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**Structure and Physical Properties  
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Hardened Portland Cement Paste**

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## Structure and Physical Properties of Hardened Portland Cement Paste

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Methods of studying the submicroscopic structure of Portland cement paste are described, and deductions about structure are presented. The main component, cement gel, is deposited in water-filled space within the visible boundaries of a body of paste. Space filled with gel contains gel pores; space not filled by gel or other solid material is capillary space. Hygroscopicity of cement gel, and capillary pores, accounts for various aspects of the properties and behavior of concrete. Data on gel and paste structure are used in discussing strength, permeability, volume stability, and action of frost.

### I. Introduction

**I**n the parlance of the cement industry, a mixture of Portland cement and water is called cement paste; the chemical reactions of the components of Portland cement with water are spoken of collectively as cement hydration; hydration of cement causes the paste to harden and thus there is the term "hardened Portland cement paste."

Studies of the structure and properties of hardened paste began in the Portland Cement Association laboratories in about 1936. The purpose was to bridge a gap between cement chemistry and concrete technology. It seemed that establishing the relation between properties of the paste and chemical constitution of cement on the one hand and between properties of paste and properties of concrete on the other hand might accomplish this purpose. Results are gradually fulfilling that hope.

The amount of water absorbed by dry paste indicated that the paste was highly porous, and at first the physical structure of hardened paste was thought of in terms of pores. Theories pertaining to capillaries were used. In about 1939 the concept changed, and pores were thought of as spaces among particles (interstitial spaces). This change marked the beginning of progress. The theory of Brunauer, Emmett, and Teller<sup>1</sup> was used to interpret data on adsorption of water vapor by predried paste, and this application of the theory, still in constant use, turned out to be a most valuable tool for studying physical structure.

By the Brunauer-Emmett-Teller method, internal surface area was measured and then the order of size of the solid particles composing hardened paste was computed. This was first accomplished in about 1940. The thermodynamics of adsorption and the freezing of water in hardened paste also were studied. Such studies were coordinated with experimental and theoretical studies of such physical properties as strength, permeability, and volume change.

After a wartime hiatus, work was resumed and new techniques were gradually added to the old ones. An experimental study of permeability has been under way on a part-time basis for about 11 years, and studies of volume changes, especially those caused by freezing of water in hardened paste, have been especially intensive. X-ray techniques are now applied to almost all aspects of studies of structure. Diffraction has been effective in establishing the stoichiometry, and structure of the solid phases of the paste, and small-angle scattering has been used recently for measuring specific surface. Electron-optic and electron-diffraction techniques are now being applied.

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<sup>1</sup> Stephen Brunauer, *Adsorption of Gases and Vapors*, Vol. I. Princeton University Press, Princeton, 1943. 511 pp.; *Ceram. Abstr.*, 23 [11] 204 (1944).

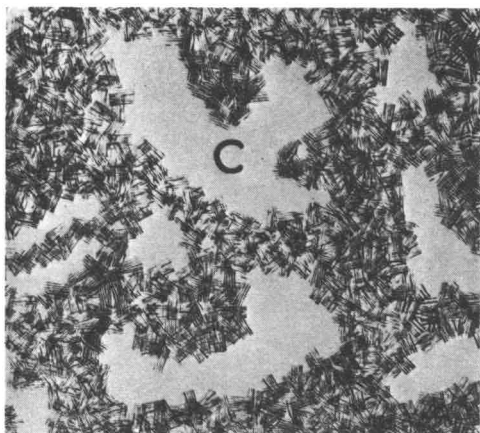


Fig. 1. Simplified model of paste structure. Gel particles are represented as needles or plates; C designates capillary cavities.  $\text{Ca}(\text{OH})_2$  crystals, unhydrated cement, and minor hydrates are not represented.

A theoretical paper about freezing of water in hardened paste based on results of studies of physical structure was published in 1945,<sup>2</sup> but a comprehensive statement about the structure and physical properties did not appear until 1947.<sup>3</sup> Since then the program has produced other papers.

The following is a brief statement about the principal concepts developed during the course of this work.

## II. Structure of Paste

Fresh cement paste is a network of particles of cement in water. The paste is plastic, and it normally remains thus for an hour or more, during which period it "bleeds"; i.e., there is a small amount of sedimentation.<sup>4</sup> After this relatively dormant period, the plastic mass sets and thereafter the apparent volume of the paste remains constant, except for microscopic but technically important variations caused by changes of temperature or moisture content, or by reactions with atmospheric  $\text{CO}_2$ .

Chemical reactions between components of cement and water produce new solid phases.<sup>5</sup> One of them is crystalline calcium hydroxide and another, the predominant one, microscopically amorphous, is "cement gel."

Cement gel is composed of gel particles and interstices among those particles, called gel pores. The solid part of the gel contains approximately  $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ . Its crystal structure, although highly disorganized, approximates that of tobermorite. Cement contains Al and Fe atoms as well as calcium and silicon atoms. They seem to play a relatively minor role as structural units but a more important role in determining rates of reaction.

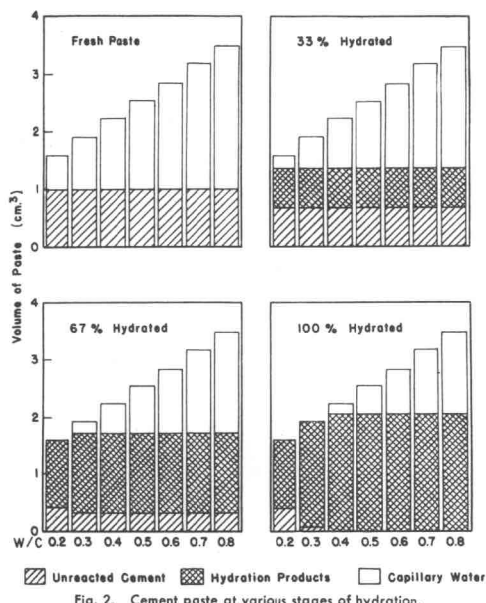


Fig. 2. Cement paste at various stages of hydration.

The Brunauer-Emmett-Teller method gives the specific surface of the solid part of the gel as about  $700 \text{ m}^2$  per  $\text{cm}^3$  of solid. This is equal to the specific surface of a sphere having a diameter of 86 a.u. The figure for specific surface was confirmed recently by small-angle scattering of X rays.

As seen with the electron microscope, cement gel consists mostly of fibrous particles with straight edges. Bundles of such fibers seem to form a cross-linked network, containing some more or less amorphous interstitial material.

The structure of paste is not identical with the structure of gel. Space within the visible boundaries of a specimen of paste contains gel, crystals of calcium hydroxide, some minor components, residues of the original cement, and residues of the original water-filled spaces in the fresh paste. These residues of water-filled space exist in the hardened paste as interconnected channels or, if the structure is dense enough, as cavities interconnected only by gel pores. These residual submicroscopic spaces are called capillary pores, or capillary cavities.

Thus two classes of pores within the boundaries of a body of paste are recognized: (1) gel pores, which are a characteristic feature of the structure of gel, and (2) capillary pores or cavities, representing space not filled by gel or other solid components of the system. Figure 1 shows a model of this concept of structure.

All the spaces, gel pores and capillary cavities, are submicroscopic. This fact, together with the hydrophilic character of the solid phase, accounts for the hygroscopicity of paste; water content is a function of ambient humidity.

Capillary porosity is greatest in a given paste when the paste is fresh. It is least when all the cement has become hydrated that can become hydrated under existing conditions. At any given stage of hydration, capillary porosity depends on the original proportion of water in the paste, which is usually expressed as the ratio of water to cement in the original mixture.

<sup>2</sup> See reference (4) of Bibliography on p. 6, this issue.

<sup>3</sup> See reference (7) of Bibliography.

<sup>4</sup> See reference (1) of Bibliography.

<sup>5</sup> (a) J. D. Bernal, "Structures of Cement Hydration Compounds," *Proc. Intern. Symposium Chemistry of Cement, 3rd Symposium, London, 1952*, pp. 216-60 (1954); *Ceram. Abstr.*, 1956, September, p. 184c.

(b) H. H. Steinhour, "Reactions and Thermochemistry of Cement Hydration at Ordinary Temperature," *Proc. Intern. Symposium Chemistry of Cement, 3rd Symposium, London, 1952*, pp. 261-333 (1954); *Ceram. Abstr.*, 1956, September, p. 184b.

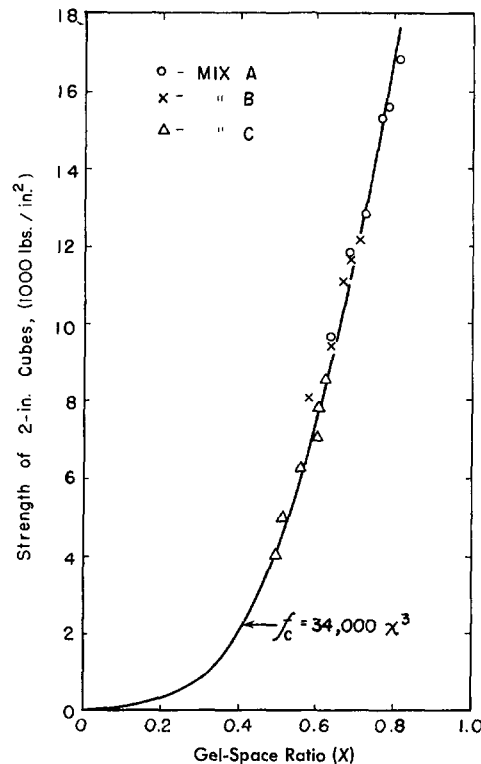


Fig. 3. Compressive strength vs. gel-space ratio for cement-sand mortars.  $f_c$  = compressive strength (lb. per sq. in.);  $x$  = gel-space ratio.

The products from 1 cm.<sup>3</sup> of cement require a little more than 2 cm.<sup>3</sup> of space. Therefore, the volume of water-filled space in fresh paste must exceed twice the absolute volume of cement, or some of the original cement must remain unhydrated. Cement gel can be produced only in water-filled capillary cavities, and when all those cavities become full, no further hydration of cement can occur. Figure 2 illustrates how hydration products gradually reduce the amount of capillary space, and in some cases eliminate it.

### III. Strength

As just indicated, cement gel is regarded as a solid substance having a characteristic relatively high porosity. From the assumption that this substance has intrinsic strength depending on its composition and structure, and that the strength of the gel is the sole source of the strength of hardened paste, it follows that the strength of a specimen of paste should be related to the amount of gel within its boundaries. Furthermore, an assumption that the relative strength of the paste depends on the degree to which gel fills the space available to it leads to the establishment of an empirical relationship between the porosity and the strength of a paste.

The degree to which gel fills available space can be expressed as a ratio of volume of gel to volume of available space. A typical relationship between compressive strength and gel-space ratio is shown in Fig. 3. The specimens repre-

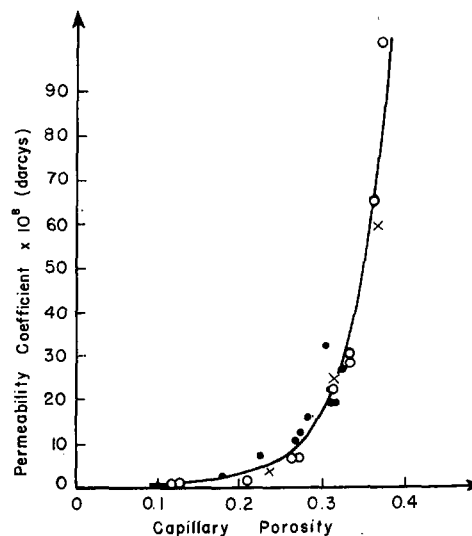


Fig. 4. Permeability vs. capillary porosity for cement paste. Different symbols designate different cements.

Table I. Comparison of Permeabilities of Rocks and Cement Pastes

Kind of rock	Permeability of rock (darcys)	Water-cement ratio*
Dense trap	$2.57 \times 10^{-9}$	0.38
Quartz diorite	$8.56 \times 10^{-9}$	.42
Marble	$2.49 \times 10^{-8}$	.43
Marble	$6.00 \times 10^{-7}$	.66
Granite	$5.57 \times 10^{-6}$	.70
Sandstone	$1.28 \times 10^{-5}$	.71
Granite	$1.62 \times 10^{-5}$	.71

\* Water-cement ratio of mature paste having same permeability as rock.

sented there contain aggregates, and whatever effect the aggregate had on strength is also reflected in the characteristics of the empirical curve. It is evident that the gel-space ratio is the dominant variable, and that strength increases in direct proportion to the cube of the increased gel-space ratio. The numerical coefficient probably depends principally on the intrinsic strength of the gel produced by this particular cement, and it would be different for a different cement.

As to the source of strength of the gel itself, there is no adequate theory. It is perhaps a fair speculation to assume that strength arises from two general kinds of cohesive bonds: (1) physical attraction between solid surfaces and (2) chemical bonds. Since gel pores are only about 15 a.u. wide on the average, it seems that London-van der Waals forces ought to tend to draw the surfaces together or at least to hold the particles in positions of least potential energy. In either case, those forces give rise to cohesion. Since water cannot disperse gel particles, i.e., since cement gel belongs in the limited-swelling category, it seems that the particles are chemically bonded to each other (cross-linked). Such bonds, much stronger than the van der Waals bonds, add significantly to

over-all strength; there is good reason to believe, however, that only a small fraction of the boundary of a gel particle is chemically bonded to neighboring particles and that physical bonds are perhaps the more important. Pertinent evidence is that converting gel to well-organized crystals by curing in steam at about 400°F. destroys cohesion.

#### IV. Porosity and Permeability

Any solid composed of particles randomly aggregated is both porous and permeable. Since cement paste has such structure, it is intrinsically porous and permeable. The densest possible completely hydrated cement paste has a porosity of about 26%. The porosity of paste as a whole is usually greater, and it depends on the original water content and on the extent to which space has become filled with hydration products. It depends, therefore, on the original water-cement ratio and on the conditions of curing.

The permeability of a granular solid depends on porosity and on the size and shape of the pores. In such solids, size of pore can be expressed in terms of hydraulic radius, which is the quotient of water-filled space by the boundary area of that space. Knowing the porosity of a paste and the specific surface of the gel it contains, one can calculate the hydraulic radius. The hydraulic radius of the pores in the gel itself is found to be about 5 a.u. Resistance to flow through pores so small is exceedingly high. Measurements show that the coefficient of permeability of the gel itself is about  $7 \times 10^{-11}$  darcys.\*

The permeability of paste as a whole depends mostly on its capillary porosity, for the resistance to flow through the capillary cavities is much smaller than that through the gel. The relationship between permeability and capillary porosity is shown in Fig. 4. Paste such as is produced normally in concrete of good quality has a capillary porosity of 30 to 40% and, as seen in Fig. 4, is from 20 to 100 times as permeable as cement gel itself. It is, however, less permeable than many natural rocks, as may be seen by the data shown in Table I.

#### V. Instability of Volume

As with other colloidal hydrophilic materials, cement gel shrinks and swells with changes in moisture content, and its response to change in temperature is complex. Noncolloidal components of paste, and the mineral aggregate of concrete, restrain most of the shrinking and swelling of gel, but the remainder, which accounts for some characteristic volume changes of concrete, is commercially significant. Typical shrinkage of paste at constant temperature, caused by drying from the saturated state, is shown in Fig. 5. Shrinkage is manifestly a complex function of the change in relative humidity in the pores of the paste.

Change in volume caused by change in temperature also is complex. In Fig. 6 the dashed line indicates the change in volume produced by a slow change in temperature with the specimen kept fully saturated at all stages of the change. This line represents the ordinary thermal contraction shown, for example, by metallic solids.

The solid line *AB* is the locus for a specimen of paste not quite saturated with water. When such a specimen is cooled, it undergoes ordinary thermal contraction and in addition a shrinkage that is called *hygrothermal shrinkage*. The amount of such shrinkage is indicated by the vertical distance from a point on line *AB* to the corresponding point directly above it on the dashed line.

The locus *BC*, showing lack of reversibility, and residual expansion, is indicative of still more complexities of behavior that are not discussed here.

The state of shrinking or swelling depends on the amount of water adsorbed by the gel. This may range from none to a maximum which represents a state of saturation. The amount of water that gel is able to adsorb increases as tem-

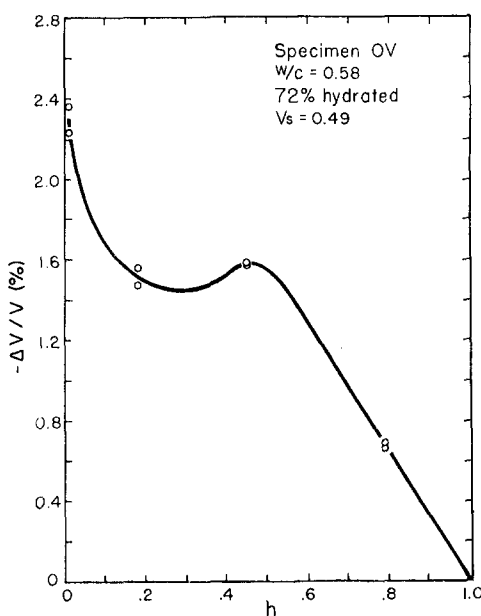


Fig. 5. Drying shrinkage of cement paste.  $\Delta V/V$  = fractional volume change;  $V_s$  = solids per unit volume of paste;  $h$  = relative humidity.

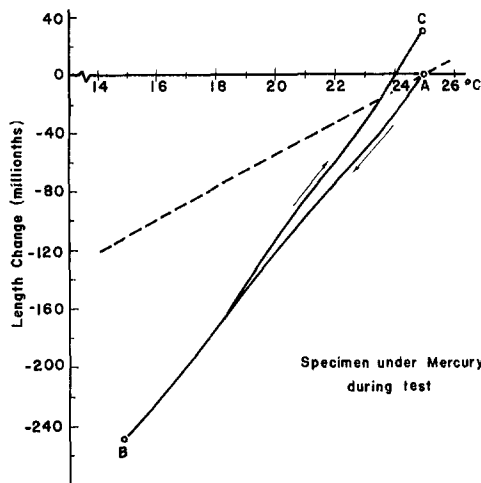


Fig. 6. Hygrothermal effects in cement paste.

\* A flow rate of 1 cm.<sup>3</sup> per second through an area of 1 sq. cm. under a pressure gradient of 1 atm. per cm. with a fluid having a viscosity equal to 1 centipoise equals 1 darcy.

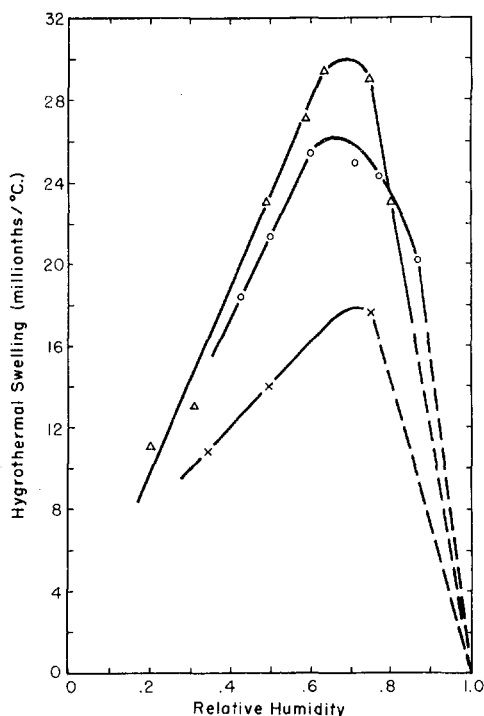


Fig. 7. Hygrothermal swelling of cement paste. Two top curves, data of Meyers (see footnote 6); bottom curve, data of Virronnaud and van Thanh (see footnote 7).

perature decreases. When temperature drops and no extra water is available, the gel becomes relatively less saturated, and it shrinks. The amount of shrinkage thus induced depends on the state of saturation of the gel and hence on the internal humidity of the specimen, as indicated in Fig. 7.

In Fig. 7 the amount of hygrothermal volume change is shown in relation to the internal humidity of the specimen. It is expressed as millionths per degree and is therefore numerically comparable with the ordinary thermal coefficient. Since a typical value for a thermal coefficient is 11 millionths per °C., these figures indicate that the maximum hygrothermal swelling effect may be two to three times as great as the normal thermal coefficient.

Such effects appear to be understandable consequences of the colloidal state of the hydration products of Portland cement. A comprehensive hypothesis about the mechanism of volume changes produced by changes in temperature and in the humidity is now being developed.

<sup>6</sup> S. L. Meyers, "Thermal Expansion Characteristics of Hardened Cement Pastes and of Concrete," *Highway Research Board, Proc.*, **30**, 193-203 (1950).

<sup>7</sup> L. Virronnaud and N. van Thanh, "Dilatometer with an Optical Tripod; Tests and Results of Experiments," *Ann. inst. tech. bâtiment et trav. publ.*, **7**, 522-40 (1954) (in French).

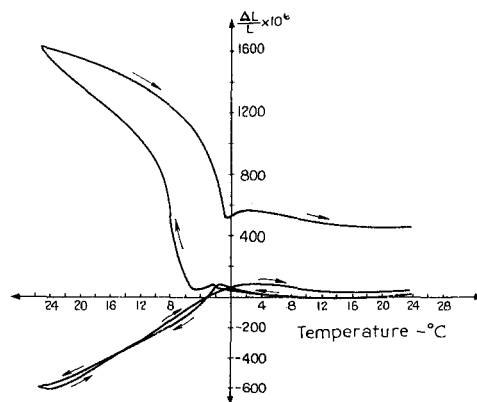


Fig. 8. Effect of entrained air in cement paste. Upper curve shows dilation produced in paste containing no bubbles. Lower curve shows same paste with entrained air.  $\Delta L/L$  = fractional length change.

## VI. Freezing

Water can be caused to freeze in capillary cavities, but it cannot freeze in gel pores. Gel pores apparently are too small to permit nucleation of ice crystals. The fraction of total evaporable water that can be frozen is a function of temperature and time, as would be expected from dimensional factors and the effects of solutes in the freezable water.

Freezing of water in a saturated paste causes the paste to dilate destructively unless special steps are taken to protect the paste from the pressure that causes dilation. The pressure that causes dilation comprises two kinds: (1) hydraulic pressure that, during freezing, forces water away from freezing sites (the water-filled capillary cavities) and (2) osmotic pressure produced by water tending to enter partly frozen capillary cavities. Either kind of pressure can be controlled by filling the fresh paste with microscopic air bubbles which remain in the hardened paste. The bubbles must be so numerous that they are separated by layers of paste only a few thousandths of an inch thick. Effects of such bubbles on dilation during freezing are shown in Fig. 8.

When the air bubbles are sufficiently close together, freezing produces shrinkage rather than dilation. Under these circumstances shrinkage is caused by transfer of water from the paste to the air bubbles by osmosis.

## VII. Other Properties

Cement gel surrounds and isolates each noncolloidal particle in concrete. Mechanical properties of concrete are therefore characterized by the mechanical properties of the gel, to an important degree. Stress-strain-time relationships are to be explained largely in terms of the characteristics of cement gel. Most of the research needed in this field is yet to be done.

## VIII. Summary

Research started in the Portland Cement Association laboratories about 20 years ago on the properties of Portland cement paste produced important basic knowledge about the properties and behavior of concrete. The principal research technique was water-vapor adsorption interpreted by the Brunauer-Emmett-Teller theory. More recently, other tech-

niques including X-ray and electron microscopy have been introduced. Knowledge of the physical and chemical constitution of cement paste provides useful conceptual models for dealing with practical problems. Strength, permeability, and volume instability are basically related to the colloidal state

of the major product of the reactions between Portland cement and water, and to the spatial concentration of this product (cement gel). The mechanics and physical chemistry of frost action in concrete was established in terms of the physical characteristics of cement paste.

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