

# The Nature of Concrete

Richard A. Helmuth<sup>1</sup>

## PREFACE

T. C. Powers authored the first version of this chapter, which was published in *ASTM STP 169A* in 1966. His chapter was reprinted without revision in *ASTM STP 169B* in 1978. Readers are advised that his version is still worthwhile reading. The present chapter condenses some of that work and includes more recent material.

## INTRODUCTION

For thousands of years, mankind has explored the versatility of materials that can be molded or cast while in a plastic state and then harden into strong and durable products [1]. As with ceramics and gypsum plasters, lime mortars and pozzolanic concretes provided engineers with economical materials for production of diverse utilitarian and aesthetically pleasing structures. Modern concretes preserve these ancient virtues while greatly extending the range of technically achievable goals.

### Concrete-Making Materials—Definitions

Concrete is defined in ASTM Terminology Relating to Concrete and Concrete Aggregates (C 125) as a composite material that consists essentially of a binding medium within which are embedded particles or fragments of aggregate; in hydraulic-cement concrete, the binder is formed from a mixture of hydraulic cement and water. Hydraulic-cement concretes are those most widely used in the United States and world wide. Hydraulic cement is defined in ASTM Terminology Related to Hydraulic Cement (C 219) as a cement that sets and hardens by chemical interaction with water and that is capable of doing so under water. Portland cement is the most important hydraulic cement. It is produced by pulverizing portland cement clinker, consisting essentially of hydraulic calcium silicates, usually by intergrinding with small amounts of one or more forms of calcium sulfate in order to control reaction rates.

Aggregate is defined in ASTM C 125 as granular material, such as sand, gravel, crushed stone, or iron blast-furnace slag, used with a cementing medium to form

hydraulic-cement concrete or mortar. Detailed descriptions of these and other materials for making concrete and their effects on concrete properties are given in other chapters in this work.

Typical hydraulic-cement concretes have volume fractions of aggregate that range approximately from 0.7 to 0.8. The remaining volume is occupied initially by a matrix of fresh cement paste consisting of water, cement, and admixtures, that also encloses air voids. While the aggregates occupy most of the volume, they are relatively inert and intended to be stable. It is the cement paste matrix that undergoes the remarkable transformation from nearly fluid paste to rock-hard solid, transforms plastic concrete into an apparent monolith, and controls many important engineering properties of hardened concretes.

### Scope

Hydraulic-cement concretes may be properly designed to provide properties required for widely varying applications at low life-cycle cost. If not properly designed or produced, or if exposed to service conditions not understood or unanticipated, premature failures may result. Successful use depends on understanding the nature of concrete.

The scope of this examination of the materials science of concrete is mainly confined to concretes made with portland cements, with or without mineral and chemical admixtures. The focus is mainly on how we understand concrete performance in ordinary construction practice. That understanding is based on knowledge of its constituents, and their physical and chemical interactions in different environments.

## FRESHLY MIXED CEMENT PASTE AND CONCRETE

### Water in Concrete

The properties of fresh cement paste (FCP) and concrete depend on the structure and properties of ordinary water, which are unusual for a substance of such low molecular weight. Each molecule has a permanent dipole moment. Strong forces of attraction between these highly polar molecules result in unusually high melting and boiling temperatures, heats of fusion and vaporization, viscosity, and surface tension [2].

<sup>1</sup> Materials research consultant, Construction Technology Laboratories, Skokie, IL 60077-1030.



## 6 TESTS AND PROPERTIES OF CONCRETE

In addition to dipole interactions, hydrogen bonding between water molecules and thermal agitation affect the structure of water and aqueous solutions. Hydrogen bonding causes formation of clusters of molecules, the degree of association depending on the temperature. Thermal agitation, including translational, rotational, and vibrational motions, tends to disrupt the structure.

In the liquid state, the molecules are easily oriented in an electric field so that water has a large dielectric constant (78.6 at 25°C). This orientation, as well as molecular, polarization means that the electric field strength and the forces between charged particles, such as ions in solution, are reduced to  $1/78.6$  relative to that in vacuum (or air). Because of its high dielectric constant, water is an excellent solvent of salts; the energy of separation of two ions in solution is an inverse function of the dielectric constant of the solvent. Ions in solution are not separate entities but have water molecules attached to them by ion-dipole bonds.

A few minutes after mixing begins, about half of the cement alkalis are dissolved so that the concentration of the alkali and hydroxyl ions may commonly be 0.1 to 0.4 mol/L, depending mainly on the water/cement ratio and the cement alkali content [3]. At 0.3 mol/L, each ion would be separated from like ions, on the average, by about 1.7 nm, or about five water molecules.

### Interparticle Forces

Atoms in solids near the surface are distorted and shifted relative to their positions in the interior because of the unsatisfied atomic bonds at the surface. These distortions of the surface produce net positive or negative surface charge, and elastic excess surface free energy. Silicon on the surface of quartz in aqueous solutions attract hydroxyl ions, reduce pH, and produce surfaces with excess negative charge [4]. Particles with surface charges of the same sign repel each other in suspensions and tend to remain dispersed. Particles of opposite sign attract each other and flocculate [5].

In addition to these coulombic and polar forces, which can be attractive as well as repulsive, there are forces between solids, atoms, and molecules that are always attractive. These van der Waals, or dispersion, forces exist because even neutral bodies constitute systems of oscillating charges that induce polarization and oscillating dipole interactions [5]. The combined action of the different forces cause sorption of water molecules and ions from solution, which can neutralize surface charge and establish separation distances of minimum potential energy between solid particles [6]. The mechanical properties of both fresh (FCP) and hardened (HCP) cement pastes and concretes depend on these forces.

### Fresh Cement Paste Structure

Modern portland cements have mass median particle sizes that are about 12 to 15  $\mu\text{m}$  (diameter of an equivalent sphere), almost all particles being smaller than 45  $\mu\text{m}$ , and very little of the cement being finer than 0.5  $\mu\text{m}$ . During grinding, calcium sulfates grind faster and usually

become much finer than the clinker. After mixing with water, the solid surfaces are covered by diffuse layers of adsorbed ions, oriented-dipole water molecules, and solvated ions, forming film thicknesses at least several times the size of the water molecule (0.3 nm). These films both separate and weakly bind the solid particles into the floc structure.

In FCP and concretes made with high doses of water-reducing admixtures, cement particles may become almost completely dispersed (deflocculated) because large organic molecules are adsorbed on their surfaces, displacing water films, and greatly reducing attractive forces between cement particles. Mineral admixtures that contain small percentages of ultrafine (submicron) particles may also produce dispersion of cement particles by adsorption of the ultrafine particles on the surfaces of the larger particles. This specific kind of fine-particle effect is responsible for the improved flow of many portland cement/fly ash mixtures [7,8].

The average thickness of films of water separating dispersed particles in the paste depends on the water-cement ratio (w/c) and the cement fineness. A first approximation to the average thickness of these films is given by the hydraulic radius: the volume of water divided by the specific surface area, if it assumed that the films are thin compared with the particle sizes. If that were so, the calculated thickness is 1.2  $\mu\text{m}$  for cement of specific surface of 430  $\text{m}^2/\text{kg}$ , mixed at 0.5 w/c [9]. Since the assumption is not valid for the finer-size fractions (Fig. 1) and much of the fine fraction in portland cement is composed of calcium sulfates and other phases that dissolve within minutes after mixing begins, the average film thickness for the larger particles in that paste is probably about 2  $\mu\text{m}$ . For flocculated particles, the films are much thinner between adjacent particles, so that much of the water is

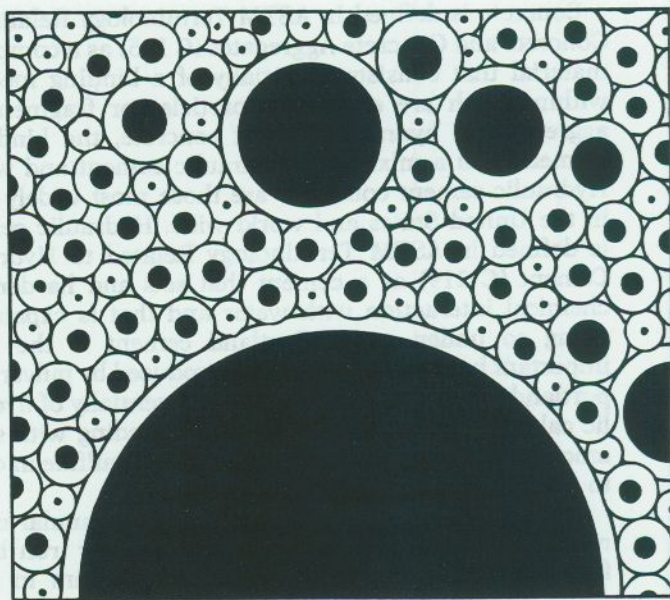


FIG. 1—Idealized model of the structure of fresh paste with cement particles (up to 30  $\mu\text{m}$  diameter) uniformly dispersed in water.



forced into relatively large cavities or capillary-like channels.

## CEMENT HYDRATION AND STRUCTURE FORMATION

### Early Hydration Reactions

Chemical reactions between portland cements, water, and admixtures are usually well controlled and follow a definite sequence [10]. Initial partial dissolution of alkali sulfates, calcium sulfates, aluminates, and silicates rapidly increase concentrations of ions in solution to supersaturation levels (except for alkali hydroxides), and produce calcium aluminate, sulfoaluminate, and silicate hydrates on the surfaces of the cement and other particles. Within minutes, these reactions are slowed by coatings of hydrates on the reaction surfaces that produce a "dormant" period of slow reaction as ettringite continues to form and calcium supersaturation persists. Eventually, calcium hydroxide begins to crystallize from solution, reducing the calcium concentration and accelerating the dissolution and reaction of the silicates. Setting results from the growth of acicular crystallites of calcium silicate hydrates that bridge the water-filled void spaces. Reaction of the aluminates to form ettringite continues until the readily soluble calcium sulfates are depleted. The concentration of sulfate in solution then decreases, causing dissolution of some ettringite, and a period of acceleration of hydration of the aluminate and ferrite phases.

During the reactions prior to setting, two and sometimes three kinds of volume changes occur. Sedimentation causes subsidence of the floc structure and collection of bleeding water on the top surface, if evaporation is not excessive. If the surface becomes partly dried, capillary tension in the water can cause plastic shrinkage and cracks. Chemical shrinkage is the volume change that results from formation of hydrates that have less solid volume than the volume of water and solids reacted. While the paste is plastic, the entire volume of paste undergoes chemical shrinkage. After setting, the external dimensions remain essentially fixed and additional water must be imbibed to keep the pores saturated with water. If sufficient water is not imbibed, the paste becomes self-desiccated.

If the early reactions of  $C_3A$  and  $C_4AF$  are not well controlled by sufficiently rapid dissolution of calcium sulfates, thin platy crystals of calcium aluminoferrite monosulfate hydrate (AFm) form in the solution instead of dense coatings of ettringite, the AFt or trisulfate phase, resulting in premature stiffening, or in extreme cases, "flash set" [11]. If, on the other hand, the aluminate reactions are too slow to consume all of the rapidly dissolving calcium sulfates, crystallization of fine needles of gypsum from solution will cause early stiffening referred to, in the extreme, as "false set." If there is a slight imbalance in reaction rate control, rapid slump loss of concrete may result from adsorption of water-reducing admixtures from solution by high surface area reaction products. The balance of these reaction rates may be upset in some (incompatible)

cement/admixture combinations so that premature stiffening occurs, especially in low water/cement ratio concrete.

### Hardening Reactions and Microstructure

Portland cements continue to react with water at diminishing rates following setting. After 24 h at room temperature, 30 to 40% of the cement is usually hydrated, forming coatings of increasing density and thickness around each particle (Fig. 2). Larger clinker particles hydrate by partial dissolution and partly by in situ reaction so that a pseudomorph of inner products is formed within the boundaries of the original grain. Depth of reaction increases with time, but at decreasing rates so that the larger particles may have unhydrated cores even after years of moist curing. The dissolved portion forms outer products in the water-filled space near the grains. The calcium silicates produce crystalline calcium hydroxide and nearly amorphous calcium silicate hydrate (C-S-H gel) that engulf crystalline phases formed by the early reactions. Capillary pores remaining in mature HCP increase in size with  $w/c$  and have diameters ranging from 10  $\mu\text{m}$  to 10 nm [12].

Powers defined the hydration products of portland cements as "cement gel," recognizing that they contained both C-S-H gel and crystalline products, and essential micropores [13]. Early research showed that typical cement gels had minimum porosities of about 30%, and specific surface areas of about 200  $\text{m}^2/\text{g}$ , as calculated by BET theory from water-vapor adsorption data obtained after first drying to remove all of the evaporable water. These studies also showed that at 0.38  $w/c$  all of the capillary pore space was just filled by maximum density gel when all the cement was hydrated. Mixtures made with water/cement ratios less than 0.38 cannot be completely hydrated; the amount of cement that can hydrate is proportionately less because hydration virtually stops when the capillary space is filled with gel of minimum porosity. Saturated HCP made at water/cement ratios above 0.38 have remaining capillary pore space (by definition), when completely hydrated, equal to the excess above 0.38. Partially hydrated mixtures have proportionately less gel and more capillary space. Cements of different compositions behave similarly, with similar values for the constants.

Later work has shown that drying and rewetting alter the microstructure and that different adsorbates measure different surface areas. The sheet-like crystallites are imperfectly stacked and separated by interlayer adsorbed water at relative humidities down to 11% relative humidity (RH). Before drying or aging, cement gels have specific surface areas of C-S-H monomolecular sheets, about 700  $\text{m}^2/\text{g}$ , as measured by small-angle X-ray scattering [14]. Because of the large internal surface area, the distances between solid surfaces of the pores in the gel approach the size of water molecules; most of the gel water is close to the surfaces. In such systems, it is not certain how much of the volume change of chemical shrinkage should be attributed to the reaction itself, and how much to the possible change of density of water in pores as it is adsorbed on newly created surfaces. If it is assumed [15] that the adsorbed solution has the same density as that



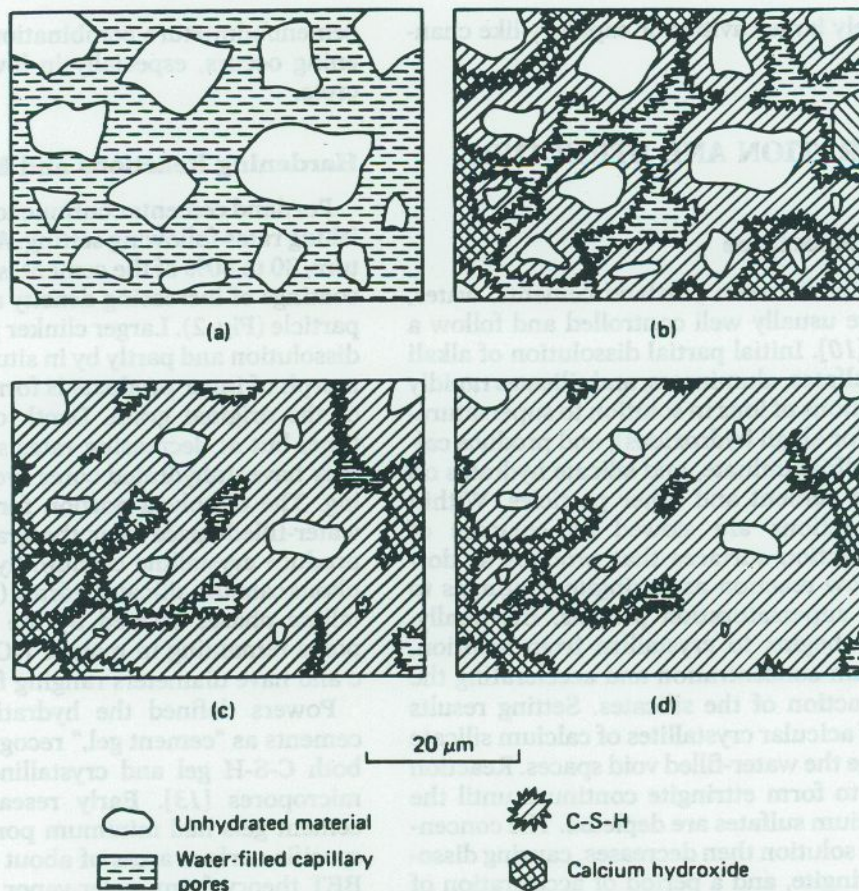


FIG. 2—Representation of microstructural development in portland cement pastes; fine particles omitted for clarity; (a) initial mix, (b) 7 days, (c) 28 days, and (d) 90 days [12]. Reprinted with permission by Academic Press.

in large pores, the apparent specific volumes of the non-evaporable (hydrate) water and solids were found to be 0.74 and 0.398  $\text{cm}^3/\text{g}$ , respectively, and minimum porosity of the gel to be 30%. The amount of chemical shrinkage is expressed in terms of the change in the apparent specific volume of the reacted water, from 0.99 to 0.74  $\text{cm}^3/\text{g}$ , and the amount,  $w_n$ , of that nonevaporable water: 0.25  $w_n$ .

Hydration of each unit volume of cement produces about 2.2 volumes of gel. This value does not depend on the assumption concerning specific volumes. Although chemical shrinkage slightly reduces the space filling by solid hydrates, cement gel is an even more effective filler of the capillary space than the solid hydrates because of the 30% porosity of the gel.

### Effects of Drying

Loss of moisture in drying atmospheres partially empties the largest capillaries at exposed surfaces. Adsorbed water remains on capillary walls as concave menisci form and progress into smaller interconnected pores. Menisci curvature and capillary tension in the remaining water are increased as the relative humidity is decreased down to about 45% RH, below which sorption effects prevail. Reductions in relative humidity slow the hydration rate;

at 80% RH, hydration is insignificant. Drying causes shrinkage of hardened cements and major alterations of the gel microstructure. Shrinkage and stabilization of HCP by drying are complex and partially irreversible processes involving capillary, sorption, and dehydration effects.

Capillary tension in the pore water increases as the relative humidity decreases below that of the pore solution. For dilute solutions, tensions increase to about 97 MPa (14 000 psi) at 50% RH. At lower relative humidities, 40 to 45% RH, the tension exceeds the cohesive strength of water in capillaries and the menisci can no longer exist [13]. Above 45% RH, capillary tensile stress in the water must be balanced by compressive stresses in the solid structure, in which stress concentrations can produce irreversible effects. When the pores are nearly water-filled, the average stress is that produced by tension in the cross-sectional area that is pore water; the resulting strain in the solid structure is the beginning of the drying shrinkage. As the capillaries empty the water-filled cross-section is reduced, but the tension increases and causes local collapse of less dense regions of the outer product, and enlargement of large pores. Desorption causes shrinkage by permitting solids to come together, and by increasing solid surface tension. Well-crystallized AFm and AFt hydrated phases also dehydrate, decreasing lattice spac-



ings, so that elastic restraint of the shrinking C-S-H gel is reduced.

HCP cured for six months before drying at 47% RH for the first time shows both reversible and irreversible water loss and shrinkage [16]. Increased drying time causes increased water loss, shrinkage, and greatly reduced internal surface area. Rewetting causes sorption and swelling that only partly reverses the first water loss and shrinkage (Fig. 3). The irreversible component of shrinkage increases with water-cement ratio (0.4 to 0.6) from 0.2 to 0.4%, whereas the reversible component (after stabilization by drying) is only 0.2% and nearly independent of porosity. Even without drying, long-term aging in moist conditions causes age stabilization at water-cement ratios above 0.4 so that even the irreversible shrinkage tends to become porosity independent at about 0.2%. The irreversible shrinkage volume is only about half of the volume of the irreversibly lost water, if we assume its specific volume to be 0.99, which suggests that some pores emptied during drying become closed off and are not accessible during rewetting [17], or have reduced capacity. Below 11% RH, loss of interlayer water is accompanied by large partially irreversible shrinkage and water loss effects [18].

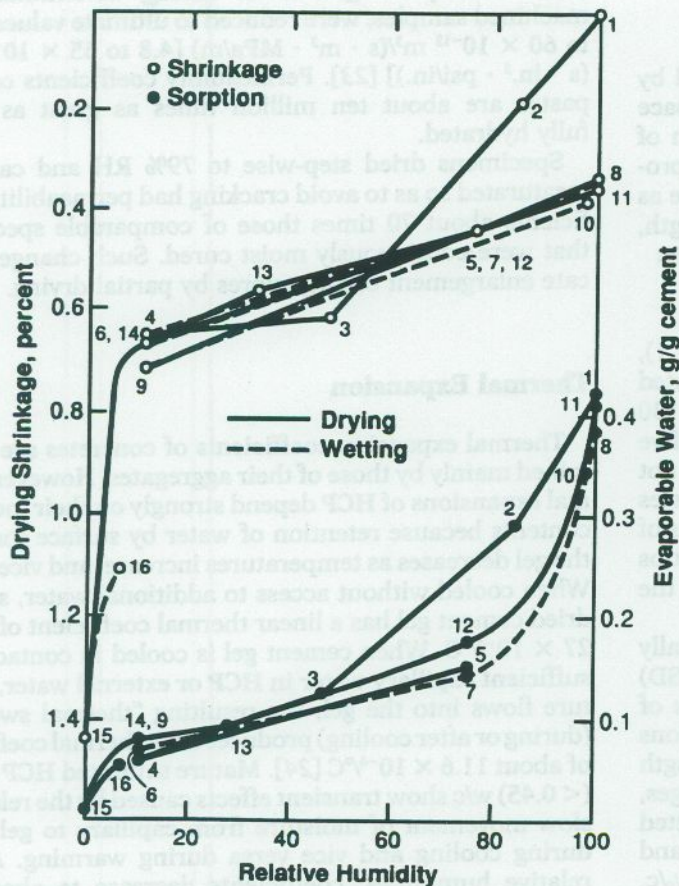


FIG. 3—Drying shrinkage, rewetting swelling, and sorption of 0.6 w/c hardened portland cement paste. Numbers indicate sequence of measurements [16]. Reprinted with permission by the Portland Cement Association.

## CEMENT PASTE STRUCTURE-PROPERTY RELATIONSHIPS

### Rheology of Fresh Cement Paste

When cements are mixed with sufficient water and intensity, dry agglomerates of fine particles are first dispersed and then tend to form a floc structure, which is continuously broken down by mixing if the early reactions are well controlled. When mixing is stopped, the floc structure reforms until it becomes an essentially continuous floc. Cement pastes in this condition are actually weak solids with measureable shear stress yield values that depend on water/cement ratio, cement fineness, and other factors. Typical values for portland cements without admixtures range roughly from 10 to 100 Pa (0.0014 to 0.014 psi) for w/c from 0.6 to 0.35 [9]. Prior to yield, the pastes are elastic and shear strains can reach about 20 deg, indicating a rubber-like elasticity.<sup>2</sup> They are also plastic solids with typical values for plastic viscosity that range roughly from 10 to 100 mPa · s (centipoise). High water/cement ratio pastes seem to be liquid and may be poured easily because their yield stress values are so low. At low water/cement ratios, they are obviously plastic and can be deformed by moderate forces. Standard test pastes made at normal consistency have w/c about 0.25 and yield stress values of about 2000 Pa (0.29 psi) [9].

At ordinary temperatures, portland cement hydration reactions cause progressive stiffening and setting during the first few hours. Yield stress values increase to  $2 \times 10^4$  Pa (2.9 psi) at initial set and  $1 \times 10^5$  Pa (14 psi) at final set [9].

### Elasticity and Creep

Hardened cement pastes are not perfectly elastic, but are viscoelastic solids. Internal friction, creep, and stress relaxation are useful in dissipating vibrational energy, and preventing excessive stress concentrations in concrete. They are a result of redistribution of moisture, viscous flow of gel, and dissolution of solids under stress and recrystallization in pores. These processes, and slow growth of cracks, are thermally activated processes in which random thermal motions provide sufficient energy, in addition to the applied stress, at sites of adsorbed water molecules, or solid-solid bonds, to exceed the bond energy. Short-term loading tests of water-saturated HCP show that creep and creep recovery versus time curves are bimodal and consist of a component with retardation times ranging from 0.2 to 2 s and a slower component that ranged over weeks. The short-time component was identified with redistribution of water in capillary pores [19]. Diffusion of strongly adsorbed and hydrate water, recrystallization, and other irreversible changes are believed to contribute to the slower processes. Long-term creep of HCP can be several times the elastic deformation.

<sup>2</sup> Unpublished work done at Construction Technology Laboratories for the Portland Cement Association under Project HR 7190.



## 10 TESTS AND PROPERTIES OF CONCRETE

Elastic moduli can be measured precisely by dynamic methods and are found to vary with porosity,  $\epsilon$ , according to

$$E = E_0(1 - \epsilon)^3$$

in which  $E_0$  is the modulus at zero porosity [20]. If the capillary porosity is used,  $E_0$  is the modulus of the cement gel, about 34 GPa ( $5 \times 10^6$  psi) for Young's modulus of water-saturated pastes. If the total porosity (including that of the gel) is used,  $E_0$  is an average modulus for the solids, about 76 GPa ( $11 \times 10^6$  psi). Equations of the same form apply for the shear and bulk moduli. Drying significantly reduces Poisson's ratio, from about 0.3 to 0.18, and the bulk modulus; stresses are carried by at least some of the water in pores.

Elastic moduli of saturated pastes increase moderately as the temperature is decreased to 0°C. At temperatures in the freezing range down to about -60°C, ice formation in capillaries increases the moduli as ice contents increase. At still lower temperatures, the moduli increase more rapidly; internal friction reaches a peak at about -90°C as the gel water viscosity increases as it approaches its glass transition temperature at -119°C [21]. The gel water (adsorbed solution) does not freeze to ice, but becomes a glassy solid.

### Compressive Strength

The fraction,  $X$ , of the available space that is filled by cement gel at any stage of hydration is called the gel/space ratio. It can be calculated from the w/c, the fraction of the cement that has hydrated, and the volume of gel produced. For fully hydrated cement pastes, it is the same as  $(1 - \epsilon)$  for the capillary porosity. Compressive strength,  $f_c$ , at different w/c and ages can be simply expressed as

$$f_c = f_{cg} X^n$$

in which  $f_{cg}$  is the intrinsic strength of the gel (at  $X = 1$ ), and  $n$  has a value of about 3. Use of this equation indicated intrinsic strengths of cement gels ranging from 90 to 130 MPa (13 000 to 18 500 psi) in mortars made with five different cements [13]. However, mortars probably do not provide accurate measures of intrinsic strengths of pastes because of transition zones at aggregate surfaces. Tests of cement pastes yielded higher strengths at gel/space ratios calculated to be equal to those of mortars made with the same cement.

More recent testing of pastes made with both normally ground and controlled-particle-size-distribution (CPSD) portland cements has shown that intrinsic strengths of the gel do not depend on cement particle size distributions over the range investigated, although rates of strength development do. However, paste strengths at several ages, defined different straight lines for each w/c when plotted against  $X^3$ , and indicated intrinsic strengths of 134 and 97 MPa (19 400 and 14 000 psi) at 0.36 and 0.54 w/c, respectively [22]. This result indicates that the intrinsic strength of the gel formed at w/c above about 0.38 decreases with increasing w/c, in contrast with Powers' mortar data at different w/c.

If we consider fresh cement pastes to have strengths equal to their yield stress values, typically 10 to 100 Pa, and ultimately harden to compressive strengths of 10 to 100 MPa, the increase is about one million times.

### Permeability

HCP and concretes are porous and permeable to water, dissolved material, and gases. When water-saturated, flow is proportional to hydraulic pressure differences, if corrections are made for osmotic effects; concentration gradients cause osmotic flow to higher concentrations, and diffusion of ions to lower concentrations. When partly dried, relative humidity and moisture gradients cause flow because of capillary tension, and diffusion along surfaces, and in the vapor phase. The same changes of microstructure that cause great changes of elastic moduli and strength of cement pastes during hardening cause reductions of permeability.

Permeability coefficients of fresh portland cement pastes of 0.5 and 0.7 w/c, calculated from bleeding data, range from  $5.7$  to  $20 \times 10^{-5} \text{ m}^3/(\text{s} \cdot \text{m}^2 \cdot \text{MPa/m})$  [ $6.1$  to  $22 \times 10^{-4} \text{ in.}^3/(\text{s} \cdot \text{in.}^2 \cdot \text{psi/in.})$ ], respectively. These coefficients for hardened pastes of the same water-cement ratios after prolonged moist curing, determined with machined samples, were reduced to ultimate values of  $4.5$  to  $60 \times 10^{-12} \text{ m}^3/(\text{s} \cdot \text{m}^2 \cdot \text{MPa/m})$  [ $4.8$  to  $65 \times 10^{-11} \text{ in.}^3/(\text{s} \cdot \text{in.}^2 \cdot \text{psi/in.})$ ] [23]. Permeability coefficients of fresh pastes are about ten million times as great as when fully hydrated.

Specimens dried step-wise to 79% RH and carefully resaturated so as to avoid cracking had permeability coefficients about 70 times those of comparable specimens that were continuously moist cured. Such changes indicate enlargement of large pores by partial drying.

### Thermal Expansion

Thermal expansion coefficients of concretes are determined mainly by those of their aggregates. However, thermal expansions of HCP depend strongly on their moisture contents because retention of water by surface forces in the gel decreases as temperatures increase, and vice versa. When cooled without access to additional water, slightly dried cement gel has a linear thermal coefficient of about  $27 \times 10^{-6}/^\circ\text{C}$ . When cement gel is cooled in contact with sufficient capillary water in HCP or external water, moisture flows into the gel; the resulting "thermal swelling" (during or after cooling) produces a net thermal coefficient of about  $11.6 \times 10^{-6}/^\circ\text{C}$  [24]. Mature saturated HCP of low ( $< 0.45$ ) w/c show transient effects caused by the relatively slow movement of moisture from capillary to gel pores during cooling and vice versa during warming. At low relative humidities, coefficients decrease to about the same value as for saturated pastes. Such differences between thermal expansion coefficients of pastes and aggregates may cause excessive local stresses in concretes unless relieved by creep.



## CONCRETE AGGREGATES

The major constituents of ordinary concretes are crushed rocks or gravels and sands used as coarse and fine aggregates. Materials used in concrete usually need to be processed to be of proper size gradation and relatively free of deleterious substances.

### Specific Gravity and Porosity

It is useful to classify aggregates by specific gravity and porosity into lightweight, ordinary, and heavy-weight materials (ASTM C 125). Lightweight aggregates are used to reduce dead loads and stresses, especially in tall structures, and to provide thermal insulation. Heavy-weight aggregates are used mainly for radiation shielding. Ordinary aggregates, such as sandstone, quartz, granite, limestone, or dolomite, have specific gravities that range from about 2.2 to 3.0. Densities of ordinary concretes range from about 2.24 to 2.4 Mg/m<sup>3</sup> (140 to 150 lb/ft<sup>3</sup>).

Porosity reduces weight, elastic moduli, and strength of aggregates and concretes, although the effect on strength may be significant only in high-strength concrete. Porosity increases permeability to fluids and ions in pore solutions, especially if the pores are open (interconnected) rather than closed. Freezing of water in pores in aggregate particles in moist concrete can cause surface pop-outs or D-cracking in concrete pavements [12].

### Strength of Aggregate Particles

Strength test results of individual samples of rock from any one source show wide variations that are caused by planes of weakness, and their different orientations, in some of the samples. Such weaknesses in the rock samples may not be significant once the rock has been crushed to the sizes used in concrete so that the higher, or at least average, strengths may be more significant. Ten different common types of rock tested at the Bureau of Public Roads had average compressive strengths that ranged from 117 MPa (16 900 psi) for marble to 324 MPa (47 000 psi) for felsite [25]. A good average value for concrete aggregates is about 200 MPa (30 000 psi), but many excellent aggregates range in strength down to 80 MPa (12 000 psi) [26]. These values are generally above strengths of ordinary concretes.

### Permeability

Measurements of coefficients of permeability to water of selected small (25-mm (1-in.) diameter) pieces of rock, free of visible imperfections, yield values several orders of magnitude smaller than for larger specimens, which probably contained flaws [23]. Values for the small specimens ranged from  $3.5 \times 10^{-13}$  m<sup>3</sup>/(s · m<sup>2</sup> · MPa/m) [ $3.8 \times 10^{-12}$  in.<sup>3</sup>/(s · in.<sup>2</sup> · psi/in.)] for a dense trap rock, to  $2.2 \times 10^{-9}$  m<sup>3</sup>/(s · m<sup>2</sup> · MPa/m) [ $2.4 \times 10^{-8}$  in.<sup>3</sup>/(s · in.<sup>2</sup> · psi/in.)] for a granite. These values are equal to those measured for mature hardened portland cement pastes made at water cement ratios of 0.38 and 0.71, respectively, despite the low (less than 1%) porosities of these rocks.

## CONCRETE PROPORTIONING, STRUCTURE, AND PROPERTIES

### Proportioning and Consistency

Two basically different kinds of concrete mixtures must be distinguished. Nonplastic mixtures made with relatively small amounts of water show considerable bulking as water is added, and after compaction have sufficient strength to support their own weight. The concrete block industry is based on such nonplastic but cohesive mixtures. Void space in such mixtures is relatively high and filled mostly by air. The strength of the cohesive mixture results from capillary tension under meniscii bounding the water films on and between the solid particles, and solid surface forces. Strength and bulking increase to a maximum as water is added, and then decrease as the void space becomes nearly water filled and capillary tension is diminished. With sufficient water, the mixture is wetted so that surface meniscii and capillary tension disappear, void contents reach a minimum, and limited plastic deformation becomes possible. The remaining cohesive force is a result of interparticle attraction between closely spaced fine particles. This minimum void space contains about 12% air when such mixtures are compacted by ordinary means, and the cement content is not below a certain limit. The water content at minimum voids content is called the "basic water content" [6].

The consistency of cement paste at its basic water content is nearly the same as the normal consistency as defined in ASTM standards. Normal consistency pastes, and mortar or concrete mixtures made with different aggregates at their basic water contents, have slump values of about 42 mm (1.7 in.) in the standard test. Such concretes are much stiffer than the plastic mixtures commonly used in American practice that usually contain chemical admixtures and higher water contents. Further additions of water increase void volume, reduce interparticle forces, and increase the capacity for plastic deformation.

The main effect of adding increments of aggregate to paste is to reduce the amounts of voids and cement per unit volume. The total effect is not just that of volume displacement, because the cement paste void space is dilated by the added aggregate surfaces, as described in the next section. Also, when aggregate is introduced, plastic strains in the paste during compaction are necessarily greater and the mixture is stiffer than the paste. If such additions are begun using cement paste of the standard normal consistency, and if the same compacting force or energy is applied to the mixtures as to the paste, that consistency can be maintained constant if increments of water are added with each increment of aggregate. The ratio of the volume of water plus air to the total volume of solids (voids ratio) decreases with added aggregate, but not as much as without the added water, until a minimum voids content is reached, and then increases.

Consistency of concrete depends on consistency of cement paste as well as on dispersion of aggregate by sufficient paste volume for each particular aggregate. Although concrete yield stress values can be calculated



from slump values, there is as yet no valid method of calculation of concrete slumps from paste yield stress values for concretes made with different aggregates and proportions. For fixed proportions, the stiffer the paste, the stiffer the concrete, and such changes can be calculated from paste data for ordinary concretes.<sup>3</sup> In mixtures that are relatively rich in cement and paste volume, adding increments of aggregate does not greatly increase water requirements for flow. In leaner mixtures, particularly those with aggregate contents above those at minimum voids ratios, but below those very lean mixtures that require excess amounts of entrapped air, the water requirement is proportional to the volume fraction of aggregate in the total solids [6]. This range comprises much of the concrete made for ordinary use.

### Structure

The fine structure of fresh and HCP were described in earlier sections. However, the HCP matrix in mortars and concretes differ in pore structures from those of neat HCP usually used for study [27–29]. Differences are caused by (1) entrapped air in normally compacted mixtures, (2) deficiencies of large cement particles and higher porosity at aggregate surfaces (Fig. 4) because particles cannot pack as in bulk paste, and (3) sedimentation of cement particles prior to setting that releases bleeding water from the paste under larger aggregate particles, creating voids, especially at high water/cement ratios. Mineral admixtures such as fly ash and condensed silica fume reduce the latter two defects and greatly reduce permeability [8].

The coarse structure of concrete is determined by the volume and particle size grading of the total aggregate, the volumes of cement, admixtures, water, and air in the concrete mixture, mixing and placement or sampling procedures, and curing conditions. Over a considerable range of proportions of adequately mixed acceptable materials, concretes form cohesive, plastic, workable mixtures. Such mixing results in cement and admixture particles being dispersed in water and aggregate particles being desegregated and distributed in a three-dimensional, apparently random, array in a matrix of paste and air voids. However, systematic local deviations are forced by flat bounding surfaces of forms where larger particles cannot pack together as they can within the mass, so that smaller particles fill more of the space adjacent to forms. Similar effects occur within the mass at surfaces of particles that are much larger than their neighbors. During hardening of the paste matrix, concrete becomes more nearly homogeneous as the paste properties approach those of the aggregates.

In order for concrete to possess plasticity, the aggregate must be dispersed by a sufficient volume of cement paste to permit deformation under shear stress. For any aggregate size gradation, the minimum voids ratio indicates

the volume required to fill the voids in compacted (dry-rodded) aggregate. If the concrete is plastic, it must contain an excess volume of paste and air above that minimum to disperse the aggregate, that is, to provide some separation between particles that would be in contact in the absence of paste. Fine aggregate disperses coarse aggregate but also reduces average paste film thicknesses. For concretes made with nearly the same voids ratios (about 0.20), at 75 to 100 mm (3 to 4 in.) slump, and different aggregate finenesses, Powers calculated the minimum separation distances between aggregate particles from the excess paste volumes, by two different methods with dissimilar results [6]. The average values by the two different methods ranged from 26  $\mu\text{m}$  to 121  $\mu\text{m}$  for lean to rich mixtures, respectively, the latter having the highest percentage of fine aggregate (43%) and being close to the minimum voids ratio. Such results indicate that many concretes, especially very lean mixtures, suffer from poor workability because of particle interference to flow by the larger ( $\geq 30 \mu\text{m}$ ) cement particles. This indication has been confirmed by recent research. Although cement pastes made with cements of 30- $\mu\text{m}$  maximum particle size were stiffer than those made with ordinary cements, improved flow was obtained using such CPSD cements in standard mortars and ordinary (not lean) concretes [30]. Particle interference by large particles is also one of the reasons that some fly ashes increase water requirements of concretes [8].

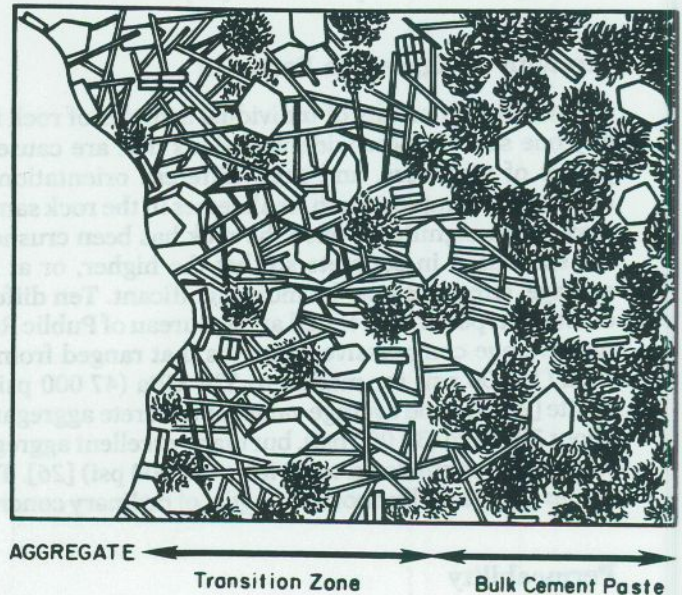


FIG. 4—Representation of transition zone at paste/aggregate interface in concrete, showing more coarsely crystalline and porous microstructure than in interzonal mass [27]. Reprinted with permission by P.K. Mehta.

<sup>3</sup> As yet unpublished research at Construction Technology Laboratories for the Portland Cement Association (Project HR 7190) and W. R. Grace & Co., (Project CR 7895) on test methods for early stiffening and slump loss.



## Hardened Concrete Properties

Other chapters in this publication give comprehensive treatments of many properties of hardened concretes. Some details are noted here to relate previous sections to specific properties of the HCP/aggregate composite.

In short-term loading tests for compressive strength, stress/strain relationships for aggregates and HCP can be sensibly linear up to near the compressive strength of HCP, while those for concrete exhibit curvature with increasing strain and pseudo-plasticity at stresses above about 0.4 times strength; microcracking at paste-aggregate interfaces develops progressively with increasing strain [26].

Creep of many concretes, except possibly those loaded at early ages, is proportional to stress/strength ratios up to 0.3 to 0.6; microcracking also begins in about this same range, depending on the heterogeneity of the mixture. Mortars, for example, exhibit proportionality up to perhaps 0.85. In concretes, stress/strength ratios near this value produce failure in time [26].

Long-term durability of concrete depends strongly on exposure and service conditions, concrete properties, especially porosity and pore structure, and structural design. Exposure to acidic or neutral waters causes leaching of calcium hydroxide from HCP, which increases its porosity and permeability, and can eventually soften even the much less soluble C-S-H. Sulfates in fresh waters can penetrate into concrete to cause sulfate attack by reaction with aluminate phases in HCP to produce ettringite, which can be destructively expansive if there is insufficient space to accommodate the volume expansion of that highly hydrated reaction product. Calcium and sodium chloride solutions react to form Friedel's salt and other complex salts, some of which are also expansive reactions under some conditions. Seawater causes leaching and contains sodium, chloride, magnesium, and sulfate ions in amounts sufficient to cause significant reactions, but the main effect is that of erosion or loss of constituents [1].

Moisture and freezing temperatures can cause damage by ice formation in large pores in the HCP and some aggregates. Ice formation at frozen surfaces is propagated through capillaries large enough to freeze. Because of ice/water interfacial tension, smaller capillaries require lower temperatures to be penetrated by the growing tips of ice crystals. These crystals in frozen capillaries, and also those in entrained air voids, grow by osmotic accretion of ice formed by diffusion of water from the gel pores. If entrained air voids are closely spaced, so that their void spacing factors are less than about 0.20 mm (0.008 in.), diffusion of moisture from both capillary and gel pores to ice in the air voids dries the HCP and prevents excessive expansions, otherwise caused by ice formation in capillary pores [31].

Approximate values for many properties of hardened concretes can be calculated from relatively simple equations for composites if values for properties of their aggregates and HCP (and water contents) are known, or can be estimated with reasonable accuracy. Density and heat capacity are simple examples. In recent years, our understanding of the nature of concrete has been formalized and exploited through mathematical modeling, despite

differences between structures of bulk HCP and HCP in mortar and concrete. Predictive models are now widely used for engineering design for creep, shrinkage, and temperature effects [32]. Modeling the development of microstructure and properties of concrete has been used to predict hydration rates, total porosity reductions, pore volumes of different sizes, heat evolution, permeability and diffusion coefficients, and compressive strength of concretes of diverse compositions at different temperatures and moisture contents [33,34]. Results of variations of mix proportions and other variables in tests for alkali-silica reactivity have also been modeled with considerable success [35]. Many other examples could be cited. Such studies continue to advance our understanding and ability to design and to test concretes and concrete-making materials, for performance in specific applications.

## CONCLUDING DISCUSSION

It must be recognized that the apparent successes of mathematical modeling have been achieved in a relatively narrow range of compositions and properties of portland and blended cements, for which decades of research and field experience have provided a large base of knowledge and understanding. This base has been used to write mainly prescription-based specifications for the materials. Such successes must also be contrasted with the limitations of standard test methods to guarantee performance or to yield results concerning performance problems that are not misleading. ASTM tests that have been subject to such criticism include ASTM Test Method for Autoclave Expansion of Portland Cement (C 151) [36,37], ASTM Test Method for Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar-Bar Method) (C 227) [8,38], ASTM Method for Sampling and Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland Cement Concrete (C 311) [8], and ASTM Test Method for Effectiveness of Mineral Admixtures or Ground Blast-Furnace Slag in Preventing Excessive Expansion of Concrete Due to the Alkali-Silica Reaction (C 441) [8].

These limitations should be overcome if we are to continue to move towards total reliance on performance testing, without the prescription-based specifications on which our knowledge base has been built, especially for long-term durability. Advocates of performance testing argue persuasively that their course will permit innovation, more extensive utilization of waste materials, and advanced technology. Performance test-based specifications will open the way for formulations of cements and concrete mixtures ranging well outside even the present base, which does not yet have altogether satisfactory test methods. Research on improved test methods, and the use of those results together with mathematical modeling to predict long-term performance, should therefore be given high priority.

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## 14 TESTS AND PROPERTIES OF CONCRETE

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