CHAPTER 6.11: CEMENTS AS POROUS MATERIALS

H.M. Jennings*, J.J. Thomas*, D. Rothstein#, and J.J. Chen*
Northwestern University
Department of Materials Science and Engineering*
Department of Civil Engineering#
Evanston, IL 60208
USA

6.11.1 Introduction

Concrete, found in roads, bridges, skyscrapers, and a myriad of other structures, is easily one of the most ubiquitous materials in modern civilization. Quite surprisingly, however, concrete is also a relatively difficult material to classify. It can easily be mistaken for a rock, possibly some form of artificial rock, or perhaps thought of as a composite. Adopting any one of these categories would not reveal the fundamental nature of concrete, namely that it is porous. In fact, the binding matrix phase of concrete, called hardened cement paste, possesses between 25 and 50% porosity. This relatively large porosity is striking in itself; however, the variation in pore size is equally impressive, ranging from nanometer-sized gel pores, to micrometer-sized capillary pores, to millimeter-sized air voids.

The complexity of concrete is compounded by its interactions with water. Hardened cement paste, formed from the reaction of the various minerals in concrete with water, will continue to react with its aqueous phase for several years, leading to progressive refinement and maturation of its porous structure. Much of this porous structure resides in the calcium silicate hydrate gel, causing the hydrate to have a surface area of several hundreds of square meters per gram. These colloidal dimensions result in an intimate association between the solid gel phase and the aqueous phase that resides in the gel pores. This coupling has important repercussions on
the properties of hardened cement paste, especially in phenomena such as drying shrinkage and creep.

Rather than attempting to cover all the peculiarities of cement science, this review concentrates on the pore structure of hardened cement paste and concrete. In Section 6.11.2, the structure of hardened cement paste is described after a brief overview of the hydration of Portland cement. Section 6.11.3 outlines pertinent issues concerning the characterization of the porous structure of hardened cement paste. Section 6.11.4 presents interpretations of the pore structure of hardened cement paste and, particularly, that of the calcium silicate hydrate product. Section 6.11.5 describes selected macroscopic properties of concrete such as strength, volume stability, and permeability, with emphasis on the influences of porosity and water on these properties. The concluding Section 6.11.6 concerns the durability of concrete and briefly reviews the debilitating effects of several important interactions between concrete and its environment. After a summary in Section 6.11.7, a glossary of terms that are relevant to cement science is given in Section 6.11.8.

6.11.2 Hardened Cement Paste

The character of concrete is largely determined by the porous structure of its primary component, hardened cement paste. As will become evident, any meaningful discussion of this porous structure requires a rudimentary knowledge of the chemical and physical reactions associated with its formation.

6.11.2.1 Portland Cement

Cement is a generic term for a material that is used to bind particulate matter together. The chemical constitution and the ultimate use of a cement are not strictly defined. Historically,
however, cement has been equated with readily available materials that could bind stones and brick together, plaster walls and ceilings, and waterproof buildings and conduits. Conceivably, the earliest cementing material was mud mixed with straw, as was typical in early civilizations [1]. The Egyptians later employed impure gypsum cement mortars to build the remarkably well preserved great pyramids along the Nile [2]. The Greeks and Romans made extensive use of lime cement mortars throughout their respective empires, the latter taking advantage of the availability of reactive volcanic rock to create hydraulic mortars, which possessed the novel ability to harden under water. Today, cements can take on an entirely different character. In the medical field, for example, organic based acrylic cements [3] have found commercial success in binding artificial implants to human bone, and the more recently developed calcium phosphate cements [4, 5] aid in bone repair and regeneration.

With the overwhelming success of the concrete industry during the modern era, the term cement has become nearly synonymous with Portland cement, the proportioned mixture of predominantly calcium silicate and calcium aluminate minerals that chemically react with water, a process known as hydration, to form a dramatically different product called hardened cement paste. Due to its inherent brittleness, hardened cement paste is usually combined with fine aggregate (sand) to form mortars, or with a combination of fine aggregate and coarse aggregate (gravel or crushed stone) to form concrete. While the properties of mortar and concrete are naturally influenced by the characteristics of the aggregate phase (particularly with regard to volume stability), they are predominately controlled by the character of the hardened cement paste.

The primary raw materials of Portland cement are a lime-rich substance (such as limestone, chalk or shells) and a clay-rich substance (such as shale, slate, or clay itself), both of
which are readily available natural resources. Before being heated in a rotary kiln, the raw materials are carefully proportioned to supply the desired amounts of lime, silica, aluminum oxide, and iron oxide. During the heat treatment at temperatures approaching 1450ºC, partial fusion (or clinkerization) of the oxides produces walnut-sized particles called clinker, a chemically different substance having an unusually high reactivity with water. Clinkers are then cooled, mixed with a 3 to 4 % addition of gypsum (to control the initial rate of hydration), and finally ground to a fine powder (usually with a size distribution ranging from 1µm to 100µm, with a mean of ~15µm to 20µm). The resulting powder is called Portland cement.

6.11.2.2 Hydration of Portland Cement

Any discussion of the structure of hardened cement paste requires a basic understanding of the chemical and physical changes that occur during hydration. The sequence of events is as follows.

When Portland cement is combined with about half of its weight in water, the result is a viscous but still fluid mixture called cement paste. Normally the wet paste remains in a state of relatively constant fluidity from 2 to 4 hours, after which time the mix starts to stiffen at a dramatically faster rate. The time at which paste loses its fluidity is denoted as initial set. Substantial increases in strength and hardening of the paste do not occur until several hours after the initial set, a time denoted as final set. Strength increases rapidly during the first two days and continues to increase at a decreasing rate for several years.

The above description of events during the hydration of cement is purposefully crude, giving little indication of the chemical complexity of the reactions taking place. Without any knowledge of cement chemistry, it would not be illogical to conclude that the hardening of cement is a result of a rewetting/drying process similar to what occurs in simpler systems such as
gypsum plaster. This theory, however, is completely incorrect and is a commonly held misconception. What is often overlooked is that Portland cement can harden under water, and in fact, the quality of the hardened cement paste cured under water is superior to that cured in air. The reason for the hardening of cement, thus, cannot be attributed to drying. Instead, the hardening process, as discovered by John Smeaton in the 1750s, is a result of chemical reactions between water and the calcium silicate phases of Portland cement.

6.11.2.2.1 Chemistry of Cement Hydration

The hydration of Portland cement has been exhaustively examined, interpreted, and reinterpreted over the last century. While the overall course of the reaction has been established, many of the details are still under debate. For the purposes of this review, only the essential features of cement hydration that are relevant to later discussions on structure will be presented; consequently, the discussion will focus primarily on the calcium silicate hydrate product. For completeness, the other hydration products will be mentioned but the reader should consult Taylor’s excellent book [6] for further information.

The primary hydration reactions involve four oxide phases formed during the clinkerization process: tricalcium silicate, $3\text{CaO}\cdot\text{SiO}_2$ ($C_3S$), dicalcium silicate $2\text{CaO}\cdot\text{SiO}_2$ ($C_2S$), tricalcium aluminate $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ ($C_3A$), and tetracalcium aluminoferrite $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ ($C_4AF$). (The abbreviations used here and throughout this review follow the conventions of standard cement chemistry notation: $C=\text{CaO}$, $H=\text{H}_2\text{O}$, $S=\text{SiO}_2$, $F=\text{Fe}_2\text{O}_3$, $A=\text{Al}_2\text{O}_3$, $\bar{S}=\text{SO}_3$.) It is important to note that all of these chemical formulas are approximations since each of the phases contains appreciable quantities of impurities. In addition to the four primary oxide phases, gypsum (CaSO$_2$H$_2$) is also present. A typical average composition of a Type I normal Portland cement (used for standard applications) is approximately (in weight-%): 50%
C₃S, 25% C₂S, 12% C₃A, 8% C₄AF, 3.5% CSH₂, with the balance consisting of small amounts of compounds of magnesium, sodium, potassium and sulfur.

When Portland cement is mixed with water, the primary chemical reactions can be approximately represented as follows:

\[
C_3S \rightarrow C_{1.7}SH_x + 1.3CH \tag{1}
\]

\[
C_2S \rightarrow C_{1.7}SH_x + 0.3CH \tag{2}
\]

\[
C_3A + 3C₃SH₂ + 26H \rightarrow C_3A·3C₃SH₃₂ \tag{3}
\]

\[
2C_3A + C₆A₃S₃₂H₃₂ + 4H \rightarrow 3C₄A₃S₁₂ \tag{4}
\]

\[
C_3A + 6H \rightarrow C_3AH₆ \tag{5}
\]

\[
C_4AF + 13H \rightarrow C_4(A₂F)H₁₃ \tag{6}
\]

where the variable \(x\) in Eqs. (1,2) represents the chemically bound water content (that is discussed below) in the calcium silicate hydrate product.

Since C₃S and C₂S constitute approximately 75% of the Portland cement, the calcium silicate hydrate (C₁₇-S-Hₓ) and calcium hydroxide (CH) phases [see Eqs. (1,2)] dominate the hydration products of Portland cement, each comprising approximately 50 to 60% and 20 to 25% of the total product volume respectively. The calcium hydroxide phase is significant since it buffers the aqueous pore solution (which contains an appreciable level of dissolved salts) to a pH of about 12.5. However, the far more important hydration product is the calcium silicate hydrate. From a practical standpoint, calcium silicate hydrate is essential for concrete since it is the phase that binds to steel reinforcing bars, aggregates, sand, and other hydration products.

On the colloidal scale, the calcium silicate hydrate phase is an amorphous gel that contains pores (appropriately called gel pores) of approximately a few nanometers in diameter. The fineness of the porosity creates a significant surface area between the calcium silicate
hydrate and its pores, reaching a magnitude of a few hundred m$^2$g$^{-1}$; this value is essentially equal to the surface area of the hardened cement paste since the contribution made by the other hydration products is comparatively negligible. As a result, calcium silicate hydrate is responsible for almost all of the important properties of hardened cement paste such as strength, volume stability and permeability. Another important consequence of its fine porosity and high surface area is the intimate association between calcium silicate hydrate and the aqueous phase that resides in its gel pores. This intimacy is revealed by the fact that a line segment which originates in a gel pore and traverses a calcium silicate hydrate particle perpendicular to its surface will emerge into another gel pore at a distance no greater than tens of nanometers. Since this type of significant intermixing between solid and porous phases is one of the defining characteristics of a colloidal gel [7], calcium silicate hydrate will often be described as a colloidal gel in this review. An immediate consequence of the finely divided colloidal structure is the fostering of significant intermolecular interactions between the calcium silicate hydrate and water (which resides in the pores). As will be discussed in Section 6.11.5.2, these interactions play major roles in properties of hardened cement paste such as drying shrinkage and creep.

In addition to the water in the fine gel pores, there is the chemically bound water of calcium silicate hydrate that is represented in the formula, C$_{1.7}$SH$_x$. The subscript $x$ on the water component indicates that the chemically bound water content in calcium silicate hydrate is not fixed. A typical formula for a water saturated calcium silicate hydrate is C$_{1.7}$SH$_{4.0}$ [6]; the water content in calcium silicate hydrate for sub-saturated conditions will be correspondingly less. Also note that the molar ratio of CaO to SiO$_2$ (C/S) in calcium silicate hydrate found in hardened cement pastes can slightly diverge from its average value of 1.7 represented in Eqs. (1,2). For example, an analytical electron microanalysis study [8] showed that a 26-year old C$_3$S paste
possess a C/S range of approximately 1.60 to 1.85, with a modal value of 1.78. To minimize any ambiguities in chemical composition, it is preferable to use the terms “C-S-H” or “C-S-H gel” to describe any poorly crystalline calcium silicate hydrate with an arbitrary water content or C/S ratio [6]. These terms will be used throughout the remainder of the review. (Note that without the dashes the term “CSH” refers to a very particular composition, CaO•SiO2•H2O.)

6.11.2.2 Kinetics of Hydration

That Portland cement and water constitute a highly dynamic system is readily seen from the hydration kinetics. Figure 2 shows a characteristic rate of heat evolution during hydration of C₃S. (Portland cement shows a very similar plot but with additional peaks associated with the aluminate phase.) A dramatic series of events occurs during the first 24 hours. Upon mixing, there is an intense but brief production of heat, lasting only a few minutes (stage 1 in Figure 1). Most of this initial activity for C₃S is from wetting effects, but in the case of Portland cement, the early heat release is also due to reaction of the aluminate phases. The heat output then stabilizes to a relatively constant rate during the induction (or dormant) period (stage 2), in which the paste remains in a relatively plastic, fluid state for approximately 2 hours. The causes of the induction period and of its termination have been debated considerably, and the relevant hypotheses differ mainly as to whether protective membranes form around cement particles or nucleation of C-S-H or CH is inhibited [9]. Regardless of the specific mechanism, the end of the induction period is marked by a dramatic increase in the rate of heat evolution caused primarily by the formation of C-S-H gel and CH. This acceleratory period (stage 3) ends in a maximum in heat output (at about 10 to 12 hours). Thereafter, the heat evolution decelerates (stage 4) to a steady state level (stage 5) during which hydration continues for a period of several months to a few years. As a result of
this extended period of reaction, the structure, and more importantly, the pore structure of hardened cement paste will continuously evolve with time.

6.11.2.2.3 Morphology of Hydration Products

Hydrated cement paste is a cohesive, albeit porous, entanglement of hydration products that differ in chemical composition and morphology. Since the solid phases ultimately bound, and thus create, the porous space in hardened cement paste, a basic knowledge of the solid phase morphology should give a greater understanding of the porous structure to be described in later sections.

As noted in Section 6.11.2.2.1, the colloidal C-S-H gel product dominates the structure of hardened cement paste. Despite being crystallographically amorphous, there are distinct morphologies of C-S-H that can be identified by techniques such as scanning electron microscopy (SEM); four morphologies of C-S-H gel have been observed [10] (see Table 1). The relative abundance and importance of each morphology are unknown, but it has been shown that the various types can be associated with specific stages of hydration [11].

The morphologies listed in Table 1 are those obtained after thorough drying of the C-S-H gel, which is a required procedure for conventional electron microscopy techniques that operate at high vacuum. The loss of evaporable water from C-S-H gel associated with the drying procedure inevitably produces irreversible changes in the microstructure, and thus, one is left to observe only relics of the actual structure. This critical issue must be kept in mind in evaluating any electron microscopy investigation of C-S-H.

Even though the amorphous, colloidal C-S-H gel dominates the structure of hardened cement paste, there are important crystalline phases embedded in the C-S-H gel network (Table 1). If there is enough space available, calcium hydroxide (CH), the most abundant crystalline
phase, can form massive hexagonal-prism crystals of approximately 100 µm across. The calcium sulfoaluminate phases of ettringite (C₃A•3C₅S₃H₃₂) and monosulfoaluminate (3C₄A₂S₁₂H₁₂) [(see Eqs. (3,4))] are other distinct crystalline phases that adopt prismatic needlelike and hexagonal plate morphologies, respectively.

6.11.2.3 Physical Structure of Hardened Cement Paste

While the chemical and morphological nature of the hydration products certainly influence properties, many phenomena associated with the hardened cement paste are the result of purely physical features of the structure such as porosity and colloidal dimensions of the solid and porous phases. Powers and coworkers at the Portland Cement Association in the USA during the 1940s to early 1960s were the first to systematically investigate these factors. Despite limitations in experimental techniques, their seminal review [12] of hardened cement paste still forms the basis of much of our current interpretation of its structure and properties.

On mixing cement with water, the cement particles are dispersed and essentially discontinuous (or only connected by van der Waals type forces). Water-filled space separates the cement grains by a distance roughly equal to the of size of the grains, which ranges from 1 to 100 µm in diameter but averages between 15 to 20 µm. Reactions take place at the surface of the original cement grains where products can either form directly on the surface of the grain (as is done by C-S-H), or precipitate in the water-filled space (as in done by both calcium hydroxide and C-S-H). As hydration continues, the cement particles become progressively smaller and the original water-filled space becomes increasingly filled with hydration product, most of which is the porous C-S-H gel. If insufficient water-filled space is available for the hydration products to deposit, the reaction can terminate before all unhydrated cement particles have reacted. Alternatively, if the original water to cement ratio was exceedingly high, hydration product will
only partially fill the original water-filled space, leaving behind an excess of unfilled space called capillary pores. As will be described in later sections, capillary pores can be significantly larger than the gel pores of C-S-H described in Section 6.11.2.2.1.

According to the above description, hardened cement paste can be thought of as consisting of unreacted cement, C-S-H gel (including its gel pores), calcium hydroxide, and capillary pores (see Figure 2). This representation is an obvious oversimplification, because we have neither taken into consideration the hydration products of the aluminate phases, nor have we admitted the evidence that the morphologies of the C-S-H gel formed in the space originally occupied by cement particles is different from those formed in the space originally filled with water. Nevertheless, numerous (but certainly not all) experimental observations can be explained on the basis of such a simplified, idealized microstructure. Among the observations easily understood by this model are the following. Increasing the initial water to cement weight ratio (w/c) results in a more porous hardened cement paste; decreasing the w/c results in a denser one. Porosity is seen to decrease with reaction time; consequently, strength, being a direct function of porosity, is seen to increase with time. Permeability, and hence susceptibility to ingress of aggressive species, is directly related to the extent of discontinuity of the capillary porosity [13, 14].

This simple model system consisting of unhydrated cement, C-S-H gel, calcium hydroxide and capillary pores forms the basis of the sophisticated three-dimensional computational simulations of cement hydration developed at the National Institute of Standards and Technology [15]. Coupled with theoretical concepts of percolation and composite theory, many of the properties of hardened cement just cited can be computed, and agreement with experimental results are often very good.
6.11.2.4 Pore Structure of Hardened Cement Paste

Any discussion of the structure of hardened cement paste will inevitably lead to a discussion of its complex porous structure. The following sections will outline the various classes of pores in hardened cement paste. These classes will be distinguished by their characteristic pore sizes, and more importantly, by the interactions between the C-S-H gel and the aqueous phase that is held within their associated pores.

6.11.2.4.1 Pore Size Distribution

A typical pore size distribution for hardened cement encompasses a large range, extending from about 10 µm to as small as 0.5 nm or less in diameter (Table 2). The larger pores, ranging from 10 µm to 10 nm, are the residual unfilled spaces between cement grains, earlier defined as capillary pores. The finest pores, ranging from approximately 10 nm to 0.5 nm, are called gel pores since it is believed that they constitute the internal porosity of the C-S-H gel phase. Pores having dimensions of 0.5 nm or smaller are formed by the interlayer spaces of C-S-H gel, where chemically bound water resides (see Section 6.11.2.2.1). It is important to note that since the range of pore sizes is a continuous one, the suggested dimensional boundaries between capillary and gel pores, and between gel pores and interlayer spaces are simply approximations to inherently blurred boundaries.

Voids greater than 10 µm often exist in concrete [16], either from the unintentional entrapment of air during the mixing procedure, or from intentional air-entrainment, which purposefully disperses air voids of approximately 50 µm in diameter throughout the paste to relieve pressures induced from the freezing of water in pores (discussed in Section 6.11.6.2.1).
Air voids can be considered essentially outside the characteristic hardened cement paste pore system, and thus, will not be discussed in ensuing sections.

6.11.2.4.2 Non-Evaporable Water: Interlayer Spaces

As noted in Section 6.11.2.2.1, C-S-H gel has a variable amount of chemically bound water in its interlayer spaces that is, at equilibrium, a function of the external saturation conditions (i.e. RH). Determination of the precise amount of chemically combined water, however, is not a trivial matter. As noted in Section 6.11.2.4.3, a distinct physical boundary between interlayer spaces (which contain the chemically bound water) and the smallest gel pores does not exist. This situation inevitably blurs the line between chemically bound and physically bound water. Facilitating a means of distinguishing between the two requires the definition of specific terms.

Non-evaporable water is strictly defined as water that is not removed from a specimen under a standard drying condition; evaporable water is the water removed under the same drying condition. The most well defined (but arbitrary) standard drying condition is vacuum drying at the equilibrium vapor pressure of water (~ 6.7 x 10^{-2} Pa) obtained at the temperature of dry ice (T = 194 K), a process known as D-drying [17]. D-drying is often approximated by the more convenient oven drying at 105°C, or vacuum drying at ambient conditions; these latter methods, however, should not be used for precise measurements of non-evaporable water since a fixed equilibrium water vapor pressure is not involved, as is the case for D-drying.

The non-evaporable water retained in the specimen after D-drying (or roughly equivalent processes) is approximately equal to the amount of water chemically combined with the cement. Taylor [6] warns, however, that the non-evaporable water measured on D-drying should not be precisely equated with the amount of chemically combined water since an unknown amount of
chemically combined water will inevitably be lost upon D-drying. Nevertheless, the non-evaporable water content is a very useful empirical measure of the extent of the hydration. Since a fully reacted Portland cement contains approximately 0.24 g of non-evaporable water per gram of cement, one can obtain the approximate degree of reaction by dividing the measured non-evaporable water content of a specimen by a factor of 0.24.

6.11.2.4.3 Evaporable Water: Capillary vs. Gel Water

The evaporable water content of hardened cement paste is often divided into two classes, capillary and gel water. The obvious distinction between the two is the difference in size of the pores the water is residing in: gel pores are roughly 10 nm or smaller while capillary pores can reach up to 10 µm (see Table 2). As mentioned, the physical demarcation between capillary and gel pores is ultimately arbitrary since the spectrum of pore sizes is continuous. The original distinction between gel and capillary pores, delineated by Powers and Brownyard [12, part 3], arose from water adsorption studies that indicated a minimum porosity when hydration products filled all available water-filled space (i.e., no capillary pores). The remaining porosity at this unique condition was thus concluded to be entirely present in the porous C-S-H gel phase, and hence, the associated pores were denoted as gel pores. When the hydration products could not fill all available space (i.e., when excess water is present), additional pores of considerably larger scale were introduced in the paste. These capillary pores were not dependent on the amount of C-S-H gel formed, but could be present in any amount depending on the original water content of the paste.

The characteristic sizes of capillary and gel pores have important influences on the behavior of liquid water that resides in these pores. The constrained dimensions of smallest gel pores (less than about 4 or 5 nm), for example, will promote important intermolecular
interactions between the C-S-H gel surface and the water molecules of the gel water. These interactions (which are present in virtually all colloidal systems [7, 18, 19]) lead to an aligning, or structuring, of the polar water molecules in the vicinity of the C-S-H gel surface. Since gel water in small pores will always be near a solid surface, the structuring of water molecules is a significant, and perhaps dominant, phenomenon in gel water. As a result, physical properties of gel water such as density, viscosity, dielectric constant and conductivity often differ from those of bulk water [19]. The density of gel water in C-S-H, for example, is seen to be slightly higher (~ 1.1 g cm\(^{-3}\)) than that of bulk water [20]. Also, the mobility of gel water in the vicinity of a surface is significantly decreased from its bulk value [7]. This reduced mobility has been postulated to play important roles in mechanisms of creep and of drying shrinkage at low humidity. Moreover, the reduced mobility of gel water is exploited in the use of nuclear magnetic resonance (NMR) [7] (see Section 6.11.3.5) to measure the surface area of hardened cement paste.

As we have seen, capillary water resides in significantly larger pores than does gel water. The important consequence of this is that capillary water does not undergo the strong intermolecular interactions with the C-S-H surface that are dominant in small gel pores. Capillary water will, in essence, behave like bulk water. However, since capillary water must possess a high surface to volume ratio (due to the physical confinement of capillary water in capillary pores), the properties of capillary water will be strongly influenced by the properties of its interfaces. These interfaces between liquid water and solid C-S-H gel or between liquid water and air are characterized by excess surface energies, or surface tensions, which arise due to the presence of unsatisfied bonds at the interface. As will be discussed further in Sections 6.11.5.2.2 to 6.11.5.2.4, surface tension is significant during the drying of C-S-H gels since its presence at
curved liquid-vapor interfaces (i.e., menisci) creates pressure differentials across these interfaces (a phenomenon embodied in the Laplace equation). Due to the negative curvature of the menisci, the evaporating capillary water will experience a negative capillary pressure, or equivalently, a tension that depends on the curvature [7, 21]. To relax this internal tension in the liquid phase, the adjacent C-S-H solid phase goes into compression. This induced compressive force causes the C-S-H gel to shrink.

6.11.2.5 Volume Relationships; Water to Cement Ratio; Self-Desiccation

Considering all of the above, one might conclude that the water to cement ratio (w/c) probably has the dominant effect on the porosity, and hence the properties, of hardened cement paste. It was stated earlier that increasing the water to cement ratio increases the initial water-filled space between unhydrated grains, which ultimately leads to a greater proportion of capillary pores in the hardened cement paste after hydration is completed. The explanation as to why this is so lies in the combined experimental observations that: (i) the hydration reaction takes place at essentially constant volume, and (ii) the hydration products at complete reaction require a finite amount of additional space over the original volume of cement from which they form. Concerning the latter point, Powers [20] estimated that 2.2 cm³ of space is required to fully hydrate 1 cm³ of Portland cement. Thus, if the original w/c ratio is high enough to create an excess of 2.2cm³ of water-filled space for every 1cm³ of cement, remnants of the water-filled space will be present even after complete reaction since the hydration products can only occupy, at most, 2.2 cm³ for every 1cm³ of cement.

An equally valid conclusion to be drawn from the two experimental observations mentioned above is that there is a unique w/c ratio below which hydration cannot be completed due to insufficient space for the hydration product to form; Powers and Brownyard [12] estimate
this w/c to be ~ 0.38. A schematic of the effect of w/c on the volumetric proportions of hydration product, unhydrated cement and capillary pores is shown in Figure 3.

It is important to note that Figure 3 assumes that a sufficient supply of excess water is available throughout hydration. It has been observed experimentally that a fully hydrated sample will take up approximately 0.06 g of additional water per gram of cement when hydration takes place under water [6, pg. 232]; this amount corresponds to the amount of water required to fill the gel pores with water. If a cement paste is sealed during hydration, water flows from the capillary pores to the gel pores until the latter are saturated. This action would effectively empty the capillary pores and reduce the amount of water available for reaction with the original cement; hydration can thus be halted from a lack of available water before space limitations come into effect. The net result of this phenomenon, called self-desiccation, is that a sealed cement specimen requires a higher initial w/c for complete reaction, estimated to be 0.44.

6.11.3 Characterizing the Pore Structure and Surface Area of Cement Paste

All of the engineering properties of cement and concrete are related in some way to the porosity, and characterization of the pore system is often a better predictor of performance than characterization of the solid phases. However, characterizing the porosity of hydrated cement paste is difficult. Because of the large range of pore sizes (from a few nanometers to tens of micrometers), no single technique can adequately characterize all of the important components of the pore system. Most standard techniques require that the pore fluid be removed, but such a drying pretreatment can sometimes significantly alter a porous structure. Therefore, measurements performed on dry paste may give an inaccurate picture of the porosity of cement paste under the conditions of its actual use.
There are three general parameters of interest in the pore system: the total porosity, the pore size distribution, and the specific surface area of the pores. Experimental techniques for characterizing the pore system can be divided into two categories: those that involve the intrusion of a fluid into the pore system (pyknometry, mercury intrusion, gas sorption,), and those that use particles or fields to probe the material (small-angle scattering, NMR). The latter category has a significant advantage, in that the cement does not need to be dried. However, these "modern" techniques require highly specialized equipment, and the data are more difficult to interpret.

Measurement of the specific surface area is by far the most commonly performed analysis of cement paste pore systems. Values reported for surface area in the literature vary over two orders of magnitude, depending on the technique used and the interpretation of the results. Despite this variability, surface area measurements are still performed. This fact attests to the utility of having a single parameter such as surface area that describes the overall fineness of the microstructure on a nanometer scale, and that correlates closely to important properties such as durability and drying shrinkage. Thomas et al. [22] have reviewed the application of different techniques to measuring cement paste surface area.

The variability of the specific surface area is related to a number of factors, some of which are listed below in approximate descending order of importance:

1) **Difficulties with data analysis.** Modern techniques, namely small angle scattering and NMR, provide important insights into the microstructure and pore system of cement-based materials. However, obtaining quantitative surface area values from these techniques is difficult due to the many models and assumptions needed to convert the raw data. The first reported surface area values for small-angle X-ray scattering and for NMR were both
extremely high (several hundred m$^2$/g). Refinements of the data analysis and improved experimental calibration methods may bring the values more into line with gas sorption values.

2) Specimen preparation. As noted above, gas sorption requires that the paste be dried, and this affects the pore system. The difference in values for the surface area obtained (1) by nitrogen sorption ($S_N^2$) after severe drying (such as oven drying) and (2) after solvent exchange, which preserves the pore structure, can approach an order of magnitude.

3) Normalization of the surface area value. Gas sorption results are reported as surface area per weight of dried paste, the unit for small-angle scattering is area per sample volume, and NMR results are generally reported as area per weight of starting cement powder. Results from any technique are occasionally reported as area per weight of ignited paste. This can generate numerical differences of up to a factor of two, making comparisons difficult. It is possible to make an approximate conversion from one type of units to another using hydration models and known properties of cement paste. Results reported here are converted to area per grams of D-dried paste where needed, following the approach of Thomas et al. [22].

4) Analytical sensitivity. Some techniques may probe features of the internal C-S-H structure not associated with the surface area, while others do not measure the full surface. It is difficult to deconvolute these effects from issues associated with data analysis (factor 1 above).

When the above factors are taken into account, surface area measurements are a useful way to characterize cement. The specific surface area varies with the age of the paste, the water/cement ratio, the cement composition, and other processing variables, which determine the
amount of finely divided hydration product in the material. Due to the above issues, these effects are best observed using a single measurement technique and method of sample preparation.

Another, more philosophical difficulty associated with surface area measurements of cement paste is defining what exactly is meant by the cement surface. The C-S-H phase has an extremely high specific surface area, and the total surface area of cement paste is essentially equal to that of its C-S-H component. In addition to the liquid water within the internal gel pores, the C-S-H in cement also contains strongly adsorbed and chemically bound water as part of its internal structure. This creates a basic uncertainty in defining the boundary between solid and pores. A satisfactory measurement of surface area for cement paste would include the gel pores, which contribute to the transport of reactive species through cement paste, and would exclude any features of the internal solid C-S-H structure that do not contribute to ionic transport. It is not clear, however, that there is a distinct structural separation between these types of features.

6.11.3.1 Pyknometry

Pyknometry measures the porosity of a specimen by simply measuring the volume of fluid that can intrude into the material. For cement paste, the total porosity is most easily obtained by measuring the loss of mass when the evaporable water is removed, normally by heating to 105°C. A true pyknometric measurement, obtained by resaturating a dried specimen in water, gives the same result. It is an interesting feature of cement paste that the intrusion of other fluids, such as helium or methanol, into well-dried specimens results in a smaller measured porosity. The reason for this is that the most tightly bound evaporable water is associated with the C-S-H gel phase in such a way that its equivalent volume is only measured by resaturation with water [6]. This is verified by the fact that when pyknometry is performed after partial drying, water, helium, and alcohols all give the same result [23]. If a water-saturated paste is
solvent-exchanged with alcohol and then fully dried, resaturation with alcohol measures a larger pore volume similar to that measured by water [24]. It thus appears that the physical changes associated with removal of all the evaporable water can be avoided by prior solvent exchange. This is in agreement with specific surface area measurements performed with gas sorption, which are highest when drying follows solvent exchange.

Equilibration of cement paste to 11% relative humidity (RH) is an accepted method of removing all the pore water while leaving more tightly bound water in place. The pore volume thus obtained (after the ingress of any suitable fluid) is called the free water porosity [6]. As would be expected, the total and free water porosities both decrease with the age of the paste and increase with the w/c ratio. Table 3 lists reported values for total and free water porosities for mature cement pastes having different w/c. In the cement literature, the difference between the total porosity and the free water porosity is often referred to as the "interlayer porosity" or "gel porosity". These terms, which arise from structural models of the C-S-H phase, are sometimes used interchangeably and sometimes have very different meanings, which should be taken in context.

6.11.3.2 Mercury intrusion porosimetry

Mercury intrusion porosimetry (MIP) is one of two methods commonly used to measure a pore size distribution in cement paste, the other being gas sorption. After the specimen is dried, mercury is forced into the pore system under increasing isostatic pressure, and the intruded volume is recorded. Because mercury does not wet the solid, it enters pores only under pressure, and the smaller the pore the greater the pressure required.

MIP is complimentary to gas sorption in the sense that it measures more of the capillary porosity while gas sorption measures the finest pores more accurately. The two techniques do not
agree within their region of overlap, however. As summarized by Taylor [6], there are serious problems with the application of MIP to cements:

1) The method measures the size of the pore entrances, not the pore itself. When a large pore can only be accessed through a small opening, the entire volume accessed is registered as small porosity. This has been shown to generate serious errors for cement paste [25].

2) Data analysis assumes cylindrical pores and a constant contact angle; these assumptions are not strictly correct for cement paste.

3) The drying treatment changes the pore structure. This is also true for other techniques, notably gas sorption. As with gas sorption, exchange with alcohol prior to drying preserves the structure to some extent.

4) The fine structure is damaged by the large stresses needed to intrude the mercury.

5) The coarsest part of the porosity (the largest capillary pores) is not fully registered.

Because of these issues, the pore-size distribution measured by MIP is very different from the true value for a saturated pore system, particularly at the coarsest and finest ends of the distribution. MIP does provide self-consistent results, however, registering useful differences for pastes of different ages and w/c ratios. The total intruded volume decreases with age and the distribution shifts sharply to smaller pore sizes during the first 7 days of hydration. MIP has also been used to measure differences in the pore systems of cement and concrete arising from a more porous interfacial transition zone (see Section 6.11.5.3.2) surrounding individual aggregate particles [26].
6.11.3.3 Gas sorption

Gas sorption is the oldest and most widely used technique for measuring the surface area of cement paste, and it is by far the technique with the most published results. Gas sorption can also provide a pore size distribution of the finer pores (<30 nm). Issues associated with drying of cement paste are particularly important for gas sorption, and methods of drying cement paste are discussed in this section as well. The physics and applications of gas sorption techniques are covered in a book by Gregg and Sing [27]. Rarick et al. [28] reviewed the application of the gas sorption method to cement paste.

The gas sorption isotherm for cement paste can be classified as type IV in the BDDT scheme [29]. This category is associated with mesoporous materials such as silica gel, porous glass, and certain naturally occurring minerals such as montmorillonite [27]. A key feature of type IV isotherms is a hysteresis loop, caused by the irreversibility of the capillary condensation process in mesopores (2 - 50 nm). The hysteresis loop for cement paste is large, reflecting the significant mesoporosity in the C-S-H gel. The specific surface area is obtained from the multilayer adsorption region of the isotherm, using the well-known BET method. The desorption isotherm can be used to calculate a pore size distribution in the mesopore region using a method developed by Barrett, Joyner, and Hallenda [30].

Most published gas sorption measurements of the surface area of cement paste have used either water vapor or nitrogen as the sorptive gas. Because equilibrium is approached very slowly when water vapor is used, the procedure requires a variation of the gravimetric method. This involves exposing the specimen to a series of closed vessels containing salt solutions with different water vapor pressures. Surface area results from nitrogen sorption are obtained using the volumetric method; an automated process provides faster results with less labor.
6.11.3.3.1 Drying Cement Paste for Gas Sorption

As mentioned above, one of the drawbacks of the gas sorption technique for application to cement paste is the requirement that the specimen be dried. There are two general problems associated with the drying pretreatment. First, any gel pores that remain filled with water due to incomplete drying will not be accessed by the adsorbate molecules and will not be included in the surface area measurement. The smallest pores are the most difficult to dry, but they also have the highest relative surface area. The second, and more serious, problem is that the drying process changes the C-S-H structure. Different drying techniques cause different changes to the C-S-H, and surface area results from gas sorption vary rather widely depending on the drying treatment. Also, if the dried paste is stored for a long period of time before measurement, exposure to even small amounts of CO₂ leads to carbonation of the C-S-H gel and significant decreases in the measured surface area.

For cement paste, the simplest techniques for removing the water in preparation for a gas sorption measurement are oven drying at 105°C or vacuum drying using a rotary pump. Although these techniques effectively remove all of the evaporable water, they also damage the specimen. To minimize this damage gentler drying techniques have been developed. The most common of these is D-drying, which involves equilibrating the specimen to the pressure of water vapor at the temperature of dry ice (see Section 6.11.2.4.2). This is the standard preparation procedure for gas sorption.

Another method sometimes used during preparation of cement paste specimens for gas sorption is solvent exchange. Before drying, the specimen is placed in a bath of a solvent having a high vapor pressure, such as methanol, thus allowing the pore water to exchange with the solvent. The solvent is then removed using a standard method such as D-drying. Preparation by
this method results in significantly higher surface area values than otherwise. Another factor affecting the nitrogen surface area is the rate of drying. Faster drying, particularly in the relative humidity range of 30-70% where capillary tension forces are greatest, results in a higher measured surface area. All the evidence from different drying methods points to an effect of capillary tension on the C-S-H phase, with harsher drying rearranging the pore structure so as to exclude adsorbate molecules from entering the finest pores.

6.11.3.3.2 Gas Sorption Results

The surface areas of cement paste measured by sorption of nitrogen and of water vapor are usually quite different, with water vapor giving higher values. For well hydrated cement dried rapidly and completely to a D-dried state, water vapor gives about 200 m$^2$ g$^{-1}$, while nitrogen gives 50-140 m$^2$ g$^{-1}$, depending primarily on the w/c ratio.

The difference between nitrogen and water vapor surface areas was the subject of a vigorous debate in the literature in the 1960s and early 1970s. One point of view was that only the smaller water molecule could fully penetrate the smallest pores and thus measure the full surface area [31, 32]. Proponents of this theory hypothesized that the C-S-H gel contained many "ink-bottle" pores with entrances of a size that allowed water molecules to enter while excluding nitrogen. Others argued that water vapor was chemically or structurally re-incorporated into the C-S-H gel phase during the measurement, causing the water vapor results to be too high [33]. C-S-H structural models are discussed in Section 6.11.4.

There are a few significant observations supporting the view that nitrogen sorption provides the more useful results. Nitrogen sorption is used with good success to characterize many other colloidal and microporous materials that have pore systems comparable to that of cement [27], suggesting that the difference between the results from nitrogen and water in
cements is due to chemical interactions rather than pore inaccessibility. When cement surface areas are measured with sorptive gases having different molecular sizes, water vapor does not match the trend observed with other molecules. As shown in Table 4, the surface area measured with water is much higher than would be expected. Finally, the surface area obtained with water vapor does not vary with the starting water/cement ratio of the cement (see Table 5), as is observed with other sorptive gases (and with small-angle scattering). The increase in the relative amount of fine pore structure with w/c (and with other variables such as chemical and mineral admixtures) is an important aspect of cement paste, and the insensitivity of water vapor to these variables certainly limits its usefulness regardless of which method measures the "full" surface area.

The surface area measured with nitrogen ($S_N^2$) increases with hydration time until it plateaus at a maximum value. The maximum surface area as well as the time to reach this plateau increases with the water/cement ratio. Figure 4 shows typical results for the variation in $S_N^2$ with age for cement pastes with different w/c. The lower w/c specimen reaches a maximum surface area value by 28 days, while the higher w/c specimen continues to increase in surface area out to 180 days. The increase in surface area of mature pastes with w/c is shown in Table 5. A logical interpretation of these results is that the amount of hydration (and the amount of surface area) is controlled by the space available for new product to form. However, hydration (defined as continued binding of free water) can continue long after the maximum surface area has been reached. In addition, all pastes, even mature pastes with low w/c, have some capillary porosity. This and other related observations have led to the proposition that two structures of C-S-H form in cements, only one of which has a high surface area. This is discussed in more detail in Section 6.11.4.2.
6.11.3.4 Small Angle Scattering

Small-angle scattering is a powerful tool for characterizing complex microstructures. It is a particularly attractive technique for characterizing cement paste because it is sensitive to features on the order of a nanometer in size and larger, and because specimens can be analyzed with water-filled pores, thus avoiding the problems associated with drying discussed in the previous section. Small angle neutron scattering (SANS) and small angle X-ray scattering (SAXS) operate on the same physical principle (diffraction), and they are discussed together in this section. The primary difference between SAXS and SANS is that neutrons are scattered by interactions with atomic nuclei, while X-rays are scattered by interactions with outer shell electrons. However, in both cases the scattering occurs at interfaces between two phases. In cement, the scattering of both X-rays and neutrons is mostly at the interface between solid C-S-H and the pore system, although information about coarser microstructural features can also be obtained.

Scattering techniques and their application to porous materials are discussed in detail elsewhere in this volume so only a brief overview focusing on issues relevant to cements is given here. The energy source consists of an intense, monochromatic (single wavelength) beam of either neutrons or X-rays. The thickness of the specimen is chosen so that majority of the incident intensity, generally 70% or more, passes through the specimen without interaction. (If the transmission is too low, multiple scattering effects limit the utility of the data. For cement paste, the maximum thickness is about 1 mm for SANS and perhaps half that for SAXS. In both cases the volume of paste that is sampled is large enough to be statistically representative of the microstructure.) Most of the remaining intensity is scattered through random, elastic collisions with atoms in the specimen, creating large incoherent background signals. Thus only a small
fraction of the incoming intensity (on the order of 1%) is scattered by diffraction through a small angle via interactions with microstructural features within the bulk of the material. These data must be separated from the incoherent background and calibrated as part of the analysis. The interpretation of SANS scattering data from highly disordered materials such as cement paste was discussed by Allen et al. [37]. Thomas et al. [22] have reviewed the application of SANS and SAXS to cement paste.

For purposes of analysis, the scattering angle, $\Phi$, is normally replaced with a scattering vector, $Q$, defined as:

$$Q = \frac{4\pi}{\lambda} \sin \left( \frac{\Phi}{2} \right)$$

where $\lambda$ is the wavelength of incident neutrons or X-rays. This substitution simplifies the mathematics.

For cement and similar porous materials, the small-angle scattering profile, which is the flux of neutrons or X-rays as a function of scattering vector, is effectively a form of Fourier transform of the solid/pore microstructure. As the scattering vector increases, the size of the microstructural features that contribute to the signal decreases, so different aspects of the microstructure can be probed by focusing on the appropriate range of data. The intensity of the small angle scattering is a strong function of scattering vector, falling off sharply as the scattering vector increases. The smallest values of $Q$ that can be resolved (and thus the largest microstructural features) are determined by the experimental setup. The effective maximum scattering angles, and associated minimum dimensions studied, are determined by the signal-to-noise ratio as the small-angle scattering becomes small compared to the incoherent background signal. This is an important issue for surface area determination.
The surface area of a specimen is determined from the small angle scattering response at the largest scattering vectors, called Porod scattering. In the Porod region the intensity of the scattering, $I$, falls off as $Q^4$, and the surface area is given by

$$S_V = \frac{C_P}{2\Delta |\Delta \rho|^2}$$

(8)

where $S_V$ is the surface area per unit sample volume, $\Delta \rho$ is the difference in the scattering length density of the two materials forming the interface associated with the scattering, and $C_P$, the Porod constant, is the intercept of a linear fit to Porod data plotted as $IQ^4$ vs. $Q^4$. The term $|\Delta \rho|^2$ is called the scattering contrast, and it represents the relative strength of the scattering interaction created by the interface between the two materials that define the surface. For cement, this contrast is between C-S-H and H$_2$O in a saturated paste, or between C-S-H and air if the paste is dried.

Once the Porod constant has been measured, there are two ways that the surface area can be determined from Eq. 8. The first, and preferred, method is to determine the scattering contrast. If the formula and density for the two phases creating the interface are known, the contrast can be calculated directly. Unfortunately, this is not the case for cement because the amount of water that should be included in the solid C-S-H phase for the purpose of this calculation is not known a priori. In the case of SANS, the contrast can be calculated experimentally by taking advantage of the difference in contrast when specimens are exchanged with D$_2$O (heavy water) [38-40].

The second method for determining the surface area is the "scattering invariant" method. The scattering invariant, $I_{inv}$, is given by:

$$I_{inv} = \int_0^\infty IQ^2 dQ = 2\Delta |\Delta \rho|^2 \phi_V$$

(9)
where $\phi_v$ is the volume fraction of the scattering phase, which is C-S-H in the case of cement. This method has two advantages: the data need not be absolutely calibrated, and the scattering contrast does not need to be known explicitly. However, these are more than offset by the difficulties associated with taking the integral in Eq. 9. The integration must be over all values of $Q$, which requires extrapolation of the experimental data. Uncertainties in the scattering profile or in the incoherent scattering subtraction create the potential for large errors, particularly at high $Q$ [22]. Another problem is that the volume fraction of C-S-H, $\phi_v$, is not easy to determine accurately.

Most SANS surface area values have been calculated using the contrast method, while SAXS studies have generally used the scattering invariant method.

An important contribution of small angle scattering to the study of cement is the discovery that the C-S-H phase has a disordered fractal structure [39, 41, 42], the non-solid spaces of which actually comprise the so-called "gel porosity" and, perhaps, part of the capillary porosity as well. In this context a fractal region can be defined as a heterogeneous microstructure that remains consistent over various length scales, and such a microstructure is readily identified by the presence of a linear region on a log-log small-angle scattering plot of $I$ vs. $Q$. Figure 5 shows a typical SANS plot of this type for a mature cement paste and the various $Q$-ranges of interest. SAXS plots are essentially similar.

At larger $Q$ values where smaller features are probed, a mass or volume fractal structure is observed with both SANS [38, 39] and SAXS [42-44] with a fractal scaling exponent, $D_V$, of 2.5-2.8. Monte Carlo simulations performed on SANS data by Allen et al. [39] indicate that this structure is generated by the random aggregation of 5 nm diameter particles of C-S-H. At $Q$ values just above the volume fractal region (the Guinier region, see Figure 5), a discrete
population of scatterers of this size can be identified [45]. These results are consistent with a C-S-H outer product structure consisting of colloidal-sized particles that are aggregated into larger clusters [39]. No evidence for an interlayer structure is observed at these length scales.

At lower $Q$ values, a surface fractal structure can be observed, with calculated scaling exponents, $D_S$, ranging from about 2.5 to 3.0 [39]. This region can be associated with the development of surface roughness on the original cement grains as they hydrate [41]. The transition from surface fractal to volume fractal regions occurs at a $Q$-value of about 0.2 -1nm. It is interesting to note, in view of the large differences in the reported surface area values, that SANS and SAXS studies of cement are in good agreement regarding the fractal nature of the microstructure.

For saturated cement paste with w/c values in the range of 0.3 - 0.6, reported SANS surface area values range from 70-147 m$^2$ g$^{-1}$ [35, 37, 39, 46] while reported SAXS values range from 210-618 m$^2$ g$^{-1}$ [44, 47-49]. These values have been renormalized to a basis of grams of dry paste (see [22]). The SANS values are in reasonable agreement with reported nitrogen gas sorption values, and show a similar trend with w/c (see Table 4). The SAXS values are 2-6 times higher than the SANS values, and there is significant variation from study to study. This suggests that different assumptions were made in the calculation of the scattering invariant, as discussed earlier. There is also the possibility that SAXS studies probe more of the C-S-H fine structure than SANS. SAXS studies use a shorter wavelength than SANS studies, and this in principle allows SAXS to reach higher scattering vectors where scattering from features smaller than (and within) the 5 nm globules would be seen. The SAXS surface area is observed to decrease significantly on drying [47-49], which may favor this hypothesis. Determining the appropriate
SAXS scattering contrast for cement (so as to avoid the need to estimate the scattering invariant) is perhaps the best way to resolve these issues.

One of the major advantages of small-angle scattering is that the same specimen can be measured repeatedly as it hydrates, allowing the development of the microstructure and surface area to be monitored during the critical first few days after mixing. Figure 6 shows the surface area development of a cement paste as measured by SANS [35]. The surface area tracks closely with the heat evolution until about 18 hours, and then levels off. This indicates that the fine-pore structure associated with a high surface area develops primarily during the rapid hydration period (Stage 3 in Figure 1), and that after the paste sets the microstructure is more static, although hydration continues.

6.11.3.5 NMR relaxation

Nuclear magnetic resonance (NMR) is another advanced technique that is used to study a wide variety of atomic-scale interactions in materials. The technique is based on the fact that most atomic nuclei have a non-zero spin state. The rate at which the spins align themselves with a static magnetic field (spin-lattice NMR), or the response of the material to an oscillating magnetic field (spin-spin NMR), provides information about atomic interactions with adjacent nuclei and with the surrounding medium. For materials with a water-filled pore system such as cement, NMR utilizes the fact that nuclear spin interactions between water and the solid pore walls are much stronger than interactions in the bulk fluid. The NMR relaxation response of mobile hydrogen is thus sensitive to the surface to volume ratio of the pore system, and this allows a surface area value to be inferred. The application of NMR relaxation techniques to porous media was reviewed by Halperin et al. [50].
The first surface area measurement of cement paste using NMR, done using spin-lattice relaxation, reported values as high as 900 m² g⁻¹ for mature cement paste [51]. However, the approach used to calculate the surface area (based on the BET approach for multilayer adsorption) was later shown to be inaccurate [52]. Halperin et al. [52, 53] developed a different approach, deriving an expression for the total surface area accessed by mobile water in a specimen:

\[ S = \frac{T_{2s}V}{\lambda T_{2i}} \]  

(10)

where \( \lambda \) is the thickness of the layer of mobile surface water, \( V \) is the volume of mobile water in the pore system (the evaporable water content, determined after the experiment), \( T_{2s} \) is the characteristic spin-spin relaxation time for mobile surface water, and \( T_{2i} \) is the experimentally measured spin-spin relaxation time for mobile water in the saturated paste. The parameter \( T_{2s} \) is determined by measuring the change in \( T_{2i} \) as the paste is progressively dried.

Using this approach, Halperin et al. [53] observed the development of the surface area during the hydration of a white cement paste (a low-iron cement quite similar to OPC with \( w/c = 0.42 \), using spin-spin relaxation. They found that the surface area increased rapidly between 6 hours and about 48 hours, and that there was essentially no surface area increase between 100 and 1000 hours. This behavior is quite similar to the SANS results shown in Fig. 6. The maximum surface area was \(~280\) m² g⁻¹ of dry paste, a value which falls between the values reported for SANS and for SAXS.

6.11.3.6 Other techniques

Scanning electron microscopy (SEM) and optical microscopy can be used to identify pores larger than about 500 nm. SEM provides higher magnifications and the potential to see
smaller pores, but requires drying the specimen and thus altering the fine microstructure. Digital image analysis can be used to separate porosity from solid phases quantitatively, and backscattered SEM images have been used [54] to measure total coarse porosity values that, although lower, correlate well with the capillary porosity. Although microscopy is one of the most widely used and valuable techniques for studying cement microstructure and morphology, the inability to characterize the gel pores limits its use as a probe of the pore system.

Another method of studying the coarse porosity is low-temperature calorimetry, which takes advantage of the depression of the freezing point of water confined in a pore. As the temperature is lowered below 0°C, ice forms in progressively smaller pores (the higher the surface to volume ratio the lower the freezing point), and the resulting change in heat capacity makes it possible to obtain a sort of pore size distribution [55]. Recently, quasi-elastic neutron scattering (QENS) has also been used to monitor the same effect [56]. QENS measures the relative amounts of bound and free water in a paste, allowing the fraction of frozen water to be monitored as a function of temperature.

Impedance spectroscopy (IS) measures the AC electrical response of a material as a function of frequency. Because the cement pore solution is much more of a conductor than the solid phases, IS is quite sensitive to the connectivity of the pore system, which is directly related to the permeability. This, combined with the relative experimental simplicity of IS, makes the technique potentially of great use both for fundamental studies and as a diagnostic technique. Christensen et al. [57] reviewed the application of IS to cement paste. The complexity of the IS data analysis invites analogy to small-angle scattering, but the latter technique has the benefit of having been widely used on related systems such as clays, and enjoys a more sound theoretical underpinning. The impedance response of a porous material is affected by a wide variety of
microstructural variables, and some features of the data obtained from cements are not well understood [6]. Reported IS results, particularly those attempting to produce quantitative values, have met some resistance in the cement research community due to a perceived lack of theoretical grounding.

6.11.4 Models of C-S-H

Historically, structural models of C-S-H have been developed in parallel with available experimental observations, and improvements in analytical techniques have often led to new models. Early work, beginning with Le Chatelier in 1887 [58], relied exclusively on direct observation and optical microscopy. These studies noted the gelatinous character of the hydration product and provided some information about the distribution of unhydrated cement clinker grains, crystals of calcium hydroxide and other compounds, but no details of the pore network. Early electron microscopy and X-ray diffraction studies provided little additional information.

Studies of the pore network were begun in earnest in 1936 by a group led by T.C. Powers at the Portland Cement Association in the United States. At that time, researchers considered the cement hydration products as a single, continuous “cement gel” phase that included C-S-H, calcium hydroxide, and other reaction products. They reasoned that an understanding of the physical properties of this gel would provide insight into the physical properties of cement paste. A general principle that has governed the development of most models for the structure of C-S-H is that macroscopic properties such as volume, strength, hardness, and permeability, and particularly changes in these properties with relative humidity, depend less on chemical composition than on the incorporation of water into the porosity.
6.11.4.1 Early Models for the Structure of C-S-H

Several early models for the structure of C-S-H are discussed below; a summary of prominent aspects of these models are listed in Table 6.

From measurements of the water content and dimensional changes as a function of relative humidity, Powers and Brownyard [12] modeled the cement gel as a colloid with a characteristic particle radius of about 5 nm. An important feature of this early model is that the cement gel contains 28% internal porosity by volume, referred to as gel porosity. This porosity is the minimum that can be contained in fully reacted cement paste, and any additional porosity is defined as capillary porosity. For purposes of comparison to later models, it is useful to recalculate the values obtained by Powers and Brownyard by assigning all of the surface area and gel porosity to the C-S-H phase alone. Using average conversion factors described elsewhere [59] for fully reacted pastes, the characteristic radius of the particles is 3.3 nm, and the gel porosity occupies 42% of the C-S-H volume. These values should be compared to values listed in Table 7.

In an X-ray diffraction (XRD) pattern from cement paste the only features that can be attributed to C-S-H gel are a diffuse peak between 0.27 and 0.31 nm and another peak at 1.82 nm, thus underlining the lack of long-range crystallographic order in C-S-H gel. The observed peaks suggest a structure on the sub-nanometer scale that is related to the lattice spacings in calcium hydroxide [61]. Using XRD and chemical analysis, Taylor [61] classified C-S-H gels into two structural types: C-S-H (I), which precipitates from aqueous solutions of soluble salts such as CaCl$_2$ and NaSiO, and C-S-H (II), which forms from the hydration of C$_2$S and C$_3$S. The XRD patterns from C-S-H (I) and C-S-H (II) are similar to those of 1.4 nm tobermorite.
(~ $\text{C}_5\text{S}_6\text{H}_9$) and jennite ($\text{C}_9\text{S}_6\text{H}_{11}$), respectively, which are naturally occurring calcium silicate hydrate minerals. The reasons for the differences between C-S-H (I) and (II) are not well understood. Taylor [62] proposed that C-S-H gel in cement paste has a disordered layer structure, with individual layers resembling 1.4-nm tobermorite with many imperfections, primarily missing silicate tetrahedra.

The Taylor model proved useful for explaining the lack of order in the structure of the C-S-H formed by cement hydration. It also strongly influenced later models of the C-S-H pore network, which generally incorporated a layered structure. The model became so well accepted that the literature of the 1950s often referred to C-S-H as the "tobermorite gel". Relatively recently, based on composition, thermogravimetric, and sorption data, Taylor modified the C-S-H gel model to incorporate a mixture of imperfect jennite and tobermorite layers [62]. This is consistent with sub-micrometer variations in the molar ratio of CaO to SiO$_2$ observed by SEM and TEM [8].

Brunauer [32] used water sorption data to argue that the C-S-H gel consists of sheets two or three layers thick that, on drying, roll into fibers. This is similar to the "Type I" morphology observed in the SEM (see Table 1). The concept that a C-S-H gel morphology consisting of intertwined fibers gives cement paste its high compressive strength and low tensile strength has been widely explored. Brunauer also advanced the idea that water is removed from C-S-H interlayers on drying and cannot re-enter these spaces when the paste is resaturated (because of irreversible collapse), thus providing an explanation for irreversible shrinkage. A controversial consequence of this theory is that, because of its small molecular size, water vapor, unlike other larger gas molecules, can enter the smallest pores and thus measures the surface area of cement paste more accurately than larger gases such as nitrogen.
Feldman and Sereda [33] proposed a different layered structure for C-S-H gel consisting of highly irregular sheets, sometimes crumpled and sometimes folded. On the basis of changes in length, weight, and modulus as a function of drying and rewetting, as well as hysteresis in gas sorption isotherms, they concluded that water could in fact re-enter the C-S-H interlayer space. Consequently they argued that gas sorption using water vapor gives an incorrectly high surface area value, and that a different molecule such as nitrogen should be used to characterize cement paste. An important property of their proposed layered structure is that water can leave and re-enter the interlayer spaces causing the material to shrink and swell. These issues are also discussed in Section 6.11.5.2.

Another colloid model was proposed by Wittmann [63]. His basic structure is that of a xerogel, and dimensional changes on drying are rationalized in terms of water adsorbed on the surface of the particles. Of greatest importance are the forces between the particles, which are generally reduced as water adsorbs and moves between touching particles.

6.11.4.2 Quantitative Colloidal Model of C-S-H

One of the authors of this Chapter (HMJ) recently proposed another colloid model [59]. Although similar in many ways to some of the models described above, this new model is more quantitative than previous models and is designed to be consistent with a wide variety of experimental measurements. As with the early Powers and Brownyard model [12], this model proposes roughly equiaxed colloidal particles, but in this case they are packed into one of two fractal structures that have densities and surface areas that apparently increase as the measurement technique increases in sensitivity to fine structure. The more open structure is called "low-density" (LD) C-S-H, and the more tightly packed structure is called "high-density" (HD) C-S-H. Both the surface and volume fractal dimensions (see Section 6.11.3.4) of the
overall structure are computed to be 2.7; the transition between these two fractal regions occurs at a length scale of about 20 nm. If the smallest model units are assumed to pack together as spheres (they may have a layered structure and be more like cubes) for computational purposes, then the density and specific surface area are related by (for either spheres or cubes):

\[ S = \frac{1}{\rho r} \]

where \( S \) is the surface area per gram of D-dried C-S-H, \( \rho \) is density of D-dried C-S-H and \( r \) is the radius of the smallest units being considered.

The idealized sphere version of LD C-S-H is shown in Figure 7. From this structure the surface area and porosity that would be measured experimentally can be calculated based on the smallest unit or grouping of units that can be resolved. As water is added to the structure, pores in the densest regions that contain the smallest pores are assumed to fill first. This allows the water content at a given relative humidity to be determined based on the volume of porosity filled, from which the density can be calculated. Measured and computed values from this model structure are listed in Table 7.

As shown in Figure 7, the smallest particles, called the basic units, pack into "globules" that are approximately 5 nm in diameter. These globules then pack into either the LD or HD morphology, depending in part on when they form during the hydration process. The LD C-S-H has more of the larger interglobular pores, which can be resolved by techniques such as neutron scattering and nitrogen sorption. This structure also has some pores that are missed by nitrogen sorption. The HD C-S-H contains only smaller interglobular pores, down to the smallest, which can be resolved only by the highest resolution techniques. In an experimental sense, the interglobular spaces correlate to gel porosity and the intraglobular spaces correlate to interlayer porosity that can be reversibly re-entered.
Separating the C-S-H gel into two morphologies with different densities is a more complex proposition than simply allowing the globules (or the basic units) to pack more or less efficiently depending on age and other local conditions, and accordingly this aspect of the model is controversial [64, 65]. The simpler scenario of a single kind of C-S-H, with varying packing density, was explored intensively during the development of the model having two morphologies; it was found that important experimental observations defied explanation when the simpler model was used. For example, if the total porosity is taken as that measured by water, it can be shown that increasing the \( w/c \) ratio leads to an increase in nitrogen surface area as well as an increase in volume of fine porosity that is inaccessible to nitrogen [60, 65]. This counter-intuitive result is best explained by invoking two types of C-S-H with different densities.

Support for the new colloidal model comes from its ability to explain a wide variety of experimental data as shown in Table 7. For example, the model is consistent with the wide range in specific surface area values measured by various techniques (see Section 6.11.3), and with the kinetics of surface area development as measured by SANS (see Figure 5). It is in agreement with the fundamental 5 nm particle size measured by SANS and with the volume and surface fractal regions in cement paste determined by small-angle scattering techniques. It also correctly predicts the water content and density of the C-S-H gel as a function of relative humidity (see Table 7).

One of the implications of this model, and of volume fractal structures in general, is that the measured surface area and porosity depend on the technique used for the measurement. The concept of surface area as an intrinsic material parameter thus becomes somewhat misleading. For example, it does not follow that the highest measured surface area is the correct one. It may be more important to measure the functional relationship between the measured surface area and
the resolution of the applied technique. Important properties of cement paste such as shrinkage appear to be governed by the structure at the length scale of the globules rather than the smaller basic units that constitute the globules.

6.11.5 Macroscopic Properties of Concrete

When considering the complexities of the porous structure of hardened cement paste, one can easily lose sight of the primary function of hardened cement paste, namely to bind sand, stone and other materials together to form concrete. Since concrete is primarily used as a structural material, it must satisfy very specific engineering property requirements. For example, concrete must possess an adequate compressive strength (~ 30 to 40 MPa), a controlled volume stability under drying conditions and external load, and adequate resistance to aggressive environmental agents. This section will address the influences of porosity and water on these properties. In addition, a section on aging phenomena in cement paste will borrow analogies from colloid and sol-gel science to help explain some of the peculiarities in concrete behavior.

6.11.5.1 Strength of Concrete

Strength is the most basic property of concrete. Simply put, if a concrete structure does not attain a sufficient compressive strength, the structure can fail when externally loaded. This, however, rarely occurs in practice, and failure is more closely related to the effects of volume instability (Section 6.11.5.2), impermeability (Section 6.11.5.3) and physicochemical deterioration (Section 6.11.6) than to compressive strength. Nevertheless, strength should not be overlooked since adequate levels of strength can only be obtained by a deliberate control of the porosity of the hardened cement paste.
6.11.5.1.1 Effect of Porosity on Strength

Porosity is the single most important parameter influencing the strength of a porous body. Intuitively, one would expect that an increase in the porosity of a material will decrease its strength due to the fact that pores, filled with air or fluid, cannot sustain load. Hardened cement paste, being a porous material, behaves according to this expectation. Figure 8 shows the relationship between capillary porosity and compressive strength for cement pastes; also contributing to the curve are cement pastes cured by autoclaving (which produces a distinctly different crystalline hydration product), and a variety of porous aggregates. The fact that all three classes of materials fall on the same curve reinforces the correlation between porosity and strength. As also indicated on Figure 8, the capillary porosity range for normal hardened cement pastes is approximately 25 to 50%; this range roughly correlates to compressive strengths between 7 to 60 MPa.

6.11.5.1.2 Gel-Space Ratio

The most important variable influencing the porosity of concrete is the original water to cement ratio \((w/c)\). In Section 6.11.2.5, it was seen that the \(w/c\) ratio defines the finite amount of space available for the hydration products; a low \(w/c\) ratio \((< \sim 0.38)\) restricts complete hydration due to insufficient space for hydration products, whereas a high \(w/c\) ratio \((> \sim 0.38)\) results in permanent residual spaces called capillary pores. Powers and Brownyard [12, part 6] utilized this physical space-filling description of cement hydration to formulate their classic interpretation of strength. According to their theory, strength is directly related to the gel/space ratio, \(X\), which is the ratio of the volume of the hydration products to the space available for the hydration products. Numerically, the gel-space ratio is defined as,
\[ X = \frac{0.68\alpha}{0.32\alpha + w/c} \]  \hspace{1cm} (12)

where \( \alpha \) is the extent of reaction and \( w/c \) is the original \( w/c \) ratio. Compressive strength, \( \sigma_C \), is related to the gel-space ratio by,

\[ \sigma_c = A X^n \]  \hspace{1cm} (13)

where \( A \) is a constant (estimated to be \( \sim 234 \) MPa for ordinary Portland cement [12, part 6]) representing the intrinsic strength of a hardened cement paste (i.e., the strength at \( X = 1 \)), and \( n \) is a constant in the range of 2.6 to 3.0 that depends on the characteristics of the cement. According to this formulation, an increase in the gel-space ratio will increase the strength of the paste, and therefore that of the concrete.

An important implication of the gel/space theory is that two cement pastes of different \( w/c \) ratios can be at similar extents of reaction (i.e., equal \( \alpha \)'s) but with considerably different compressive strengths. A paste with a \( w/c \) ratio of 0.4, for example, requires only 60% hydration to equal the strength expected from a \( w/c \) ratio of 0.6 at 90% hydration.

### 6.11.5.2 Shrinkage and Creep

Concrete undergoes small, but significant, dimensional changes when exposed to stimuli such as applied stress and changes in relative humidity or temperature. The deformation response of the concrete to these various stimuli is complex, often exhibiting reversible, irreversible and time dependent deformations. The following section discusses two types of deformations, shrinkage and creep. The former relates to changes in volume associated with the loss of water, while the latter refers to the time dependent deformation that occurs under an externally applied constant load.
Shrinkage and creep are clearly interrelated as evidenced by the comparable magnitudes of deformation, and the similar dependencies on certain variables. Their most important similarity, however, is the fact that both are dependent on the water content in concrete: shrinkage cannot occur without loss of water, whereas creep is essentially non-existent without the presence of water. These simple observations suggest that the two phenomena result from the same characteristic of the hardened cement paste, namely its porosity.

6.11.5.2.1 Definitions of Shrinkage

The term shrinkage is a general term used to describe the changes in volume accompanying the loss of water from concrete. Since water can be lost in different ways, there are different types of shrinkage. Unless stated otherwise, shrinkage is generally taken to mean drying shrinkage, the deformations associated with the loss of moisture from hardened concrete by evaporation. Shrinkage that occurs from the loss of water from fresh (or unhardened) concrete is called plastic shrinkage. Autogenous or chemical shrinkage is a special case in which the removal of moisture occurs internally from chemical combination of water during hydration in a sealed curing environment, a process defined as self-desiccation in Section 6.11.2.5. Carbonation shrinkage is another special case that refers to the reduction in volume accompanying the chemical reaction between hydrated cement and atmospheric carbon dioxide.

6.11.5.2.2 Drying Shrinkage

Drying shrinkage is generally considered the most important of the shrinkage phenomena since its debilitating effects can readily occur throughout the lifetime of a concrete structure. If the dimensional changes associated with drying shrinkage are neglected in design and
construction considerations, significant shrinkage cracking of structural elements can occur, ultimately leading to a reduction in the functional life of the structure. An understanding of the causes of drying shrinkage is thus an essential criterion for ensuring concrete durability.

As introduced in Section 6.11.2.4.3, drying shrinkage is a direct manifestation of the intimate association between C-S-H gel and water that is caused by the colloidal structure of C-S-H. This association is so significant that the deformation of hardened cement paste (which dictates that of concrete) depends on the response of both the liquid and solid phases, and especially the interaction between them. A change in the one phase necessarily induces a change in the other. As we shall see, in drying shrinkage, for example, a change in the external relative humidity will induce a response in the liquid phase, which in turn will prompt a counterbalancing effect in the solid phase to regain equilibrium.

It should be noted that several researchers have shown that the extent of drying shrinkage in hardened cement pastes can usually be directly related to surface area and porosity as measured by nitrogen. Although there are some exceptions (most notably, in the cement mixes containing chemical additions called admixtures), hardened cement pastes with higher nitrogen surface areas will experience greater shrinkage strains.

6.11.5.2.3 Effect of Relative Humidity on Drying Shrinkage

When the relative humidity is lowered from 100% (saturation), water evaporates from the pores of hardened cement paste, and the body will shrink (Figure 9). Shrinkage is measured as a linear deformation, $\Delta L/L$, where $\Delta L$ is the change in length from the initial length, $L$. Increasingly stringent drying conditions are also noted on Figure 9, beginning at the top with the
saturated state (100% RH), continuing through the range of relative humidities, and ending with D-drying (defined in Section 6.11.2.4.2) and high temperature heating.

The presence of several distinct linear regions in Figure 9 suggests that several different mechanisms of drying shrinkage may operate over different ranges in RH. Regions (1) and (2), which extend from 100% RH to approximately 45% to 50% RH, represent the loss of water from the capillary pores. Region (3), extending from 45% to approximately 11% RH, is generally attributed to the loss of adsorbed water on the surface of the C-S-H gel particles. Further drying results in a loss in interlayer water in region (4). Heating to high temperatures ultimately leads to the decomposition of C-S-H gel in region (5). Although regions (4) and (5) might represent what happens when concrete is exposed to fire, they do not reflect normal conditions. Hence, only the mechanisms involved in regions (1), (2), and (3) will be considered further.

6.11.5.2.4 Mechanisms of Drying Shrinkage

Four mechanisms are generally associated with drying shrinkage: capillary pressure (as introduced in Section 6.11.2.4.3), disjoining pressure, surface tension, and removal of interlayer water. A brief review of these phenomena is presented here; details on these particular mechanisms [1, 68, 69] and related issues concerning the drying of gels (see Chapters 7 and 8 in Ref. [7], [21]) can be found elsewhere.

A. Capillary Pressure. As predicted from the Kelvin equation, increasingly negative capillary pressures (i.e., increasing tension) develop in the liquid phase of hardened cement paste when the relative humidity of the external environment is lowered. To relax the tension in the liquid phase, the neighboring solid phase, which is essentially the C-S-H gel, goes into compression. This counterbalancing compressive force causes the C-S-H gel to shrink; depending on the size of the pores from which evaporation is occurring, capillary pressures can be on the order of tens of
MPa [70]. At this magnitude, the formation of cracks can readily occur in the hardened cement paste. It is important to note that theoretically capillary pressures cannot exist below about 40 to 45% RH, since below that point, the fracture strength of liquid water (~ 120 MPa [20]) is exceeded, and liquid/vapor menisci are unstable.

**B. Disjoining Pressures.** C-S-H gel particles are separated by strongly adsorbed thin films of water that adopt a repulsive swelling pressure to counteract the attractive van der Waals interactions between the solid surfaces[71, 72]. During drying, the thickness of adsorbed films decreases due to a migration of the adsorbed water to neighboring capillary pores, which thus creates a net shrinkage in the C-S-H gel [71].

**C. Surface Tension.** A solid C-S-H gel particle, being no more than a micrometer in dimension, is under compression due to the large curvature of its surface and to its surface tension (a phenomenon described by the Laplace equation). When water is adsorbed on the surface of such a particle, the surface tension is relaxed (i.e., decreases) causing a dilatation of the particle that is directly proportional to the change in surface tension (a relationship described by the Bangham equation). Alternatively, during drying, the surface tension is intensified and the particle will contract. These effects of surface tension on dimensional changes become appreciable only for RH less than ~ 30% [69].

**D. Interlayer water.** If drying is conducted below 11% RH (the RH at which a monolayer of water is believed to be stable), interlayer water in the C-S-H gel is lost, creating a concomitant shrinkage and a potentially irreversible collapse of the structure.

**6.11.5.2.5 Irreversible Shrinkage**

With the possible exception of shrinkage from loss of interlayer water, the above mechanisms imply that drying shrinkage is a reversible process (i.e., if rewet, the sample should
return to its original dimensions). Experimental observations, however, show that the total shrinkage occurring on first drying is largely irreversible. Helmuth and Turk [73] further showed that irreversibility occurs on first drying only, and that subsequent deformation induced by additional wetting and drying cycles is reversible. In the same study, it was also shown that it is only the irreversible part of the total shrinkage that increases with original porosity; the reversible shrinkage is independent of the original porosity. Together, these findings concerning irreversible shrinkage suggest that permanent microstructural changes are induced in the hardened cement paste as a result of first drying, evidence is found in several studies [74-76].

Another peculiarity unique to cement paste is that irreversible shrinkage is strongly influenced by its drying history. The ultimate total shrinkage will, for example, decrease if the paste is conditioned at progressively lower RH’s before reaching the lowest RH (i.e., the total shrinkage of a cement paste dried directly from saturation to 50% RH will be greater than that of a paste dried in stages from saturation, to 85% RH, to 50% RH). Moreover, it has also been noted that extended exposure to a constant low RH will tend to progressively increase the irreversible shrinkage in a cement paste [73].

At present, the exact causes of irreversible shrinkage in hardened cement pastes have not been determined. As discussed in Section 6.11.5.4, there is evidence [77] that irreversibility could be due to the formation of additional silicate bonds when the surfaces of C-S-H are brought closer together by capillary pressures. Irreversible behavior has also been postulated to be a result of the formation of new interlayer spaces in C-S-H during shrinkage and creep [78]. Recently, technique based on image analysis has revealed large microscopic deformations in the C-S-H phase during drying from 100% to 40% RH [79]. It was suggested [59, 79] that the collapse of the C-S-H gel from the associated capillary pressures was analogous to what happens
during the “constant rate period”. (The “constant rate period” denotes the initial stage of drying where the shrinkage of a gel is equal to the volume of evaporated liquid [21]; the shrinkage can account for over an order of magnitude reduction in volume in colloidal gels [7].)

6.11.5.2.6 Definitions of Creep

Creep refers to the time dependent deformation of concrete that occurs under an externally applied constant load. The phenomenon of creep is present in other classes of materials such as metals and ceramics; however, the process of creep in concrete is unique in the sense that it readily occurs at ambient temperature, and is considerably affected by the presence of water. Creep is significant since the strains under a constant stress can be several times larger than the initial elastic strains on loading, and, if not taken into consideration can lead to excessive deflection and other serviceability problems. However, creep can be beneficial, and is in fact essential in relieving stress in anchored concrete structures[16] which are unable to relax internal stress by shrinkage because of their fixed dimensions.

As with shrinkage, there are several types of creep. Basic creep refers to the creep strains occurring in a closed environment, where no loss or gain of moisture can take place. If concrete is allowed to dry and creep simultaneously, the total deformation is not equal to the expected sum of the drying shrinkage strains ($\varepsilon_{sh}$) and the basic creep strains ($\varepsilon_{bc}$), but is, in fact, greater by an amount denoted as drying creep (a phenomenon also called the Pickett effect [80]). Total creep strain ($\varepsilon_c$) is the sum of the basic creep strains ($\varepsilon_{bc}$) and the drying creep strains ($\varepsilon_{dc}$). It should also be noted that all creep strains are taken as the excess strain above the initial elastic strain ($\varepsilon_i$), which is often significantly smaller than the creep strains. A summary of the relationships between the strains defined above is represented in Figure 10 and summarized as,
\[ \varepsilon_c = \varepsilon_{hc} + \varepsilon_{dc} = \varepsilon_{tot} - \varepsilon_{sh} - \varepsilon_i \]  \hspace{1cm} (14)

where \( \varepsilon_{tot} \) represents the total time-dependent strain.

Also, as with drying shrinkage, creep is a mostly an irreversible process. When a concrete specimen is unloaded, there is an instantaneous recovery of the small initial elastic strain followed by a gradual, but very incomplete, recovery of the creep strain.

6.11.5.2.7 Effect of Water Content on Creep

Creep is directly related to the water content in the pores of hardened cement paste. When there is no evaporable water prior to creep testing, little, if any, creep is observed (Figure 11) [82, 83]. The relative humidity is also a significant factor since, as mentioned earlier, the effects of drying shrinkage and creep symbiotically produce additional drying creep strains, which can be quite significant (Figure 12).

6.11.5.2.8 Other Effects on Creep

In addition to the dramatic effects of moisture content on creep, there are numerous other variables that are also significant [1, 16, 85]. The following is a short list:

A. **Applied Stress.** Creep increases approximately linearly with the applied stress up to a stress/strength ratio between 0.4 and 0.6. For comparative purposes, specific creep (creep strain per unit stress) is a useful unit for tests in this range.

B. **Strength/Age.** Generally the lower the w/c ratio and the older the concrete specimen, the lower the creep strains.

C. **Temperature.** Concrete creep increases linearly with temperature up to at least 80°C; beyond that, there is uncertainty as to whether creep strains peak at a maximum or the linear relation persists [1].
D. Aggregate. Since aggregates are dimensionally stable (i.e., they do not creep or shrink by appreciable amounts), aggregates in concrete act as restraining phases to the hardened cement paste, which has been shown to be highly susceptible to the dimensional changes of creep and shrinkage. Hence, a greater volume of aggregates will reduce the ultimate creep and shrinkage. Moreover, at a fixed volume fraction of aggregates, concrete will exhibit lower creep with aggregates of higher elastic moduli.

6.11.5.3 Permeability

Permeability is a highly significant property of concrete since most of the chemical and physical processes that are responsible for the degradation of the material (to be described in Section 6.11.6) are dependent on the ingress of external sources of water or ionic species or both. Naturally, the intrinsic pores of hardened cement paste, namely capillary pores and gel pores, control the permeability of concrete. Additional pores of concrete such as the interfacial transition zone (ITZ) that separates the aggregate and hardened cement paste phases, and cracks or microcracks that result from chemical or physical stresses also contribute to the permeability of concrete.

The following sections briefly review the effects of the above-mentioned pores on the permeability of concrete. Also, a summary of the relevant transport processes of matter through these porous networks will be given.

6.11.5.3.1 Effect of Capillary and Gel Pores on Permeability

The capillary pores predominantly control the permeability of hardened cement paste. Immediately after mixing Portland cement with water, the capillary pores (which initially constitute the space between cement grains) form a continuous (or percolating) network of pores,
which corresponds to a high permeability in the hardened cement paste. As hydration products
(mostly porous C-S-H gel) fill space, the capillary pores become increasingly smaller until
eventually they are segmented (or made discontinuous) by the intrusion of hydration products.
During this process, the permeability decreases by several orders of magnitude; in one study [86]
the permeability of a hardened cement paste decreased by 6 orders of magnitude after 28 days of
hydration. The above description accounts for the converse observation that the permeability of
cement paste increases exponentially with capillary porosity and depends primarily on the water
to cement ratio and age [12].

Even when the capillary pores become discontinuous, or are perhaps eliminated by being
completely filled with hydration products, there is a considerable amount of remaining porosity
in hardened cement paste, which is typically around 30%. Most of this porosity consists of gel
pores in the colloidal C-S-H. These small gel pores (of approximately 10nm or less in
dimension), residing in the finely divided colloidal structure of C-S-H are responsible for the
especially low permeability of mature hardened cement paste compared to other materials with
similar porosity. In fact, the flow of liquid in gel pores is so restricted that the permeability of a
30% porous mature hardened cement paste (typically in the range of $10^{-13}$ to $10^{-11}$ cm s$^{-1}$ [31]) is
comparable to that of many natural rocks, which possess porosities in the range of 0.5 to 2% [31,
86, 87].

6.11.5.3.2 Effect of Other Types of Pores on Permeability

Measuring the contributions of capillary and gel pores to the permeability of concrete is
difficult since they are obscured by the influences of other pores in concrete such as interfacial
transition zones and cracks, which are described below.
A. The Interfacial Transition Zone (ITZ). The presence of aggregates in concrete introduces significant changes in the pore structure of hardened cement paste. The most important change is the formation of additional porous regions of hardened cement paste around aggregates. These porous zones, designated as interfacial transition zones (ITZs), are characterized by fundamentally different microstructures than are found in the bulk hardened cement paste [6, 88-90]. The primary characteristics of the 25-50 µm wide ITZ include a higher porosity than observed in bulk hardened cement paste and also the presence of coarse grains of CH and ettringite. In detail, the ITZ displays both mineralogic and textural zoning [88, 91, 92]. De Rooij [92, 93] critically reviewed several models that offer explanations for the characteristics of ITZ, and suggested that syneresis effects could, together with the wall effect (i.e., the inability of hydration products to pack densely near an aggregate surface), account for the width of the ITZ. Since the ITZ can contribute a significant additional porosity to hardened cement paste, it has an important influence on properties such as strength and permeability. Concerning the latter, computer simulation has shown [94] that, at sufficiently high aggregate concentrations, the ITZs in concrete can form a continuous network of ITZ porosity (i.e., a percolation path). As with capillary pores in hardened cement paste, this percolation path can dramatically increase the permeability of concrete.

B. Cracks and Microcracks. Cracks or microcracks result from a multitude of different physical and chemical processes, such as mechanical loading, shrinkage, creep, thermal variations, and expansive chemical reactions. To some extent, almost all cementitious materials are affected by each of these processes to varying extents at different points in time, and consequently, cracks are endemic to the material. As with the ITZ, cracks constitute important features in the microstructure of since they introduce additional porosity in the hardened cement paste phase.
When these cracks coalesce they can form interconnected porous channels that dramatically increase the permeability of concrete, which, however, is seen only when the width of the microcracks exceeds approximately 200 µm [95, 96]; when the widths are below approximately 50 µm [95], there is little gain in permeability.

6.11.5.3.3 Transport Processes

The transport processes relevant to hardened cement paste and concrete are summarized in Table 8 and discussed briefly below; for more information, one should consult the review by Kropp [100]. Permeation, defined by Darcy’s Law (see Table 8), involves the flow of liquids or gases under a gradient in pressure. Diffusion, defined by Fick’s Laws (see Table 8), is characterized by the random motion of ions or molecules from areas of high concentration toward areas of low concentration. Capillary suction involves transport due to the surface tension of the-water in the capillary pores and can be expressed by a modification of Darcy’s Law for unsaturated flow. Adsorption and desorption of vapor are important for the transport of gaseous species such as atmospheric carbon dioxide and water vapor. Migration refers to the movement of ions driven by an electrical field.

6.11.5.4 Aging Processes in Cement Paste

Aging of a gel can be defined as the changes in the structure and properties that occur under ambient or hydrothermal conditions. For cements, aging should be further defined as changes over time that are unrelated to the hydration reactions. Aging of cement primarily involves chemical changes in the C-S-H gel, and these changes also affect the pore size distribution, so aging affects all the properties of cement paste to some extent. This section is predicated on the assumption that cement paste behaves in many important ways as if it were a colloid gel.
Recognition of the colloidal and gel-like properties of cement paste dates back to at least the 1950s. However, during the intervening half-century of research the colloidal properties of the C-S-H gel were often ignored in favor of alternate structural interpretations based on layered calcium silicate minerals (see Section 6.11.4). Since the 1980s there has been significant growth in the field of processing inorganic sol-gel, and this has led to an increased understanding of the fundamental properties of inorganic gels and colloids [7]. At the same time, experimental observations from techniques such as small-angle scattering have provided new evidence for a colloidal structure in cement paste (see Section 6.11.3.3). Consequently, there is at present renewed interest in the colloidal nature of cement paste.

As a background for a discussion of aging in cement paste, a brief review of the silica sol-gel process is useful (see ref. [7] for more details). A solution of colloidal silica particles (the sol) is transformed into a gel via the bonding of individual particles into clusters. The basic reaction driving this process is called condensation, which for silicates can be written as

\[-\text{Si-OH} + \text{HO-Si} \rightarrow -\text{Si-O-Si} + \text{H}_2\text{O}\]  (15)

If the condensation process is irreversible, as it is here, the clusters will grow into diffuse fractal structures that occupy more and more of the sol until they link together and fill the space completely, thereby reaching the "gel point" with the liquid phase completely trapped within the solid phase. The setting of cement paste, which is caused by individual cement grains growing together, is analogous (but not identical) to the gelling of a sol [70]. If the reaction conditions are such that condensation is highly reversible (i.e. only a fraction of collisions permanently stick), the polymeric clusters will restructure and reorganize themselves as they grow, creating dense particles rather than a space-filling colloidal solid.
Intermediate between these cases are those involving moderately reversible reactions that can lead to highly cross-linked clusters that grow in size and density until they settle out of the suspension. These precipitates are gel-like in nature, in that their internal structure contains colloidal-sized regions of liquid and solid, but they are too dense to fill the entire space and so the overall system does not become a true gel. According to Scherer [70], the C-S-H gel phase of cements can be classified as a colloidal precipitate of this nature. The presence of capillary porosity in cement pastes is good evidence of this, as it represents the volume fraction of sol that was not filled by the precipitated clusters.

For the silica sol-gel process, the condensation reaction that drives the sol-gel transition can continue long after gelation, causing a continued increase in the polymerization of the silicate network. This is the root cause of the multiple effects known collectively as aging. The most significant result of aging is generally an increase in the strength and stiffness of the gel. Condensation, and thus aging, is accelerated at higher temperatures. Aging can be considered to be a continued interaction between the solid phase and the pore liquid, and aging processes generally do not occur when the pore liquid is removed.

In a fractal space-filling gel, condensation reactions can bind together adjacent branches of the silicate network after the gel point, thereby bringing them closer together. As a result, the solid network shrinks uniformly and expels the pore fluid, a process known as syneresis. Under certain conditions syneresis can cause the volume of a gel to decrease by more than half, without changing its original shape. More commonly, inorganic gels shrink by 5-10% over the course of a few months [7].

Because cement paste contains significant amounts of non-gel phases, it might be expected that the solid network as a whole would not contract and syneresis would not be observed. In fact, syneresis has recently been observed in thin sections of paste [92], but only during the first few hours of hydration when the paste is plastic. After set, macroscopic shrinkage of cement paste via syneresis does not occur.
However, it is possible that syneresis is related to "bleeding" of higher w/c cement pastes (separation of some water at the surface shortly after mixing) and to the formation of a porous interfacial transition zone between paste and aggregate in concrete [92]. These issues deserve further research.

Aging in cement paste can be quantified in a chemical sense by measuring the degree of polymerization of the silicates. Results (see Taylor [6] for a fuller summary) have shown that there is a progressive increase in polymerization with hydration time, and that this process is accelerated by an increase in temperature. Under ambient conditions the silicate dimer dominates at early times, but is slowly replaced with polymeric species such as pentamer in a process that continues for decades -- long after hydration of the cement minerals has stopped. However, at higher hydration temperatures the increase in polymerization is much more rapid, and polymeric species with more then 100 silicate ions can form. Aging processes in cement are thus most easily monitored by comparing pastes hydrated at different temperatures. It should be noted that heating a hardened cement paste for a short period of time after hydrating at normal temperatures increases the amount of silicate polymerization and causes many of the macroscopic effects associated with high temperature curing (e.g. Refs. [101-103]). This underlines the fact that aging phenomena in cements occur independently of the hydration reaction.

Hydration of cement at higher temperatures is known to coarsen the pore structure. While the total amount of porosity is unaffected, paste hydrated at 65°C was found to have a larger capillary pore volume and correspondingly smaller volumes of mesopores (3-30 nm) and micropores (<3 nm) than paste hydrated at 25°C to the same degree of reaction [104]. The surface area is correspondingly lowered by high temperature curing [103, 105]. SEM studies have shown that the hydration product is denser after high temperature curing [106], and that the paste-aggregate interface in concrete is more porous [107]. All these physical changes can be related to aging: the density of the C-S-H gel phase is
increased at higher temperatures due to an increased rate of condensation within the precipitated particles.

Because diffusion of reactants through this denser C-S-H product layer is more difficult, the ultimate degree of hydration is usually lower at higher temperatures. This, along with the increase in the capillary porosity of the hardened cement paste, causes the permeability of the paste to be higher. For this reason, concrete placed and cured in hot weather often exhibits subsequent durability problems [107]. The increased capillary porosity associated with a higher hydration temperature also causes the ultimate strength of concrete to be lower, even though the early strength develops more rapidly due to accelerated hydration. In this case, the analogy between cement paste and pure gels breaks down: while the strength of a pure gel is determined by the degree of crosslinking of the solid network, hardened cement paste behaves like a brittle ceramic material with the strength controlled primarily by the size of the largest pores, namely the capillary pores. However, since the C-S-H phase alone does not contain large capillary pores, C-S-H is expected to behave more like a gel and experience an increase in strength with heat treatment. Thus hardened cement paste has properties that come from both the gel properties of C-S-H and the large pores (as well as other restraining phases).

Another important result of aging is a reduction in drying shrinkage. Aging causes the C-S-H phase (and the paste itself) to become stiffer, thus reducing the amount of shrinkage that occurs for a given degree of capillary tension. Thus it is observed that older pastes and pastes hydrated at higher temperatures shrink less on drying [1].

As discussed in Section 6.11.5.2.5, the phenomenon of irreversible shrinkage is puzzling from a purely physical point of view because all of the mechanisms of drying shrinkage are intrinsically reversible. We can look to the known behavior of inorganic gels for an answer [7]. As a gel dries and shrinks, the solid phase is compressed. This brings adjacent areas of the silicate network into closer
contact, giving them the opportunity to bond together via condensation. This reaction is not reversible, so on resaturation the gel does not return to its original dimensions. There is significant evidence that this is also the cause of irreversible shrinkage in cement paste. Younger cement pastes exhibit more irreversible shrinkage than do older pastes, and pastes hydrated at higher temperatures also have less irreversible shrinkage [1]. Clearly, if a paste has a high degree of silicate polymerization before drying then little or no further bonding is likely to occur during drying. For younger pastes, the degree of polymerization of the silicate is observed to increase significantly after drying and rewetting [77], so there is a direct relationship between aging and irreversible shrinkage. It can thus be concluded that the drying process itself causes aging of cement paste. This also provides a good explanation for the otherwise puzzling observation that pastes that are dried and resaturated twice develop much less irreversible shrinkage during the second cycle.

6.11.6 Durability of Concrete

As attested by the survival of ancient concrete structures such as the Roman Pantheon and Coliseum, concrete can be a remarkably durable material. However, it is certainly not invulnerable. Under certain conditions or exposures to certain chemical species, concrete will degrade, thereby leading to a premature termination of its functional life. As mentioned in Section 6.11.5.3, most of the chemical and physical processes that degrade concrete (see reviews [6, 108-113]) occur because water or other chemical agents have permeated the porous network of concrete. The debilitating changes in the microstructure of concrete that result from the interactions between these chemical species and the internal constituents of concrete (particularly hardened cement paste) will be discussed in the following sections.

The most important kinds of deterioration of concrete are freeze-thaw damage, leaching, alkali-aggregate reaction, sulfate attack, carbonation, chloride penetration, and acid attack. As
will be discussed in ensuing sections, the interactions between concrete and the aggressive agents can be distinguished by the accompanying volume changes of solids that generally increase the porosity. Some interactions, for example, will involve the precipitation of additional products in the pore space of concrete. If conditions allow for significant formation of these products, expansive pressures can develop in the pores of hardened cement paste, leading to cracks and associated increases in porosity and permeability. On the other hand, interactions between aggressive agents and concrete can lead to the dissolution of cementitious phases such as CH and C-S-H. This leaves behind additional porosity in the hardened cement paste, which leads to increases in permeability and reductions in strength of concrete.

6.11.6.1 Freeze-Thaw Damage

The freezing and thawing of water in the pores of concrete is one of the principle degradation mechanisms in cold climates [114-118]. While there are several ways freeze-thaw damage can occur, the most damaging mechanism is believed to be the generation of hydraulic pressures in the liquid phase. Hydraulic pressures originate from the approximate 9% increase in volume associated with the transformation of water into ice; this expansive transformation causes water to be pushed away from a growing ice crystal, thereby causing a pressure gradient in the pore liquid. This hydraulic pressure can only be relieved if the displaced water can escape to empty pores or spaces within concrete. If the distance traveled by the displaced water before reaching an empty pore is large, hydraulic pressures in the liquid phase can reach sufficient magnitude to cause fracture of the hardened cement paste. To counter this, a sufficient concentration of air-voids (mentioned in Section 6.11.2.4.1) is intentionally introduced in concrete mixes to minimize the distance that displaced water must travel before reaching an empty space into which it can escape. Laboratory and field studies show a dramatic improvement
in the resistance to freeze-thaw damage when the spacing between air-voids is below a critical threshold value, which is generally found to be as approximately 200 to 250 µm [117].

6.11.6.2 Leaching

Leaching of concrete occurs when soft waters (i.e., sources of water such as rainwater that have low concentrations of dissolved salts) continuously percolate through or flow around concrete structures such as dams or pipes. Leaching is also of particular concern for concrete structures designed for the long-term storage of nuclear waste. The basic mechanism involves the removal of alkali hydroxide from the pore solution of concrete and the loss of calcium from hydration products of hardened cement paste. The leaching of calcium from these hydration products is achieved by sequential dissolution of CH, monosulfate, and ettringite, followed by progressive dissolution of C-S-H [119]. Further damage results from the increases in porosity and permeability associated with the dissolution [120].

6.11.6.3 Alkali-Aggregate Reaction

Alkali-aggregate reaction (AAR) [6, 110, 111] refers to a set of chemical reactions between reactive components in the rock aggregates used to manufacture concrete and alkali hydroxides that are usually derived from the minor oxide components of Portland cement, but may come from external sources as well. The reaction produces a highly mobile gel of indefinite chemical composition, which generates expansive pressures when it imbibes water and migrates through the pore network. AAR increases porosity and permeability via the production of cracks, which originate from the migration of the gel through the pore network. Mitigation of AAR requires elimination of reactive aggregates and control of the alkali content and permeability of the concrete.
6.11.6.4 Sulfate Attack

Sulfate attack, the reaction of sulfate ions with cementitious phases, is perhaps the most widespread and common form of chemical attack on concrete [1]. It can involve the infiltration of sulfate-bearing aqueous solutions (external sulfate attack) or reaction with sulfates derived from the original components of the cement or aggregates constituting the concrete (internal sulfate attack and delayed ettringite formation (DEF) [6, 109]). The alteration of the pore network includes an increase in crack porosity associated with the expansive reactions that produce ettringite and gypsum. Further alterations include an increased porosity and loss of cohesion via leaching of calcium from CH and C-S-H and leaching of silica from C-S-H [6, 109]. Strategies for mitigating external sulfate attack include physically reducing the permeability of concrete (by installing protective membranes or barriers) and limiting the concentration of aluminate phases in Portland cement (which are necessary for the formation additional ettringite and gypsum when sulfate is introduced to concrete). Mitigation of DEF requires sound understanding of the interrelationships between cement chemistry, aggregate chemistry, and curing and manufacturing practices.

6.11.6.5 Carbonation

Carbonation occurs on the surfaces of all Portland cement-based materials that are exposed to the atmosphere. The process involves the reaction of CO₂ with CH to produce calcium carbonate. The most significant result of this reaction is the consumption of CH and subsequent lowering of the pH of pore solution from its equilibrium value of 12 or 12.5. Reductions of the pore solution pH below 11.0 destroys the passive iron oxide layer that surrounds steel reinforcements, facilitating corrosion. The corrosion products are expansive gels that imbibe water, swell, and create fracture porosity. However, the precipitation of calcium
carbonate can also decrease porosity and enhance the performance of the material, provided corrosion does not occur [6, 121]. Mitigation of damage relating to carbonation requires the use of low-permeability concrete and thick cover zones (i.e., the outer layer of concrete between the exterior surface and the steel reinforcement).

6.11.6.6 Chloride

The most detrimental consequence of chloride penetration into concrete involves the corrosion of reinforcing steel. It is one of the most significant durability problems throughout the world, ranging from marine environments in the tropics to parking garages in colder climates [108]. The presence of chloride ions destroys the passive oxide layer that surrounds steel, facilitating corrosion and the formation of the expansive corrosion products. Sources of chloride include contamination in the aggregates, calcium chloride added as a hydration accelerator, saline waters and soils in arid regions, and de-icing salts. Mitigation of corrosion relating to chloride penetration requires the use of low-permeability concrete and thick cover zones.

6.11.6.7 Acid Attack

Concrete is not durable when exposed to acidic solutions and decomposes rapidly when exposed to solutions with pH of less than 4.0 [109]. The general reactions are similar to those involved in leaching by water except they proceed much more rapidly. CH dissolves congruently while C-S-H and hydrated aluminates dissolve incongruently to produce Ca^{2+} ions and silica and alumina gels. Mitigation requires the installation of protective membranes or barriers on the surface of concrete structures.
6.11.7 Summary

Although concrete is one of the most essential materials of modern civilization, it is arguably the most under-appreciated and misunderstood man-made material in existence. This review has described the complexities of hardened cement paste, from its intricate porous network, to its colloidal nature, and to its debilitating interactions with the environment. Characterization of the pore structure is particularly challenging since C-S-H gel, the dominant phase in hardened cement paste, is a constantly evolving phase that is quite susceptible to changes in relative humidity, stress, temperature and other variables. Not surprisingly, this inherent difficulty in analyzing C-S-H has lead to several different models of its pore structure. However, a current assessment of data from pyknometry, water vapor and nitrogen sorption, and neutron and X-ray scattering leads to the conclusion that C-S-H is best described as a colloidal precipitate. This is supported by numerous similarities between the properties of C-S-H and other colloidal gels. With a renewed interest in the colloidal nature of C-S-H, cement science has been returned to its early roots incorporated in the works of Powers [12]. It is hoped that a further understanding of the colloidal nature of C-S-H can assist in resolving the fundamental questions that still persist in cement science.
Aggregate: granular material usually derived from natural rock, crushed stone, or sand. Hardened cement paste binds fine aggregate (sand) to form mortar and coarse (rock and crushed stone) aggregate to form concrete.

Aqueous phase: the aqueous solution found in the pores of hardened cement paste that is saturated with various ions and has a pH of at least 12.5. All evaporable water (i.e., capillary and gel water) in hardened cement paste can be referred to as an aqueous phase. The aqueous phase of hardened cement paste is equivalent to its pore solution.

Calcium hydroxide (CH): the most abundant crystalline phase in hardened cement paste; the presence of CH buffers the pore solution to a pH of at least 12.5.

Capillary pores: in fresh cement paste, the space occupied by the water that separates cement grains; in hardened cement paste, the residual space between cement grains that is not filled with hydration product.

Capillary water: the aqueous phase in capillary pores.

Cement: a generic term for a material that is used to bind particulate matter together; usually synonymous with Portland cement.

Chemically bound water: water in the interlayer spaces of C-S-H that is bound by molecular bonds.

Colloid: a system in which a dispersed phase, with characteristic dimensions between approximately 1 to 1000 nm, is immersed in another phase. The small size of the dispersed phase creates a significant interfacial surface area between the two phases. Consequently, interfacial effects (i.e., surface tension) significantly influence the properties of a colloidal system. C-S-H can be considered a colloid since its solid gel phase, which is believed to be composed of particles of approximately 5 nm, is dispersed in an aqueous phase.

Concrete: a composite of fine aggregate (sand), coarse aggregate (rock, crushed stone), and usually steel reinforcement, that is held together by a matrix of hardened cement paste.

C-S-H (or C-S-H gel): a nearly amorphous calcium silicate hydrate that is the main hydration product of Portland cement. An average chemical formula for water-saturated C-S-H in hardened cement paste is 1.7 CaO•SiO_2•4.0 H_2O. (Note that the dashes in the term “C-S-H” reflect the fact that the composition can slightly diverge from its average value.) At the molecular scale, C-S-H has a disordered layer structure. At the colloidal scale, C-S-H is a porous gel that is characterized by its high specific surface area (approximately several hundreds of square meters per gram) and its intimate interactions with water. Compared with other hydration products, C-S-H has the dominant influence on the properties of concrete such as strength, dimension stability, and permeability.
**Curing**: process for promoting the hydration of Portland cement. Portland cement systems are normally cured at ambient conditions, and, ideally, under water. For concrete structures in the field, curing is a deliberate process of maintaining moist surface conditions during the first several days of hydration.

**D-Dry method**: standard drying condition that involves vacuum drying at the equilibrium vapor pressure of water (\( \sim 6.7 \times 10^{-2} \) Pa) at the temperature of dry ice \( (T = 194K) \). This procedure is often approximated by oven drying at 105°C.

**Drying shrinkage**: the deformations associated with the loss of water from hardened cement paste by evaporation. The deformations can lead to cracking and other deleterious effects on concrete.

**Evaporable water**: aqueous phase that is removed by a standard drying condition, which is usually D-Drying or oven drying at 105°C.

**Fresh cement paste**: fluid mixture of Portland cement and water before hardening occurs.

**Gel pores**: the pores that constitute the internal porosity of C-S-H.

**Gel water**: the aqueous phase in gel pores.

**Hardened cement paste (or cement paste or hcp)**: the porous solid that is produced from the hydration of Portland cement and is typically used to bind aggregates in concrete and mortar. Hardened cement paste (HCP) is composed of hydration products, unhydrated cement, and pores.

**Hydration**: the complex set of chemical and physical changes that occurs when Portland cement is mixed with water.

**Hydration products**: the reaction products produced from the hydration of Portland cement. Hydration products include C-S-H, CH, and calcium sulfoaluminate phases such as ettringite and monosulfate.

**Interfacial transition zone (ITZ)**: the 25 to 50 µm wide porous regions of hardened cement paste surrounding an aggregate in concrete or mortar.

**Interlayer spaces**: the molecular sized spaces in the layered structure of C-S-H where chemically bound water resides.

**Mortar**: composite of fine aggregate (sand) in a matrix of hardened cement paste.

**Non-evaporable water**: water that is not removed from a standard drying condition, which is usually D-Drying or oven drying at 105°C. The amount of non-evaporable water in a hardened cement paste is a useful empirical measure of the extent of hydration.
Ordinary Portland cement (OPC): the most common variety of Portland cement that is used in general building applications; equivalent to the ASTM Type I Portland cement that is specified in American standards or the CEM Type I 42.5 Portland cement that is specified in European standards.

Oven drying: drying at 105°C at atmospheric pressure; a convenient approximation to the D-drying procedure.

Pore solution: the aqueous solution found in the pores of hardened cement paste that is saturated with various ions and has a pH of at least 12.5. The pore solution of hardened cement paste is equivalent to its aqueous phase.

Portland cement: a powder with definite proportions of various minerals (predominantly, calcium silicates and calcium aluminates) that react with water to produce hardened cement paste.

Unhydrated cement: unreacted Portland cement in hardened cement paste.

Water to cement ratio (w/c): the ratio of the mass of mixing water to the mass of Portland cement.

6.11.9 References


116. T.C. Powers, in *Durability of Concrete, Freezing Effects in Concrete*, SP-47, American Concrete Institute, Detroit, MI, 1975, p. 1-11.


6.11.10 Figure Captions

**Figure 1.** Heat evolution of C₃S paste during hydration; the initial (1), induction (2), acceleratory (3), deceleratory (4) and continued (5) stages of hydration are noted.

**Figure 2.** Backscattered electron image of polished section of a 28-day-old C₃S paste. In descending order of brightness are, unhydrated cement grains (white), C-S-H gel (dark gray), CH (light gray) and capillary pores (black).

**Figure 3.** Effect of w/c ratio on the volumetric proportions of C-S-H gel (including gel pores), unhydrated cement, and capillary pores under saturated curing conditions.

**Figure 4.** Surface area development with time as measured by nitrogen gas sorption, after Hunt [36].

**Figure 5.** Typical small-angle scattering plot for a hydrated cement paste.

**Figure 6.** Surface area as measured by SANS (left axis) and the heat evolved (right axis) during early hydration of cement paste, from [35].

**Figure 7.** A two-dimensional representation of LD C-S-H.

**Figure 8.** Dependence of strength on porosity for normally cured cement pastes, autoclaved pastes, and a variety of aggregates; the 25 to 50% capillary porosity range indicated on the graph represents the normal range for a normally cured cement paste (after [66]).

**Figure 9.** Shrinkage-weight loss curve with corresponding drying conditions noted at right. Mechanisms associated with drying regions 1 through 5 are described in the text (from [1], after data from [67]).

**Figure 10.** Creep of concrete under simultaneous loading and drying; \( \varepsilon_{\text{tot}} = \) total strain, \( \varepsilon_c = \) total creep strain, \( \varepsilon_{dc} = \) drying creep strain, \( \varepsilon_{bc} = \) basic creep strain, \( \varepsilon_{sh} = \) shrinkage strain.

**Figure 11.** Effect of evaporable water content on creep of concrete at w/c ratios of 0.30 and 0.60 (based on [81]).

**Figure 12.** Creep of concrete during drying from saturation to 50% and 70% RH (RH change commenced at the time of initial load); basic creep at 100% RH is shown for comparison (after [84]).
Table 1: Morphological summary of the main hydration products of Portland cement.

<table>
<thead>
<tr>
<th>Product</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Amorphous</strong></td>
<td></td>
</tr>
<tr>
<td>C-S-H gel</td>
<td>Can vary considerably, at least 4 types observed (after [9]).</td>
</tr>
<tr>
<td>Type I</td>
<td>Characterized by spines or fibers (1 µm in length, 0.1 µm across)</td>
</tr>
<tr>
<td>Radiating from cement grains into water filled space.</td>
<td></td>
</tr>
<tr>
<td>Type II</td>
<td>Interlocking structure with a honeycomb resemblance in which the gel encapsulates unhydrated cement grains and other products; only found in Portland cement pastes, and only in C₃S pastes with impurities.</td>
</tr>
<tr>
<td>Type III</td>
<td>Small irregularly flattened particles, usually no greater that 0.3 µm across.</td>
</tr>
<tr>
<td>Type IV</td>
<td>A noticeably denser structure associated with the C-S-H gel product formed within the volume of the original cement grain.</td>
</tr>
<tr>
<td><strong>Crystalline</strong></td>
<td></td>
</tr>
<tr>
<td>CH</td>
<td>Non-porous, striated, crystal typically having a typical hexagonal-prism morphology (10 µm to 100 µm across); morphology is affected by available space, temperature, and impurities.</td>
</tr>
<tr>
<td>Ettringite</td>
<td>Acicular needles (10 µm in length, 0.5 µm across).</td>
</tr>
<tr>
<td>Monosulfate aluminate</td>
<td>Thin (~0.1 µm) hexagonal plates (1 µm by 1 µm).</td>
</tr>
</tbody>
</table>

Table 2: Classification of pores in concrete (with data taken from [1]).

<table>
<thead>
<tr>
<th>Type of Pore</th>
<th>Description</th>
<th>Size</th>
<th>Water</th>
<th>Technique</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capillary Pores</td>
<td>Large</td>
<td>10 µm – 50 nm</td>
<td>Evaporable</td>
<td>SEM(^a), OM(^b)</td>
<td>Permeability, strength</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>50 – 10 nm</td>
<td>Bulk water</td>
<td>SEM</td>
<td>Permeability, strength, shrinkage (high RH(^c))</td>
</tr>
<tr>
<td>Gel Pores</td>
<td>Small</td>
<td>10-2.5 nm</td>
<td>Evaporable</td>
<td>Adsorption/MIP(^e)/IS(^d)</td>
<td>Shrinkage (to 50% RH)</td>
</tr>
<tr>
<td></td>
<td>Micropores</td>
<td>2.5-0.5 nm</td>
<td>Non-evaporable</td>
<td>Adsorption/MIP/IS</td>
<td>Shrinkage, creep (35-11% RH)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- No menisci</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- Intermolecular interactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interlayer Spaces</td>
<td>Structural</td>
<td>Non-evaporable - Ionic/covalent bond</td>
<td>Adsorption/Thermal</td>
<td>Shrinkage, creep (&lt; 11% RH)</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>------------</td>
<td>-------------------------------------</td>
<td>-------------------</td>
<td>-----------------------------</td>
<td></td>
</tr>
<tr>
<td>Other Pores</td>
<td>ITZ(^f)</td>
<td>20-50 µm</td>
<td>Bulk Water</td>
<td>SEM/OM</td>
<td>Permeability, strength</td>
</tr>
<tr>
<td></td>
<td>Microcracks</td>
<td>50 - &gt; 200 µm</td>
<td>Bulk Water</td>
<td>SEM/OM</td>
<td>Permeability, strength</td>
</tr>
</tbody>
</table>

\(^a\) SEM: scanning electron microscopy; \(^b\) OM: optical microscopy; \(^c\) MIP: mercury intrusion porosimetry; \(^d\) IS: impedance spectroscopy. \(^e\) RH: relative humidity. \(^f\) ITZ: interfacial transition zone.
Table 3: Measured total and free water porosities for mature OPC pastes [23].

<table>
<thead>
<tr>
<th>w/c ratio</th>
<th>Free Water Porosity / %</th>
<th>Total Porosity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>23.3</td>
<td>37.8</td>
</tr>
<tr>
<td>0.50</td>
<td>34.5</td>
<td>44.8</td>
</tr>
<tr>
<td>0.60</td>
<td>42.1</td>
<td>51.0</td>
</tr>
<tr>
<td>0.80</td>
<td>53.4</td>
<td>58.7</td>
</tr>
</tbody>
</table>

Table 4: Effect of the molecular size of the sorptive gas on the BET surface area of a mature OPC paste with w/c=0.4, after Mikhail and Selim [34].

<table>
<thead>
<tr>
<th>Sorptive Gas</th>
<th>Cross-sectional area / nm²</th>
<th>Surface Area / m² g⁻¹ of dry paste</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.114</td>
<td>202.6</td>
</tr>
<tr>
<td>N₂</td>
<td>0.162</td>
<td>79.4</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>0.181</td>
<td>62.5</td>
</tr>
<tr>
<td>C₃H₇OH</td>
<td>0.277</td>
<td>45.0</td>
</tr>
<tr>
<td>C₆H₁₂</td>
<td>0.390</td>
<td>44.5</td>
</tr>
</tbody>
</table>

Table 5: Effect of w/c on the surface area of cement paste, as measured by BET gas sorption with nitrogen and water on mature paste [34] and by small-angle neutron scattering (SANS) on 28 d old paste [35].

<table>
<thead>
<tr>
<th>w/c ratio</th>
<th>H₂O BET / m² g⁻¹</th>
<th>N₂ BET / m² g⁻¹</th>
<th>SANS / m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>208.0</td>
<td>56.7</td>
<td>99</td>
</tr>
<tr>
<td>0.40</td>
<td>202.6</td>
<td>79.4</td>
<td>100</td>
</tr>
<tr>
<td>0.50</td>
<td>194.6</td>
<td>97.3</td>
<td>106</td>
</tr>
<tr>
<td>0.57</td>
<td>193.8</td>
<td>132.2</td>
<td>123</td>
</tr>
<tr>
<td>0.70</td>
<td>199.6</td>
<td>139.6</td>
<td>132</td>
</tr>
<tr>
<td>0.60</td>
<td></td>
<td></td>
<td>147</td>
</tr>
</tbody>
</table>
Table 6: Summary of models for the structure of C-S-H.

<table>
<thead>
<tr>
<th>Name of Model</th>
<th>Primary Experimental Basis</th>
<th>Type of Model</th>
<th>Selected Characteristics of Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powers</td>
<td>Water sorption</td>
<td>Colloid</td>
<td>All products are gel</td>
</tr>
<tr>
<td></td>
<td>Volume of pores</td>
<td></td>
<td>Particle radius, 5 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Gel pore volume, 28%</td>
</tr>
<tr>
<td>Taylor</td>
<td>X-ray TGA</td>
<td>Imperfect</td>
<td>Atomic structure of C-S-H</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tobomerite</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jennite</td>
<td></td>
</tr>
<tr>
<td>Brunauer</td>
<td>Water Sorption</td>
<td>2-3 layers</td>
<td>Structure changes upon drying</td>
</tr>
<tr>
<td>Feldman-Sereda</td>
<td>Nitrogen sorption</td>
<td>Layers</td>
<td>Crumpled and folded layers with</td>
</tr>
<tr>
<td></td>
<td>Length vs. RH</td>
<td></td>
<td>interlayer water reversibly removed upon drying</td>
</tr>
<tr>
<td></td>
<td>Modulus vs. RH</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Weight vs. RH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wittmann</td>
<td>Modulus vs. RH</td>
<td>Colloid</td>
<td>Structure not defined</td>
</tr>
<tr>
<td>Jenning</td>
<td>Density vs. RH</td>
<td>Colloid</td>
<td>Fractal: density and surface area</td>
</tr>
<tr>
<td></td>
<td>Composition vs. RH</td>
<td></td>
<td>depend on length scale</td>
</tr>
<tr>
<td></td>
<td>Surface area</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 7: Water content and density of C-S-H as predicted by the quantitative colloidal model of C-S-H.

<table>
<thead>
<tr>
<th>Name of unit in structure</th>
<th>Radius of unit (nm)</th>
<th>Computed density (kg m(^{-3}))</th>
<th>Surface area (m(^2) / g of C-S-H)</th>
<th>Model porosity (%)</th>
<th>Relative humidity condition</th>
<th>Measured composition</th>
<th>Measured density (kg m(^{-3}))</th>
<th>Porosity based on composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic Building Block</td>
<td>1.1</td>
<td>2800 2800</td>
<td>1000(^f)</td>
<td>-</td>
<td>Dry</td>
<td>1.7 CaO•SiO(_2)•1.4 H(_2)O</td>
<td>2800</td>
<td>0</td>
</tr>
<tr>
<td>Globules</td>
<td>2.8</td>
<td>2300 2480</td>
<td>460(^g)</td>
<td>18</td>
<td>11%</td>
<td>1.7 CaO•SiO(_2)•2.1 H(_2)O</td>
<td>2450</td>
<td>16</td>
</tr>
<tr>
<td>LD</td>
<td>8.3</td>
<td>1440 1930</td>
<td>250(^e)</td>
<td>49</td>
<td>Saturated</td>
<td>1.7 CaO•SiO(_2)•4.0 H(_2)O</td>
<td>2000</td>
<td>42</td>
</tr>
<tr>
<td>HD</td>
<td>&gt;100</td>
<td>1750 2130</td>
<td>0</td>
<td>38</td>
<td>Saturated</td>
<td>1.7 CaO•SiO(_2)•4.0 H(_2)O</td>
<td>2000</td>
<td>42</td>
</tr>
</tbody>
</table>

\(^a\) Assuming spherical particles; using relation, \(r = 3/(SSA \times \rho)\) where \(r = \) radius, SSA = specific surface area, and \(\rho = \) density.

\(^b\) Based on volume fraction of solid and pores.

\(^c\) Calculated as \((1 - \rho_{\text{unit}} / \rho_{\text{basic building block}}) \times 100\).

\(^d\) Computed from the molar volume of dry C-S-H and the molar volume of water. The molar volume of dry C-S-H (1.7CaO\(\cdot\)SiO\(_2\)\(\cdot\)1.4H\(_2\)O) was computed by dividing the molecular weight by the measured density to obtain a value of 6.45 \(\times\) \(10^{-5}\) m\(^3\)/mol. The molar volume of water was taken to be 1.80 \(\times\) \(10^{-5}\) m\(^3\)/mol.

\(^e\) Values were optimized [60] by maximizing the statistical fit between reported values of nitrogen surface areas, pore volumes and capillary porosity with predicted values of the model.

\(^f\) Based on SAXS [44, 49] data.

\(^g\) Based on SANS data, assuming that only the LD C-S-H structure contributes to the surface area.
**Table 8: Summary of relevant transport processes.**

<table>
<thead>
<tr>
<th>Relevant Equation</th>
<th>Typical Values in Concrete</th>
<th>Factors affecting measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Permeation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas Permation:</td>
<td>$K_g = \frac{Q}{l \cdot a \cdot p \cdot (p_1 - p_2)}$</td>
<td>$K_g = 10^{-8}$ to $10^{-13}$ m s$^{-1}$ [97]</td>
</tr>
<tr>
<td>Darcy’s Law:</td>
<td>$K_w = \frac{Q}{l \cdot A \cdot \Delta h}$</td>
<td>$K_w = 10^8$ to $10^{13}$ m s$^{-1}$ [98]</td>
</tr>
<tr>
<td><strong>Diffusion</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fick’s First Law:</td>
<td>$F = -D \frac{dc}{dx}$</td>
<td>$10^{-11}$ - $10^{12}$ m$^2$ s$^{-1}$ (iodine)</td>
</tr>
<tr>
<td>Fick’s Second Law</td>
<td>$\frac{dc}{dt} = \frac{\partial (D \frac{dc}{dx})}{\partial x}$</td>
<td>1. Sample size. 2. Conditioning/drying. 3. Boundary conditions/leakage. 4. Driving pressure. 5. Chemical reactions during test.</td>
</tr>
<tr>
<td>Modified Darcy’s Law:</td>
<td>$F = \frac{k_p}{\eta} \frac{d}{dx} \left[ p_w + \rho g h(x) \right]$</td>
<td>$\sim 10^{-10}$ ml m$^{-2}$ [99]</td>
</tr>
<tr>
<td><strong>Capillary Suction</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nernst-Planck equation:</td>
<td>$J = D \frac{dc}{dx} + \frac{ZF}{RT} \frac{dc}{dx} + CV_e$</td>
<td>$10^{-10}$ - $10^{-12}$ m$^2$ s$^{-1}$ (chloride)</td>
</tr>
<tr>
<td><strong>Migration</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Symbols:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_{g,w}$</td>
<td>coefficient of permeability (m$^2$; $g$ = gas; $w$ = water)</td>
<td></td>
</tr>
<tr>
<td>$\eta$</td>
<td>viscosity (Ns/m$^2$)</td>
<td></td>
</tr>
<tr>
<td>$Q$</td>
<td>volume of gas or liquid flow (m$^3$)</td>
<td></td>
</tr>
<tr>
<td>$l$</td>
<td>thickness of penetrated section (m)</td>
<td></td>
</tr>
<tr>
<td>$A$</td>
<td>penetrated area (m$^2$)</td>
<td></td>
</tr>
<tr>
<td>$p$</td>
<td>pressure at which volume $Q$ is measured (N/m$^2$)</td>
<td></td>
</tr>
<tr>
<td>$p_1$</td>
<td>pressure at entry (N/m$^2$)</td>
<td></td>
</tr>
<tr>
<td>$p_2$</td>
<td>pressure at exit (N/m$^2$)</td>
<td></td>
</tr>
<tr>
<td>$p_w$</td>
<td>pore water pressure (N/m$^2$)</td>
<td></td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
<td></td>
</tr>
<tr>
<td>$\Delta h$</td>
<td>pressure head (m)</td>
<td></td>
</tr>
<tr>
<td>$x$</td>
<td>distance</td>
<td></td>
</tr>
</tbody>
</table>
**Figure 1:** Heat evolution of C₃S paste during hydration; the initial (1), induction (2), acceleratory (3), deceleratory (4) and continued (5) stages of hydration are noted.

**Figure 2:** Backscattered electron image of polished section of a 28 day old C₃S paste. In descending order of brightness are, unhydrated cement grains (white), C-S-H gel (dark gray), CH (light gray) and capillary pores (black).
Figure 3: Effect of w/c ratio on the volumetric proportions of C-S-H gel (including gel pores), unhydrated cement, and capillary pores under saturated curing conditions.

Figure 4: Surface area development with time as measured by nitrogen gas sorption, after Hunt [36].
Figure 5: Typical small-angle scattering plot for a hydrated cement paste.
Figure 6: Surface area as measured by SANS (left axis) and the heat evolved (right axis) during early hydration of cement paste, from [35].
Figure 7: A two-dimensional representation of LD C-S-H.
Figure 8: Dependence of strength on porosity for normally cured cement pastes, autoclaved pastes, and a variety of aggregates; the 25 to 50% capillary porosity range indicated on the graph represents the normal range for a normally cured cement paste (after [66]).
Figure 9: Shrinkage-weight loss curve with corresponding drying conditions noted at right (RH = relative humidity). Mechanisms associated with drying regimes 1 through 5 are described in the text (from [1], after data from [67]).
Figure 10: Creep of concrete under simultaneous loading and drying; $\varepsilon_{\text{tot}} = \text{total strain}$, $\varepsilon_c = \text{total creep strain}$, $\varepsilon_{dc} = \text{drying creep strain}$, $\varepsilon_{bc} = \text{basic creep strain}$, $\varepsilon_{sh} = \text{shrinkage strain}$. 
Figure 11: Effect of evaporable water content on creep of concrete at w/c ratios of 0.30 and 0.60 (based on [81]).
Figure 5.5. Creep of concrete during drying from saturation to 50% and 70% relative humidity (RH); RH change commenced at the time of initial load. Basic creep at 100% RH is shown for comparison (after [84]).