on a single particle moving under gravitation through a large body of fluid. The driving force is the net weight of the particle multiplied by the gravitational constant:

$$F = (\rho_s - \rho_f) \left( \frac{\eta \delta^3}{6} \right) g \quad (1)$$

as compared with 1 percent, more or less, for typical rocks. Yet the coefficient of permeability of paste is as low as that of most rocks (5). This is a manifestation of the paste's fineness of texture; the pores and particles are exceedingly small and numerous. A considerable fraction of, if not all, the water contained in these pores is adsorbed; that is, it is within the range of mutual attraction between water molecules and the solid surface. The question arises, therefore, as to whether all the water is mobile. Adsorbed water might have ice-like structure, and might show a "yield point," so that, at some threshold pressure, water immobile at a given pressure becomes mobile. If some of the water is immobile at a given pressure it is likely to be that in the first adsorbed layer, or that held in the densest portions of the structure, and in the wedge-shaped spaces where fibers cross each other. So far as flow is concerned, such immobile water would be part of the solid phase. All the

in which  $F$  = driving force;  
 $\rho_s$  = density of the solid material;  
 $\rho_f$  = density of the fluid;  
 $g$  = gravitational constant (= 980 cm per sec per sec); and  
 $\delta$  = diameter of a sphere having the same volume as the actual particle.

The drag is a function of size and shape of particle, of velocity, and of viscosity of the fluid; that is (Stokes),

$$R = 3\pi\eta(\theta) V d_d \quad (2)$$

in which  $R$  = resistance (drag);  
 $\eta(\theta)$  = viscosity of fluid at  $\theta$  C, in poises;  
 $V$  = velocity of fall, in cm per sec; and  
 $d_d$  = drag diameter (that is, the diameter of a sphere having the same viscous drag as the actual particle) (6).

When force and drag are equal, the rate of fall is constant at "Stokes velocity," or

$$V_s = \frac{(\rho_s - \rho_f) g \delta^3}{18\eta(\theta) d_d} \quad (3)$$

Then, if

$$d_s^2 = \frac{\delta^3}{d_d},$$

$$V_s = \frac{(\rho_s - \rho_f) g d_s^2}{18\eta(\theta)} \quad (4)$$

which is "Stokes velocity" in terms of "Stokes diameter"; that is, Stokes Law for the fall of an isolated particle.

When there are many equal particles suspended in a fluid medium, the fall of the suspension is slower than that of an isolated particle of the same kind, and the rate is lower the higher the concentration of particles. Thus,

$$V(c, \theta) = V_s \phi_0(c) \quad (5)$$

in which  $V(c, \theta)$  is the rate of fall of the suspension at temperature,  $\theta$ , in which the volume of concentration of particles is  $c$ , and in which the particles are characterized by Stokes velocity,  $V_s$ ;  $\phi_0(c)$  is some function of the total volume of particles. The latter function operates as a reduction factor.

From theoretical and empirical considerations, Steinour (3) found, for isothermal conditions,

$$\phi_S(c) = (1 - c)^2 \exp(-kc) \quad (6)$$

where  $k_1$  is a constant. (For spheres of tapioca and for microscopic glass spheres, he found  $k_1 = 4.19$ .)

From theoretical deductions by Vand (7), Hawksley (8) found

$$\phi_H(c) = (1 - c)^2 \exp - \left( \frac{k_2 c}{1 - Qc} \right) \quad (7)$$

Here  $k_2$  is the same as the constant in Einstein's (9) equation for the effect of rigid particles in a fluid on the apparent viscosity of the fluid. Its theoretical value, 2.5 for spheres, has been confirmed experimentally for low values of  $c$ .  $Q$  is Vand's "hydrodynamic interaction" constant. Its theoretical value for spheres is about 0.6.

Mooney (10) also arrived at Eq. 7 with the same value for  $k_2$ , but with a different interpretation and evaluation of  $Q$ . From his point of view,  $Q$  is a "crowding factor" and depends on the range of particle sizes, if the system is polydisperse.

Eqs. 6 and 7 were compared by applying them to Steinour's data for tapioca suspended in oil. These data included a well-established rate of fall for an isolated particle, and values of  $c$  ranging up to about 0.5. Three assumptions were made:

$$\phi_S(c) = (1 - c)^2 \exp(-k_1 c) \quad (\text{Steinour})$$

$$\phi_H(c) = (1 - c)^2 \exp \frac{-kc}{1 - 0.6c} \quad (\text{Hawksley})$$

$$\phi_M(c) = (1 - c)^2 \exp \frac{-kc}{1 - Qc} \quad (\text{Mooney})$$

These expressions were used in place of  $\phi_0(c)$  in Eq. 5 and the constants not arbitrarily fixed were evaluated from the data by means of an electronic computer. The results were:

$$\text{For } \phi_S(c), \quad V_S = 0.120 \pm 0.003; \quad k_1 = 4.25 \pm 0.08.$$

$$\text{For } \phi_H(c), \quad V_S = 0.102 \pm 0.002; \quad k = 2.87 \pm 0.05; \quad Q = 0.6 \text{ (arbitrary).}$$

$$\text{For } \phi_M(c), \quad V_S = 0.110 \pm 0.004; \quad k = 3.51 \pm 0.27; \quad Q = 0.31 \pm 0.11.$$

The average of 150 tests of rate of fall of a single particle in a 1,000-ml oil-filled cylinder gave a velocity of  $0.1120 \pm 0.009$  cm per sec. Correcting for wall effect increased this figure to  $0.1194 \pm 0.0095$  cm per sec. Steinour's function apparently gives the most accurate prediction of the Stokes velocity.

Although the other functions do not fit the data quite as well as Steinour's, they might seem preferable because they include explicitly factors called for by analysis based on hydrodynamic considerations. However, they apparently are not valid expressions of theory, for not only do they give a relatively inaccurate prediction of Stokes velocity, but also they give incorrect values of  $k$ . The Einstein constant should have come out as 2.5 or perhaps slightly higher, because the tapioca particles were spherical, but it did not do so for either  $\phi_H(c)$  or  $\phi_M(c)$ . On the whole, it seems that Steinour's simpler function takes into account adequately what the more explicit functions failed to do. As will be seen later, a still different function is required for the present case. At this point, the function will be left unspecified, except for the quantity  $(1 - c)^2$ ; all agree on that, because it arises from fairly obvious considerations of the influence of presence of particles in the suspension on the buoyancy of a given particle, and on the upward velocity of water relative to a given particle. Hence, it may be assumed that

$$\phi(c) = (1 - c)^2 \exp(1 - \phi(c)) \quad (8)$$

for the specific case to which the ensuing discussion pertains.

The fall of a thick suspension of equal particles (monodisperse) or of a flocculated suspension of unequal particles (polydisperse) leaves an accumulation of clear fluid above the suspension. The velocity of fall, in cm per sec, is equal to the rate at which the clear fluid appears in the container above the suspension. Thus, using Eqs. 3 and 5, it is found that

$$V(c, \theta) = \frac{dq}{dt} \frac{1}{A} = \frac{(\rho_s - \rho_f) d_s^2 g}{18\eta(\theta)} \phi_0(c) \quad (9)$$

in which  $q$  is the efflux from the suspension, in cc;  $t$ , is time, in seconds; and  $A$  is the area of the suspension, in sq cm.

By Darcy's law

$$\frac{dq}{dt} \frac{1}{A} = \frac{K_1 \Delta h}{L} \quad (10)$$

in which  $K_1$  is the coefficient of permeability, in cm per sec, and  $\frac{\Delta h}{L}$  is the hydraulic gradient in terms of hydraulic head.

In the suspension, the excess hydraulic gradient is due to the weight of the solids, minus the weight of the fluid they displace; that is,

$$d_f \frac{\Delta h}{L} = (\rho_s - \rho_f) c \quad (11)$$

$$K_1 = \frac{\rho f g d_s^2}{18\eta(\theta)} \frac{(1-c)^2}{c} \exp(-\phi(c)) \quad (12)$$

If Eq. 12 represents a thick polydisperse suspension in which all particles fall at the same rate, regardless of size, Stokes diameter,  $d_s$ , represents a "typical particle" which is not easy to define. In the present case, Stokes diameter will be replaced by a "surface diameter," as will be seen further on.

Hawksley pointed out that in using a formulation such as Eq. 12, the streamlines around each particle are assumed to be symmetrical with the general direction of flow, as in the fall of an isolated particle. In a thick, flocculated suspension, or in a granular bed, where the individual particles are not free to adjust themselves so as to equalize couples of forces acting on them, the patterns of flow deviate from the general direction. Citing arguments of Fowler and Hertel (11), he inserted an "orientation factor,"  $\zeta$ , which would appear in the first right-hand term of Eq. 12. This factor is essentially the "tortuosity factor" required by the Kozeny-Carman approach, which is practically constant (at least its product with the "shape factor" is constant) for a considerable range of  $c$ . Nevertheless, it is a function of  $c$  such that as  $c$  diminishes

$$\lim_{c \rightarrow 0} \zeta(c) = 1.0$$

For flocculated thick suspensions and for granular beds,  $\zeta(c)$  may be assumed to be  $\frac{2}{3}$ . In terms of the foregoing development this means that if the streamlines around an isolated particle could be caused to deviate from the general direction of fall to the same extent that the streamlines in a bed of particles deviate from the general direction of flow, the average rate of fall of the isolated particle would be about  $\frac{2}{3} V_s$ . Thus, Eq. 12 should be written

$$K_1 = \frac{\rho f g d_s^2}{18\eta(\theta)} \zeta(c) \frac{(1-c)^2}{c} \exp(-\phi(c)) \quad (13)$$

in which  $\zeta(c) = \frac{2}{3}$  for thick flocculated suspensions or granular beds. Using Steinour's data for uniform emery particles for both the dispersed and flocculated states, Hawksley (8) found  $\zeta = 0.71$  for the flocculated state, which is considered satisfactory agreement with the theoretical value,  $\frac{2}{3}$ .

#### APPLICATION TO HARDENED PASTE

Hardened paste, composed of hydrated portland cement, is a porous solid and not an aggregation of discrete particles. Nevertheless, it is composed of particles, and the connections between particles apparently involve but a small fraction of the total surface of each particle. Therefore, to treat the material as an aggregation of discrete particles involves no conceptual difficulty. The particles in hard paste are exceedingly small, but smallness per se would not seem to preclude application of the theory as long as the particles are large relative to water molecules. A major difficulty does arise, however, from extreme smallness of interparticle spaces. Because of this, most of the fluid is in the force-field of the solid particles; that is, much of the water is adsorbed, as previously noted. Moreover, the force-field contains hydrated ions. The net effect is that the viscosity of the fluid cannot be treated as a constant at a given temperature; it is a function of the dimensions of interparticle space, and of the kinds and amounts of dissolved materials.

Adsorption forces probably cause the pattern of flow to be different from laminar flow in a uniform field. Nevertheless, experiment shows that for any given specimen of paste, the rate of flow is proportional to the pressure gradient (see Figs. 1 to 4). Therefore, in a given specimen, the coefficient of viscosity indicates the average rate of shear under unit stress. In other words, a coefficient of viscosity found in a given specimen of paste has the same significance that it ordinarily has. It differs from the ordinary coefficient in that it is not a property of the fluid alone.

Because some of the water in saturated hydrated cement paste, perhaps all of it, is subject to adsorption forces, viscosity should vary from point to point in the specimen,

and because the effects of adsorption are various, the average viscosity could be a function of the concentration of particles. Accordingly,  $\eta(\theta)$  in Eq. 13 should be replaced by  $\eta(\theta)\eta(c)$ , the function  $\eta(c)$  being a factor by which the normal viscosity is multiplied to obtain the actual average viscosity in the specimen. Making this substitution and taking logarithms

$$\ln K_1 = \ln B + \ln \frac{(1-c)^2}{c} - \ln \eta(\theta) - \ln \eta(c) - \phi(c) \quad (14)$$

in which

$$B = \frac{\zeta(c) \rho_f g d_s^2}{18} = \frac{\rho_f g d_s^2}{27} \text{ for a granular solid} \quad (\zeta = \frac{2}{3}).$$

#### Empirical Relationship

Differentiation of Eq. 14 with respect to the reciprocal of temperature gives

$$\frac{d \ln K_1}{d \frac{1}{T}} = - \left[ \frac{d \ln \eta(\theta)}{d \frac{1}{T}} + \frac{d \ln \eta(c)}{d \frac{1}{T}} \right] \quad (15)$$

According to the theory of Eyring (12), this derivative of viscosity is a measure of the activation energy for flow. The first of the two derivatives in brackets would be the normal activation energy of the fluid; the second, the added activation energy required when the fluid is adsorbed. For non-associated liquids, activation energy, hence the first derivative on the right side, would be constant for a considerable range of temperature. However, for water it varies about 10 percent from the average for the range 0 to 30 C. The empirical plots in Figure 5 show, however, that it is nearly constant for water in paste; the variation of the derivative representing the effect of adsorption is apparently equal and opposite to the variation of that for free water over the temperature interval of these experiments. It is assumed, however, that the derivative of the part due to adsorption is a constant at a given particle concentration.

The effect of particle concentration on activation energy should depend on average distance between solid surfaces; here it is assumed to be proportional to the inverse of hydraulic radius, which is proportional to  $\frac{c}{1-c}$ . Thus,

$$\frac{d \ln \eta(c)}{d \frac{1}{T}} = \alpha \left( \frac{c}{1-c} \right) \quad (16)$$

in which  $\alpha$  is an empirical constant. Integrated, this gives

$$\ln \eta(c) = \frac{\alpha}{T} \left( \frac{c}{1-c} \right) + \text{constant} \quad (17)$$

Since  $\lim_{c \rightarrow 0} \eta(c) = 1.0$ , the constant of integration is 0.

If it is assumed that  $\phi(c)$  of Eq. 14 is proportional to the inverse of hydraulic radius, and is independent of temperature,

$$\phi(c) = \gamma \left( \frac{c}{1-c} \right) \quad (18)$$

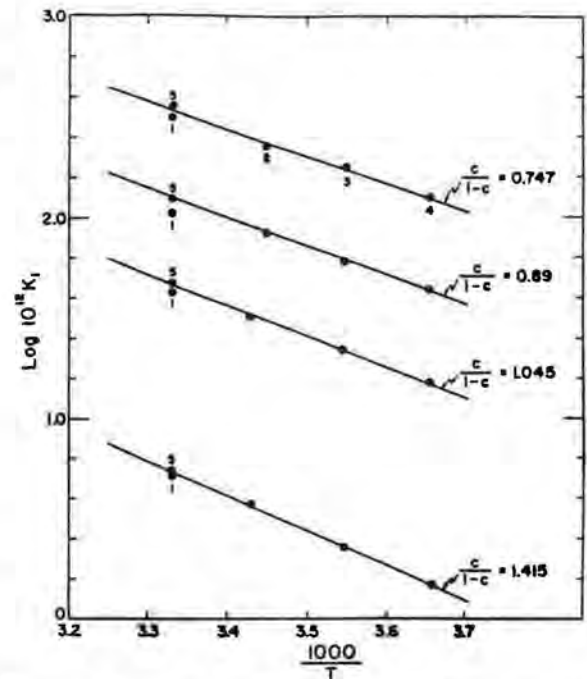


Figure 5. Permeability as a function of temperature:  $T$  = absolute temperature;  $K$  = permeability coefficient, in cm per sec; and - slope =  $896 + 647 \left( \frac{c}{1-c} \right)$ .



with  $\gamma$  being an empirical constant.

Substituting from Eqs. 17 and 18 into Eq. 14 gives

$$\ln \frac{K_1 c}{(1-c)^2} = \ln B - \ln \eta(\theta) - \left( \frac{\alpha}{T} + \gamma \right) \frac{c}{1-c} \quad (19)$$

This semi-empirical equation indicates that for data obtained at a given temperature, experimental values of the member on the left plotted against  $\frac{c}{1-c}$  should

produce straight lines, one for each temperature. Trial plots of the data in Table 1 (not reproduced here) show that the points conform very well to the expected relationship.

#### Fit of Data

The fit of the data in Table 1 to Eq. 19 was determined by the method of least squares. The first item of each group of four was omitted from calculations because of the following considerations:

The five points of each set were obtained in the sequence indicated in the first column. The first flow rate was established at 27 C, the second, third, and fourth at successively lower temperatures, and the fifth at the original temperature. The first test at 27 C gave a lower value of  $K_1$  than did the last. This change was probably caused by loss of alkali from the specimen during the first test. The indications are that there was little or no further loss of alkali during the four subsequent tests. From the other 16 values, the least square calculation, done by electronic computer, gave the following values and standard deviations:

$$B = (1.36 \pm 0.1) 10^{-10}$$

$$\alpha = 1242 \pm 133$$

$$\gamma = 0.7 \pm 0.5$$

Using these values the following empirical equation for the coefficient of permeability of the specimens represented in Table 1 is obtained:

$$K_1 = \frac{1.36 \times 10^{-10}}{\eta(\theta)} \frac{(1-c)^2}{c} \exp - \left[ \left( \frac{1242}{T} + 0.7 \right) \frac{c}{1-c} \right] \quad (20)$$

Values of  $K_1$  computed from Eq. 20 are compared with observed values in Table 2.

#### INDICATED PARTICLE SIZE

One object of this investigation was to determine what size of particle would be indicated by measurement of fluid flow, and to compare the result with indications from other kinds of measurement. Along with size there is also shape of particle to be considered. Studies by Åke Grudemo<sup>1</sup> during 1957 showed, by means of electron microscopy, that the particles in hardened paste have various shapes. The calcium silicate hydrates are (a) ribbon-like fibers, somewhat rolled up edgewise, and (b) sheets or foils aggregated as fluffy masses. The calcium aluminate hydrate and the calciumaluminoferrite hydrates occur as flat plates individually surrounded by calcium silicate hydrate. Something of size and shape can be expressed in terms of appropriate "equi-

<sup>1</sup>During 1957, Åke Grudemo, of the Swedish Cement and Concrete Institute, was a guest scientist in the Portland Cement Association Laboratories, Skokie, Ill. His work is to be published.

TABLE 2  
COMPARISON OF OBSERVED VALUES OF  $K_1$  AND  
VALUES CALCULATED FROM EQ. 20

B = 1.36 x 10 <sup>-10</sup> , α = 1242 and γ = 0.7			
Temperature (deg C)	10 <sup>12</sup> K <sub>1</sub>		Observed Minus Calculated
	Observed	Calculated	
Specimen 13 <sub>b</sub> - B			
18.54	3.75	3.43	0.32
8.92	2.28	2.16	0.12
0.20	1.48	1.35	0.13
26.97	5.55	4.95	0.60
Specimen 14 <sub>a</sub> - A			
18.54	32.2	34.4	-2.2
8.92	21.9	22.8	-0.9
0.20	15.1	15.0	0.1
26.97	48.2	47.4	0.8
Specimen 20 <sub>a</sub> - C			
16.67	85.1	87.7	-2.6
8.70	60.8	63.3	-2.5
0.52	44.2	43.5	0.7
26.87	121.0	126.9	-5.8
Specimen 28 <sub>b</sub> - C			
16.67	230.0	229.0	1
8.70	170.0	160.0	10
0.52	127.0	118.0	9
26.87	361.0	324.0	37

valent spheres" and a "sphericity factor." Hawksley (6) summarizes the following hypothetical sphere diameters, three of which were previously defined:

- $\delta$  = volume diameter: diameter of sphere having the same volume as the particle.
- $d_d$  = drag diameter: diameter of sphere having the same viscous drag as the particle in a fluid of the same viscosity and same velocity.
- $\Delta$  = surface diameter: diameter of sphere having the same external surface area as the particle.
- $d_s$  = Stokes diameter: diameter of sphere having the same density and same free-falling speed as the particle in a given fluid.
- $d$  = specific-surface diameter: diameter of a sphere having the same ratio of external surface area to volume as the particle.
- $\phi$  = sphericity factor: the ratio of surface area of a sphere having the same volume as the particle to the actual surface area of the particle.

$$d = \phi \delta \quad (21)$$

$$d = \phi^{3/4} d_s \quad (22)$$

$$d_s^2 = \frac{\delta}{\Delta} \quad (23)$$

$$\Delta = \frac{\delta}{\phi^{1/2}} \quad (24)$$

Owing to the smallness of interparticle spaces and to the force field within such spaces, streamlining of irregular particles probably does not occur. Viscous drag would seem to depend, therefore, on the extent of surface presented by the solid phase, and the average interparticle distance. The shape of the "typical particle" is probably not important in that respect. Accordingly, it is possible to identify the drag diameter with the surface diameter under the conditions of flow presumed, and thus, with reference to the relationship shown after Eq. 3:

$$\frac{\delta^3}{d_d} = \frac{\delta^3}{\Delta}$$

From Eq. 24

$$\frac{\delta^3}{\Delta} = \phi^{1/2} \delta^2$$

The definition of B given with Eq. 14 thus becomes

$$B = \frac{\rho_f g \phi^{1/2} \delta^2}{27}$$

where

$$\rho_f = 1.0 \text{ (assumed) and } g = 980 \text{ cm per sec per sec.}$$

Using the value of B given above,

$$\phi^{1/2} \delta^2 = \frac{1.36 \times 10^{-10}}{36.3} = 3.75 \times 10^{-12}$$

$$\phi^{1/4} \delta = 194 \text{ \AA}$$

From definitions previously given, the specific-surface diameter is  $\phi \delta$ . Hence, to evaluate  $\phi$  the specific-surface diameter is needed.

#### Specific-Surface Diameter

In 1947, Powers and Brownyard (15) gave the specific-surface diameter of the particles in hardened cement paste as 140 Å. This value has been revised downward because of the following considerations:

According to the BET theory,

$$\sigma = a \frac{N}{M} \frac{V_m}{c} \quad (26)$$

in which

- $\sigma$  = specific surface area by BET method, in  $\text{cm}^{-1}$ ;  
 $N$  = Avagadro's number,  $6.023 \times 10^{23}$ ;  
 $M$  = molecular weight of water, 18 g per mol;  
 $V_m$  = water required to cover the surface with a monomolecular layer, g; and  
 $a$  = area covered by 1 molecule, in sq cm.

Powers and Brownyard let  $a = 10.6 \text{ \AA}^2$  per molecule, and their equation was

$$\sigma = (35.7 \times 10^6) \frac{V_m}{c} \quad (27)$$

More recently, Brunauer (16) showed that  $a = 11.4 \text{ \AA}^2$  is a better value for these systems than is 10.6. On this basis the numerical coefficient becomes  $38.5 \times 10^6$ , which gives a specific-surface diameter about 7 percent smaller than that given by the first coefficient.

As described by Copeland and Hayes (14) in 1953, the method of drying samples of paste preparatory to adsorption measurement has been changed since the work reported by Powers and Brownyard was done, so that the non-evaporable water content is about 8 percent less than it was when determined by the original method. This change also increased  $V_m$  by about 13 percent; therefore, a present-day estimate of specific surface diameter from  $V_m$  would be further reduced. (There is reason to believe that the present method of drying gives more nearly the desired result than did the old.) A given sample treated by the 1953 method would give a higher value of  $\sigma$  than it would by the 1947 method, as follows:

$$\frac{\sigma_{53}}{\sigma_{47}} = \frac{38.5}{35.7} \times 1.13 = \frac{d_{47}}{d_{53}}$$

Hence if  $d_{47} = 140 \text{ \AA}$ ,  $d = 114 \text{ \AA}$ .

This is a partial correction of the 1947 estimate. A further correction is based on the amount of unhydrated cement in the sample. The "typical paste" for which Powers and Brownyard calculated  $d = 140 \text{ \AA}$  probably contained about 5 percent of unhydrated cement in the form of relatively large particles of clinker. Therefore, the estimate, revised not only for new value of  $a$  and new method of drying (new value of  $V_m$ ), but also for unhydrated cement, would be

$$d = 114 \times 0.95 = 108 \text{ \AA}$$

which is the final corrected value corresponding to the original  $140 \text{ \AA}$ .

For the specimens represented in Table 1, determinations of  $V_m$  were made by the 1953 method. The samples contained no unhydrated cement, and the cement was chemically the same as that to which the Powers and Brownyard value pertained. Therefore, the values obtained are directly comparable with the corrected Powers and Brownyard value. The results are given in Table 3.

These data indicate that

$$\sigma = (38.5 \times 10^6) 0.143 = 5.5 \times 10^6 \text{ cm}^{-1}$$

and

$$d = \frac{6}{\sigma} = 109 \text{ \AA}$$

which is in good agreement with the corrected value of Powers and Brownyard.

Data in Table 3 show that the value of  $\frac{V_m}{c}$ , and hence of the specific surface of the solids, is the same in each of the four specimens regardless of differences in

TABLE 3  
WATER VAPOR ADSORPTION

Ref. No.	$\frac{c}{1-c}$	$\frac{V_m}{c}$
13b - B	1.415	0.144
14a - A	1.045	0.143
20a - C	0.890	0.141
28b - C	0.748	0.143
	Average	0.143

density. This means that the specific surface of the hydration products is independent of the original water/cement ratio of the paste. Various other data not given here support this indication that the hydration product of a given cement, hydrated at standard temperature, has a characteristic specific surface. Other data show that specific surface varies with chemical composition of the cement, but the variation is small.

#### Sphericity Factor

If it is assumed that values of  $d$  and  $\phi^{1/4} \delta$  obtained in the foregoing pertain to the same particles, the value of  $\phi$  can be computed. Since  $d = \phi \delta$  (by definition) and  $\phi^{1/4} \delta = 194 \text{ \AA}$  (by experiment), it follows that  $\phi^{3/4} = 109/194 = 0.56$ , and  $\phi = 0.46$ . This value for sphericity factor may be compared with values in Table 4, cited by Hawksley (6).

The value  $\phi = 0.46$  may be considered a first approximation. A second approximation may be obtained by considering the effect of calcium hydroxide crystals. Besides gel, the specimens contained crystalline calcium hydroxide, the crystals being much larger than gel particles and thus having a relatively low specific surface. Studies of related systems by Brunauer (17) indicate that the specific surface is not greater than  $0.5 \times 10^6 \text{ cm}^{-1}$ . If it is assumed that  $\sigma_g$  = specific surface of gel particles,  $n_1$  = their volume, and  $n_2$  = the volume of calcium hydroxide,

$$\frac{n_1 \sigma_g + n(0.5 \times 10^6)}{n_1 + n_2} = \sigma = 5.5 \times 10^6$$

The weight of total solids in these specimens was about 1.234 g per g of original cement in the specimen, and the weight of calcium hydroxide was about 0.163 grams. Hence,

$$n_1 + n_2 = \frac{1.234W}{\rho_S}$$

$$n_1 = \frac{1.071W}{\rho_1}$$

$$n_2 = \frac{0.163W}{\rho_2}$$

in which

$W$  = original weight of cement in the specimen; and

$\rho_S, \rho_1, \rho_2$  = density of total solids, gel, and calcium hydroxide, respectively.

For the present purpose, it will suffice to assume that  $\rho_1 = \rho_2 = \rho_S$ , which is not far from the truth. Then

$$\frac{n_1}{n_1 + n_2} = \frac{1.071}{1.234} = 0.868$$

$$\frac{n_2}{n_1 + n_2} = \frac{0.163}{1.234} = 0.132$$

$$\sigma_g = \frac{5.5 \times 10^6 - 0.666 \times 10^6}{0.868} = 6.26 \times 10^6,$$

say  $\sigma_g = 6.3 \times 10^6 \text{ cm}^{-1}$ . This gives a revised specific-surface diameter of  $d = 95 \text{ \AA}$ .

It is now necessary to calculate a corresponding correction to the particle size indicated by the permeability measurement. Because crystals of calcium hydroxide are much larger than gel particles, they may be thought of as impermeable bodies embedded

TABLE 4  
SPHERICITY FACTORS FOR VARIOUS PARTICLES

Kind of Particle	$\phi$
Sphere	1.0 <sup>a</sup>
Portland cement	0.7 to 0.8
Emery	0.68 to 0.72
Ground glass	0.71 to 0.82
Fusain fibers	0.38
Mica flakes	0.28

<sup>a</sup> By definition.

in gel, reducing the fractional area through which flow may occur. If for the present purpose gel is defined as the porous substance occupying space not occupied by calcium hydroxide crystals, it follows that for a given gel (so defined) the coefficient of permeability is proportional to the gel content. In a hypothetical specimen containing no crystals of calcium hydroxide, the gel content is unity. In a real specimen the coefficient is smaller; that is,

$$\frac{K_g}{K_1} = \frac{1}{1 - \left(\frac{n_2}{n_1 + n_2}\right)c} = \frac{1}{1 - 0.132c}$$

where  $K_g$  is the coefficient of permeability of pure gel. It is apparent that the magnitude of the correction depends on  $c$  and is therefore different for each specimen. It will suffice to use the average  $c$  for the four specimens, which is 0.50. This value gives

$$K_g = 1.07 K_1$$

Referring now to  $B$  as defined by Eqs. 14 and 15,  $B_g$  will be considered that parameter for pure gel. Then, with  $c$  constant,

$$\frac{K_g}{K_1} = \frac{B_g}{B} = \frac{\phi^{1/2} \delta_g^2}{\phi^{1/2} \delta^2} = 1.07$$

hence  $\phi^{3/4} = \frac{95}{201} = 0.47$  and  $\phi = 0.36$ .

#### Indicated Size and Shape

On the basis of these values arrived, the "typical particle" in hydrated cement paste may be described as follows:

	<u>First</u> <u>Approximation</u>	<u>Second</u> <u>Approximation</u>
Sphericity factor, $\phi$	0.46	0.36
Spec. surf. dia., $d$	109Å	95Å
Volume diameter, $\phi$	237	264
Surface diameter, $\Delta$	350	440
Stokes diameter, $d_s$	195	205

These values and Grudemo's electron-micrographs agree in that each indicates the particles in cement gel to be not spherical. From the electron-micrographs already mentioned, and electron diffraction patterns, it appears that paste is composed mostly of ribbon-like fibers, plates, and crumpled sheets, the substance being mostly amorphous or poorly crystallized. A value for specific surface estimated from measurements of micrographs indicates (but does not prove) that these are the very particles that adsorb water vapor.

The foregoing values rest on the assumption that water-vapor adsorption measures the same surfaces that are presented to flowing water. To test this assumption let it now be assumed that the particles are layered structures such that water vapor can penetrate and measure two "inside" surfaces for every two outside surfaces (edge areas can be neglected). If it is assumed that the outside surfaces are accessible to flowing water whereas the inside surfaces are not, the specific-surface diameter,  $d$ , of the particles as felt by flowing water is one-half that indicated by adsorption. On this basis the calculation of  $\phi$  would be, using the second approximation of  $d$ ,

$$\phi^{3/4} = \frac{2 \times 95}{194} = 0.98; \phi = 0.97$$

This result indicates that the particles felt by flowing water are spheres, which is known to be false.

Let it now be assumed that interlayer water can measure only one internal surface;

that is, that only one layer of water molecules can be accommodated in the crystal lattice. In this case the specific surface of the particles felt by flowing water would be two-thirds that indicated by adsorption. The indicated sphericity factor would be

$$\phi^{3/4} = \frac{1.5 \times 95}{194} = 0.73; \phi = 0.66$$

According to Table 4, such a sphericity factor is typical of shapes found in crushed brittle materials. This result also is contrary to evidence from electron-micrographs.

Alternatively, it could be assumed that water vapor measures only the outer surfaces of gel particles, and that the particles felt by flowing water are aggregations of those gel particles. This would mean approximately that the "permeability particle" is some multiple of the "adsorption particle." Any such assumption leads to sphericity factors exceeding unity if the number of particles per aggregation exceeds 2, and the result is therefore useless.

Thus, it seems that the original calculation, based on the assumption that adsorption measures the same particles that produce drag in the permeability test, is the only one that gives an acceptable result. Possibly, a paste contains some crystals so well developed as to admit interlayer adsorption, and possibly water could not flow through such crystals. However, these data indicate that if such crystals exist, and if they do exclude flowing water, they constitute a minor fraction of the solids in the paste. It seems absurd to suggest the possibility of flow through a crystal, it should be recalled that the flow under consideration is exceedingly slow, as shown in Figure 1. A typical average rate is  $20 \times 10^{-9}$  cm per sec, which is about  $\frac{1}{4}$  in. per year. Since viscosity is not uniform, flow in some portions of the structure may be several orders of magnitude slower than the average rate. There seems to be no reason to suppose that physically adsorbed molecules would be immobile under a hydrostatic pressure gradient, whatever their situation might be.

#### GENERAL REMARKS

These data indicate that all the evaporable water (as defined by Copeland and Hayes (14)) is mobile under a hydrostatic pressure gradient, although some of it has high viscosity. If this is so, none of the evaporable water has a finite yield point under stress. Any change of stress in a concrete member, however small that change may be, should start a redistribution of evaporable water in the member, and such redistribution should be accompanied by shrinkage where the water content diminishes and swelling where it increases. This has long been recognized as a factor characterizing creep of concrete under sustained stress. It may be inferred that as far as this aspect of creep is concerned "seepage," the threshold stress for creep of concrete members, is zero, as indeed it seems to be in some experiments.

Of the two kinds of pores in hardened paste, gel pores and capillaries, the capillaries are continuous in some specimens, but not continuous in others. When they are not continuous, they are called capillary cavities, and are interconnected only by gel pores. Absence of continuous capillaries in the specimens used for this study is implied by the conclusion that adsorption measures the same surface area as that presented to flowing water. This conclusion is strengthened by data from other specimens not presented here showing unmistakable evidence of continuous capillaries in those specimens. This subject is to be dealt with in a separate paper.

If the volume diameter of a gel particle is about  $260\text{\AA}$ , as indicated by these data, the corresponding number of particles per unit volume of gel can be computed. The solid content of a unit volume of gel (exclusive of capillary cavities) is about 0.65. Hence, the quotient of 0.65 and volume per particle is the desired number. The volume per particle turns out to be  $9 \times 10^{-18}$  cc, or  $0.6 \times 10^{-18}$  cu in. Hence, the number of particles is about  $7 \times 10^{18}$  per cc, or  $10^{18}$  per cu in. of gel.

A major component of the gel is probably a tricalcium disilicate trihydrate having a volume of about 140 cc per gram-molecular weight (16). This corresponds to about  $2.3 \times 10^{-22}$  cc per molecule. A gel particle having a volume of  $9 \times 10^{-18}$  cc would thus contain about 40,000 molecules. This indicates the degree to which the water-solid

relationship in cement gel approaches (and misses) that of a homogeneous solid solution.

### CONCLUSIONS

1. The flow of water through a given specimen of hydrated cement paste complies with Darcy's law, but it is liable to be complicated by effects of osmotic pressure.
2. Within the range of paste porosity included in this report, part of the evaporable water, perhaps all of it, is adsorbed. Consequently, viscosity is higher than that of free water. (Also, viscosity is increased by the presence of solutes.)
3. Average viscosity of water in hydrated cement paste is a function of gel-particle concentration and temperature.
4. Temperature dependence of rate of flow in paste indicates a relatively high activation energy for flow, reflecting the effect of adsorption.
5. The theory of permeability based on the concept of viscous drag on particles as developed by Steinour, but modified to allow for variable viscosity, and modified by considerations advanced by Hawksley, gives a good fit to these data.
6. The particle size and shape indicated by permeability data, combined with adsorption data, are as follows: (second approximation) sphericity factor, 0.36; volume diameter, 264Å; surface diameter, 440Å; Stokes diameter, 205Å; specific surface diameter, 95Å. These data are compatible with electron-micrographs.
7. The sphericity factor obtained by combining permeability data with adsorption data indicate the particles to be sheets, or fibers, or both, in agreement with electron-micrographs.
8. All the evaporable water appears to be mobile.
9. The particles giving rise to viscous drag in the permeability test are apparently the same particles, which, when dry, adsorb water vapor.
10. In the specimens studied, there apparently were no continuous capillaries by-passing clusters of gel particles.

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