

Percolation Aspects of Cement Paste and Concrete – Properties and Durability

by

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Synopsis: Portland cement concrete is a composite material, where the matrix consists of portland cement paste. Cement paste forms from the hydration reaction of portland cement with water. The microstructure of cement paste changes drastically over a time period of about one week, with slower changes occurring over subsequent weeks to months. The effect of this hydration process on the changing microstructure can be represented using computer simulation techniques applied to three dimensional digital image-based models. Percolation theory can be used to understand the developing microstructure of cement paste in terms of three percolation thresholds: the set point, capillary porosity percolation, and the percolation of the C-S-H phase. The percolation of the interfacial transition zones also plays an important role in concrete microstructure, and can be displayed using computer simulation models. These percolation aspects help determine the transport properties and therefore the durability and service life of concrete.

Keywords: cement; chlorides; diffusivity; durability; materials science; microcomputers; microstructure; percolation; permeability; simulation; transport

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INTRODUCTION

Percolation theory plays an important role in interpreting and understanding the microstructure of cement-based materials. Much can be learned about 3-D systems from 2-D images, about quantities like volume fraction and surface area. However, nothing can be learned about percolation aspects of the microstructure, as percolation is quite different in 2-D and 3-D. Therefore to learn about the 3-D percolation aspects of the microstructure requires some kind of 3-D analysis. This paper shows how a cellular automaton model of cement hydration can give accurate 3-D microstructures and accurate predictions of percolation phenomena in cement paste, and a different computer simulation model can perform similarly for concrete.

Cement paste, formed from the reaction of portland cement in water, has more percolation thresholds of importance in it than any other material known to the authors. The three most significant of them play an important role in relating microstructure to properties. Concrete microstructure is also dominated by an important percolation threshold. The transport properties of concrete (ionic diffusion, fluid permeability, etc.) are controlled by these percolation thresholds. Durability is dominated by transport properties, so that the percolation thresholds directly affect durability and thus service life. To understand the meaning of these thresholds, one must first know something about percolation concepts, and then something about cement paste and concrete microstructure.

PERCOLATION THEORY

The ideas of percolation theory were put together formally by Hammersley in the 1950's (1). The main idea of percolation theory is to formalize and quantify the meaning of "connectedness" in a random process. Thus, percolation theory can be

seen as a branch of topology. Although there are many kinds of percolation, for the point of this paper, we will restrict ourselves to considering the connectedness of the phases in a random multi-phase material. This aspect of percolation theory is called "continuum percolation."

For a material phase, the idea of connectedness is whether a mathematical "ant," moving in only this phase, can get from one side of the material to the other, in any direction. In a random material, each direction is equivalent. Add to this a process, such that the amount and geometry of a phase is changing in time, and we then have the classic percolation problem: at what volume fraction of the phase will the phase percolate, or form a connected phase? This assumes that the phase starts out as isolated bits, and we are trying to find out when it forms into a connected cluster. We could have the alternative problem: a phase starts out connected, and as material is lost, it gradually becomes disconnected. In either event, the point at which the phase connectivity changes is called the percolation threshold, and the volume fraction the phase present at this point is usually given as the value of the percolation threshold.

A specific 2-D example of these concepts is illustrated in Fig. 1. Here we have a two-phase composite, gray and white, with gray circles being added randomly over time. The center of the gray circles can be located anywhere in the field. Each point of the white field is equally probable, and each gray circle is the same size as all the rest. Figure 1a shows the case where 22% of the material is gray and 78% white. Note that there are already some overlaps between gray circles. The gray phase is discontinuous, and the white phase is continuous. Figures 1b and 1c show the gray phase increasing to 39% and 60%, respectively, but still discontinuous. However, Fig. 1c shows that the gray phase is "almost" continuous, as it is mainly made up of large clusters of overlapping gray circles. Finally, in Fig. 1d, the gray phase has become connected. For this process, careful computer simulation studies have shown the percolation threshold to be about 68% for the gray phase (2). Note that the percolation threshold for the white phase, the point at which it loses connectivity, is then 32%. In 2-D, for random phases, only one phase can be continuous at a time, so if one phase becomes continuous, the other phase(s) must become or remain discontinuous (non-random phases, like in regular laminar or fibrous composites, can have many phases continuous at the same time).

This is not the case in 3-D, however. This is the main reason why the study of 2-D slices cannot tell us much, if anything, about 3-D percolation. Figure 2a shows a slice through the three dimensional equivalent of Fig. 1, randomly placed monosize spheres. The volume fraction of the sphere phase in the figure is 40%, which is beyond the percolation threshold for the sphere phase (3). Therefore, in 3-D, the spheres are percolated, while in this 2-D slice, they clearly are not. In 3-D, an infinite number of phases can be percolated at the same time, and so when one phase becomes connected, the other phases can retain their connectivity (4).

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Figure 2b further illustrates this point with a system of 3-D randomly placed ellipsoids (shown in white). The ellipsoids are prolate ellipsoids of revolution, with an aspect ratio (long to short semi-axis length) of 10. There are about 7% by volume of the ellipsoids. In the 2-D slice shown in Fig. 2b, the ellipsoids look very much disconnected, but a numerical study (3) showed that most of these do form a connected phase in 3-D, with less than half still being isolated.

The ellipsoid example shows us that at percolation, only part of a phase can initially make up the connected cluster, with the other parts connected over time as more of the phase is added. We define the “fraction connected” by counting how much of the phase is contained in a percolated cluster, and dividing by the total amount of that phase present. If the entire phase is isolated, then this ratio is zero. If all of the phase makes up a percolated cluster, then this ratio is 1.

The concept of “fraction connected” is illustrated by Fig. 1c, reproduced as Fig. 3. In Fig. 3, the section of the white phase enclosed by the black line is isolated, even though most of the white phase is still percolated. This would cause the fraction connected of the white phase to be less than one, but still greater than zero.

This concept is more clearly illustrated by Fig. 4, which shows two systems of randomly placed ellipses, 550 in Fig. 4a, and 700 in Fig. 4b (5). The ellipses were randomly chosen to be oriented in either the x or the y directions with equal probability. The right-hand image in each set shows the ellipses that are accessible from the top (white). In Fig. 4a, clearly 550 ellipses, or an area fraction of about 40%, were not enough for percolation of the ellipses to occur. In Fig. 4b, 700 ellipses or an area fraction of about 47% were placed, and the companion image shows that there is now a percolated pathway from top to bottom. A substantial number of ellipses were not contained in this pathway, however, giving a fraction connected of about 0.60.

MICROSTRUCTURE OF PORTLAND CEMENT PASTE

The starting point for portland cement paste (cement + water), cement powder, is obtained by grinding cement clinker with about 5% of gypsum (calcium sulphate dihydrate). The gypsum is added to moderate the hydration process. After grinding, the cement powder consists of multi-size, multi-phase, irregularly shaped particles generally ranging in size from less than 1 μm to about 50 μm , with an average diameter of about 15-20 μm . Cement paste is therefore a micrometer scale material.

The scanning electron micrograph of cement particles in Fig. 5 shows that even before hydration takes place, the cement powder is itself a random composite, with even most particles themselves being multi-phase composites. When the cement is mixed with water, hydration reactions occur which ultimately convert the water-

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cement suspension into a rigid porous material, which serves as the matrix phase for mortar and concrete. The degree of hydration at any time is the fraction of the cement that has reacted with water, and is often denoted by the symbol α . The ratio of water to cement in a given mixture is specified by the water to cement ratio (w/c), which is the ratio of the mass of water used to the mass of cement used. The various chemical and mineral phases within the cement powder hydrate at different rates, depending on their size and composition, and interact with one another to form various reaction products. Some products deposit on the remaining cement particle surfaces (surface products) while others form as crystals in the water-filled pore space between cement particles (pore products). For simplicity, and because it still correctly captures the main features of the pore structure, cement paste can be thought of as consisting of four types of phases: 1) unreacted cement grains, 2) surface products like C-S-H (calcium-silicate-hydrate), which is the main amorphous "glue" of cement paste and is itself nanoporous, 3) pore products like CH (calcium hydroxide), which forms crystalline masses, and 4) capillary pore space, which is the remaining water-filled space around the cement grains and hydration products. Surface products grow outward from the unreacted cement particles, while pore products nucleate and grow in the pore space.

While images of both initial and hydrated cement microstructures can be experimentally obtained in two dimensions, acquiring quantitative three-dimensional information is much more difficult. It is for this reason that computer models of the 3-D microstructure development of cement paste have been developed. The actual process of cement hydration, for the purposes of modelling the development of microstructure, can be broken down into three parts: 1) dissolution from the original cement particle surfaces, 2) diffusion within the available pore space, and 3) reaction with water and other dissolved or solid species to form hydration products. Each of these processes may be conveniently simulated using cellular automaton-type rules as has been previously described (6,7). Figure 6 shows four steps of simulated hydration for a C_3S cement paste in 2-D. The original particle shapes are taken from a backscattered SEM image.

A qualitative comparison between a real backscattered scanning electron micrograph of a cement paste and a model version, in which a gray scale has been used to match that of the real picture, is shown in Fig. 7. Reasonable comparison with various experiments have been obtained by the model.

This brief description of the chemical hydration process, which is the basis of the microstructural formation of cement paste, of course glosses over a number of chemical details, many of which are not clearly understood. However, this simple description is sufficient to be able to go on and investigate the various important percolation thresholds that occur in cement paste.

MICROSTRUCTURE OF CONCRETE

If we go up in length scale, to the millimeter length scale, cement paste is used as the matrix for concrete, surrounding the rock and sand inclusions. Because of the particulate nature of cement paste, the cement grains do not pack as well around the inclusions as out in the bulk paste regions. This gives an interfacial transition zone (ITZ) around each inclusion that has less cement, and, therefore, more porosity than the bulk paste. This is often called the wall effect (8). In concrete, we can then think of each inclusion being surrounded by a 10-30 μm (the typical size of a cement particle) thick shell, representing the ITZ, which has a higher porosity and larger pores than does the rest of the cement paste. Figure 8 shows a 2-D schematic picture of how these regions look in a concrete. To first order, the amount of ITZ regions is just the product of aggregate surface area and ITZ thickness. Therefore, a mortar will have a greater amount of ITZ per aggregate volume than does a concrete, as the smaller aggregate has a greater value of surface area per unit volume. We would then expect that the ITZ regions to have a greater effect on mortar properties than on concrete properties. Mortar and concrete microstructure are difficult to handle theoretically, as both the millimeter aggregate length scale and the micrometer cement length scale in the ITZ must be dealt with simultaneously.

A computational model for handling mortar and concrete microstructure has been constructed (9). Aggregate particles following the correct sieve analysis are placed into a computational box. Each particle's geometric parameters and location are stored in a file. Particles can be spheres (9) or tri-axial ellipsoids (10). An ITZ shell of the proper thickness is put around each particle. The volume fraction of the ITZ regions can be assessed numerically, via point counting, or analytically, via approximate but highly accurate formulas (11,12). Figure 9 shows slices through two 3-D models, with different shape aggregates (gray = cement paste, black = ITZ, white = aggregate). This model can easily handle up to a million aggregates, necessary for a computational box size of up to 27 cm^3 in volume. Larger models are not a problem, but do need more computer time and memory.

PERCOLATION THRESHOLDS IN CEMENT PASTE

Set point

Immediately after mixing together water and cement, a dense suspension of cement particles in water is achieved. Set is the phenomenon where the dense suspension, which is a viscoelastic liquid with a high plastic viscosity and a finite but small yield stress (13,14), turns into a viscoelastic solid, with a finite long-time shear modulus.

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This is a variation of what is well-known in the polymer literature as a sol-gel transition.

Set is a percolation phenomenon, since it is achieved when the solid cement grains become linked together with enough hydration products, mainly C-S-H, so that they form a rigid backbone with a finite long-time or zero frequency shear modulus. This process is illustrated schematically in Fig. 10. On the left, cement grains (light gray) form an isolated phase when they are first mixed into water. As time goes by, however, and hydration products like C-S-H (dark gray) form, the cement grains gradually become linked together by C-S-H to form a continuous phase (13,15). The phase that actually percolates is a composite phase of cement grains plus C-S-H. Set usually occurs at a low degree of hydration, about $\alpha = 0.02-0.08$ (13). This has been successfully predicted by the cement paste microstructure model (15).

Capillary porosity percolation and transport phenomena

As hydration products consume both water and cement and fill in the capillary pore space, the capillary porosity is reduced. Just as in the 2-D gray-white case illustrated in Fig. 1 above, the connectivity of the capillary pore space (white) is gradually reduced as it is filled-in by hydration products (gray). This process can be followed experimentally by measuring transport properties like electrical conductivity (16,17), and theoretically using the cement paste microstructure model (18). Figure 11 shows the model results for the connectivity of the capillary pore space for a variety of w/c ratios, for pure C₃S cement pastes. Figure 11a shows how this percolation is a function of degree of hydration as expected, with w/c ratio pastes above about 0.6 having their capillary pore spaces remaining percolated throughout hydration. Figure 11b reports this data vs. capillary porosity, and shows that all the data roughly fall on a single curve, with a percolation threshold of about 18% porosity. The pastes with w/c ratio of 0.6 or more still follow this curve, but since their porosity never can reach the percolation threshold (too much water initially for the amount of cement used), their capillary pore space remains percolated. The threshold has been found to depend on cement particle size distribution and cement chemical type, and usually ranges between volume fractions of 0.14 to 0.24 (19).

C-S-H percolation: Cement paste at -40°C

The cement paste microstructure model discussed above predicts that the C-S-H phase in a cement paste will itself percolate at a volume fraction of 15-20% (6). Figure 12 shows a schematic view of this process.

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Experimentally, the only way one can investigate this phase is through transport studies using electrical conductivity, for example. However, the main transport paths through cement paste are through the much larger capillary pores. These only become discontinuous at later stages of hydration, as was seen above, so that transport at that time, even though it is mainly through C-S-H pores, does not tell us anything about C-S-H at earlier stages of hydration, when its volume fraction is near its predicted percolation threshold.

Upon dropping the temperature of the cement paste to -40°C , it has been found that the larger capillary pores freeze, thus sharply reducing the conductivity of the ionic pore solution contained in them, while the solution in the smaller nano-scale pores in the C-S-H phase does not freeze. At this temperature, it is then found that the C-S-H phase becomes the main transport pathway (20). In an electrical conductivity experiment, there is only conduction through the sample when the C-S-H phase is continuous. Figure 13 shows the results of such measurements, for two different w/c ratios and for model predictions and experiments (20). When plotted against the volume fraction of C-S-H present in the material, all the data falls on a single curve and shows a percolation threshold of about 15-20% volume fraction of C-S-H, as predicted by the model (6,20).

PERCOLATION THRESHOLD IN CONCRETE

In Fig. 8, the schematic picture of concrete microstructure, the ITZ regions did not percolate. However, remember that a 2-D picture cannot give 3-D percolation information. These ITZ regions have higher transport properties like ionic diffusivity and fluid permeability than does the bulk paste, so it is important to know whether these rims or shells form a percolating phase in 3-D. This geometry is a classic percolation problem--the hard-core soft-shell problem (21). For most concretes, the ITZ regions usually do percolate, depending on the volume fraction of rocks and sand present and the thickness of the ITZ regions (9).

Figure 14 shows the fraction connected of the ITZ phase for a mortar model, with up to 50% sand by volume (9). For a given ITZ width, the amount of sand needed, for the ITZ phase to percolate, is plotted on the abscissa, and the fraction connected of the ITZ phase on the ordinate. Figure 15 shows the difference between a mortar and a concrete, in terms of the volume fraction of cement paste matrix that is within a distance d from any aggregate surface. Because of the higher surface area of the mortar aggregates, more cement paste is closer to an aggregate surface, so that the ITZ will tend to play a bigger role in mortars than in a concrete.

Mention should be made here of the different effects of the ITZ on ionic diffusivity and fluid permeability. A material phase that has a percolation threshold only makes its presence known in the transport properties if its

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individual transport property is much different from that of the other phases. For example, it has been recently shown experimentally and theoretically that for chloride diffusivity, the ITZ regions do not play a large role, because the ITZ diffusivity is only a few times greater than the bulk matrix diffusivity (22). Therefore, the diffusivity of a concrete, at equal degrees of hydration and saturation, is almost always smaller than that of the cement paste from which it is made. This is because diffusivity depends little on pore size. However, it has also been shown that for fluid permeability, the ITZ regions play a very important role (22), so that concrete almost always has a much greater fluid permeability than the cement paste from which it is made. This is because fluid permeability is a strong function of the pore size, while ionic diffusivity is dependent more on the porosity and only weakly on the pore size. For example, suppose we have a pore that is a straight cylindrical cross-section tube, of radius R . Suppose also that there is a concentration gradient inducing diffusion along the tube. Then the diffusive flow is proportional to R^2 , or the cross-sectional area A . Now suppose that there were a pressure gradient, inducing fluid flow along the tube. The fluid flow is proportional to R^4 , or A^2 (23). The bigger pores in the ITZ regions cause a large contrast in fluid permeability between ITZ and bulk paste, while the somewhat larger porosity between the two regions causes only a small contrast, of order 2-6, in the ionic diffusivity (22).

DISCUSSION AND CONCLUSIONS

Cement paste, a micrometer scale material, has the most percolation thresholds of significance of any material known to the authors. These are three in number, and include the set point, the C-S-H percolation threshold, and the capillary porosity percolation threshold. These thresholds affect the transport properties of cement paste directly and significantly.

In concrete, at the millimeter length scale, the percolation of the ITZ regions takes place at usual aggregate loadings. The enhanced porosity and pore size of the ITZ regions can play an important role in determining the transport properties of the concrete, depending on how great the contrast is between the properties of the ITZ and the properties of the bulk matrix cement paste.

In most degradation mechanisms, the rate of damage or the time to damage is strongly influenced or even dominated by the rate of transport of deleterious ions or of water (rate of chloride ions through concrete, conductivity of concrete near the reinforcing steel, etc.). Since these transport processes are controlled by the percolation thresholds in cement paste and concrete, the percolation thresholds have a direct influence on durability and therefore service life.

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So we see that percolation ideas, along with composite ideas, explain and link the microstructure of cement-based materials across many length scales, from nanometers to millimeters and beyond, and are particularly important at the micrometer length scale of cement paste and the millimeter length scale of concrete in their effect on transport properties and thus durability. More detailed exploration of these multi-scale ideas, combined with percolation and composite theory ideas, can be found at <http://ciks.cbt.nist.gov/garboczi/>, "An electronic monograph: Modelling the structure and properties of cement-based materials."

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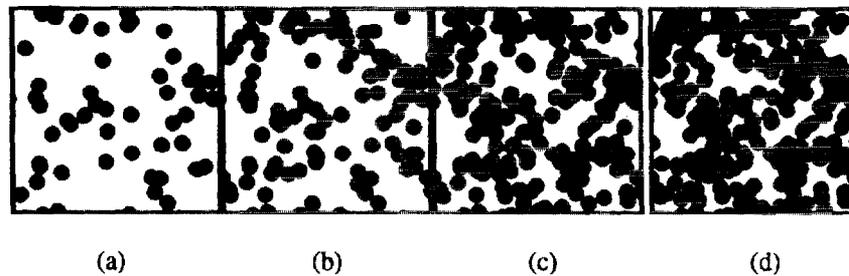


Fig. 1—Four cases of monosize circles (gray) randomly placed on plane (white) with different area fractions: (a) gray = 0.22, white = 0.78; (b) gray = 0.39, white = 0.61; (c) gray = 0.60, white = 0.40; and (d) gray = 0.70, white = 0.30.

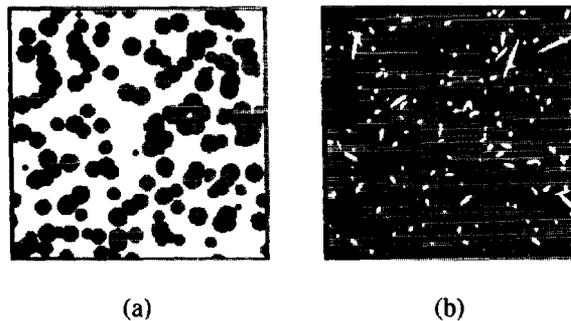


Fig. 2—(a) slice through 3-D system of 40% by volume randomly placed monosize spheres; and (b) slice through 3-D system of 7% by volume randomly placed prolate (10:1 aspect ratio) ellipsoids of revolution. In 3-D, both sets of objects are percolated, while in 2-D slices, they are not.

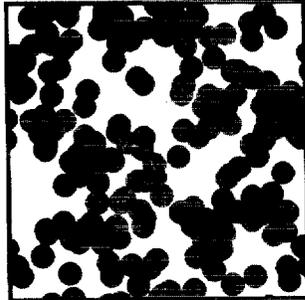
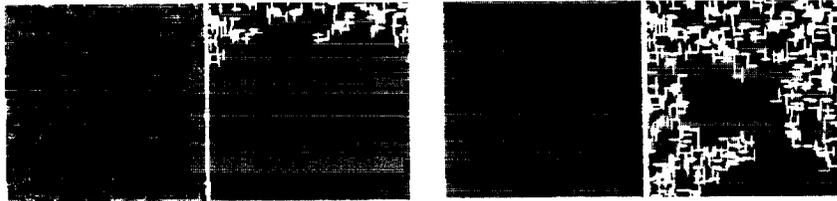


Fig. 3—Area fractions: gray = 0.60, white = 0.30. Black line encloses region of white phase that isolated from rest of continuous white phase.



(a)

(b)

Fig. 4—Ellipses (gray) randomly placed on black background. Right-hand image in each pair shows how much of ellipse phase is accessible (white) from top down: (a) 40% ellipses; and (b) 47.5% ellipses. In (b), fraction connected of ellipse phase is approximately 0.60.

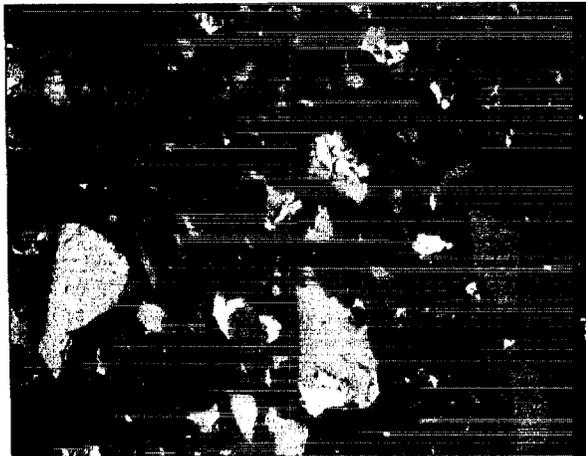


Fig. 5—Back-scattered scanning electron micrograph of portland cement powder embedded in epoxy. Gray scales show random mineral composition of grains. Main phase is calcium tri-silicate = C_3S .

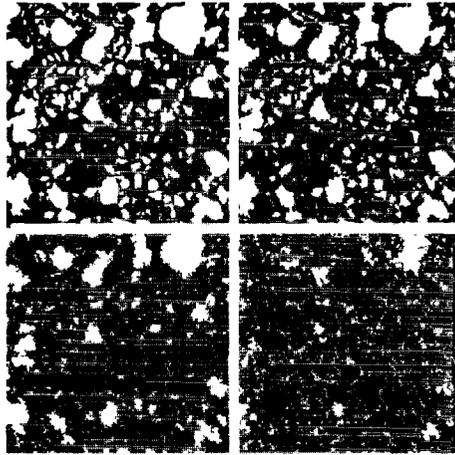


Fig. 6—Stages of hydration in microstructural model of C₃S hydration. Degrees of hydration are: top left—0, top right—20%, bottom left—50%, and bottom right—87%. White = unreacted cement, light gray = CH, dark gray = C-S-H, and black = porosity.

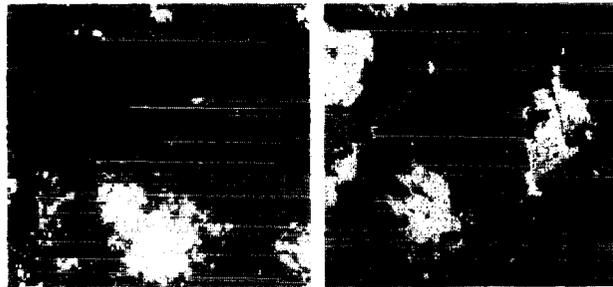


Fig. 7—Qualitative comparison between: (right) backscattered scanning electron micrograph of real cement paste; and (left) model version with realistic gray scale.

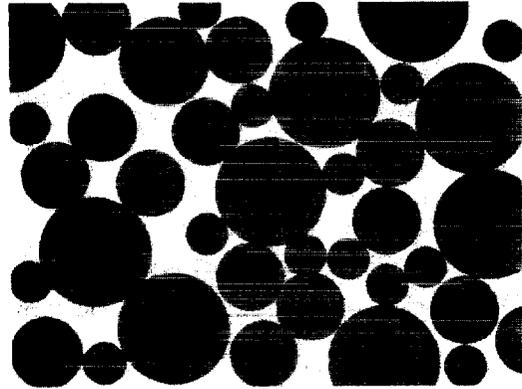


Fig. 8—Schematic picture of many sand and rock grains (dark gray) packed into cement paste matrix (light gray), each surrounded by interfacial transition zones (black).

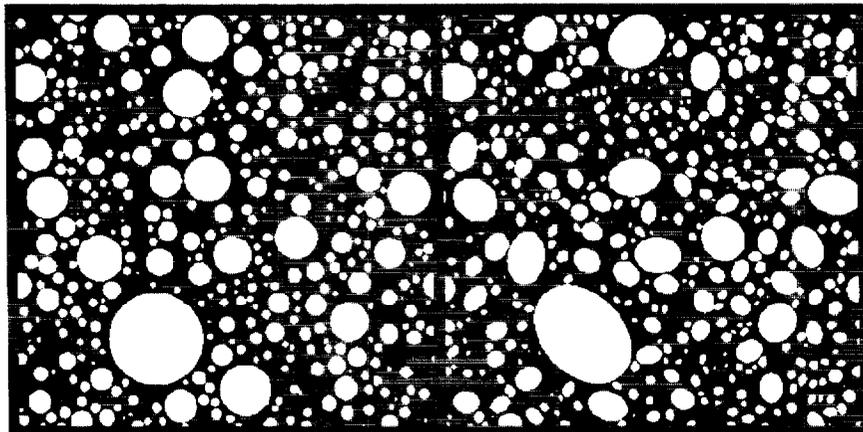


Fig. 9—Slices through two different 3-D concrete models showing different aggregate shapes and sizes (gray = cement paste, black = ITZ, and white = aggregate).

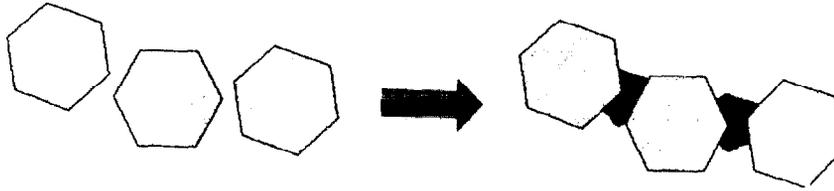
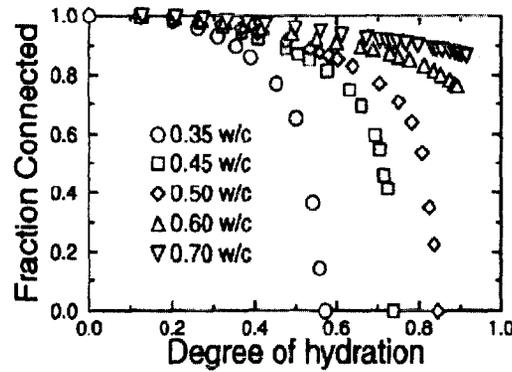
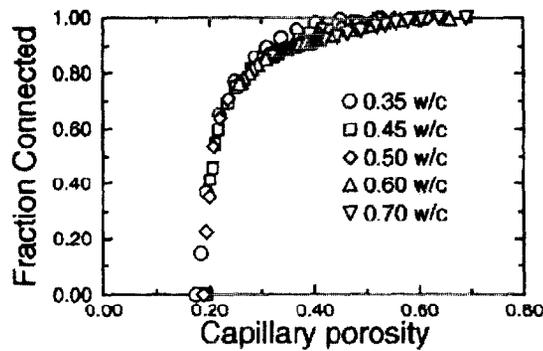


Fig. 10—Schematic illustration of setting process for cement paste. Light gray grains are cement, dark material linking cement grains is C-S-H, and dark arrow shows elapse of time, usually approximately 3-6 h at ordinary temperatures using typical cements.



(a)



(b)

Fig. 11—Fraction connected for capillary porosity for various *w/c* cement pastes: (a) plotted versus degree of hydration; and (b) plotted versus capillary porosity. Note that this particular cement particle size distribution gave percolation threshold of approximately 18%.

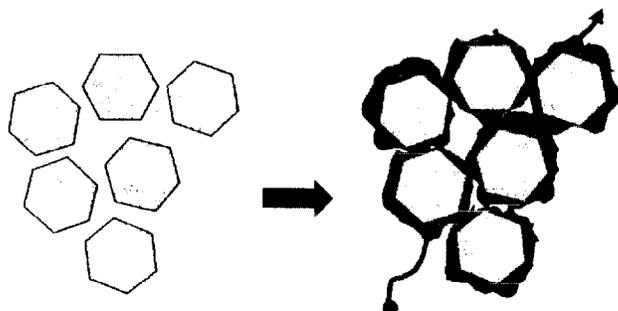


Fig. 12—Schematic illustration of C-S-H percolation process: light gray = cement, dark gray = C-S-H; arrow indicates elapse of time (approximately 12-24 h); and curved arrow shows continuity of C-S-H phase.

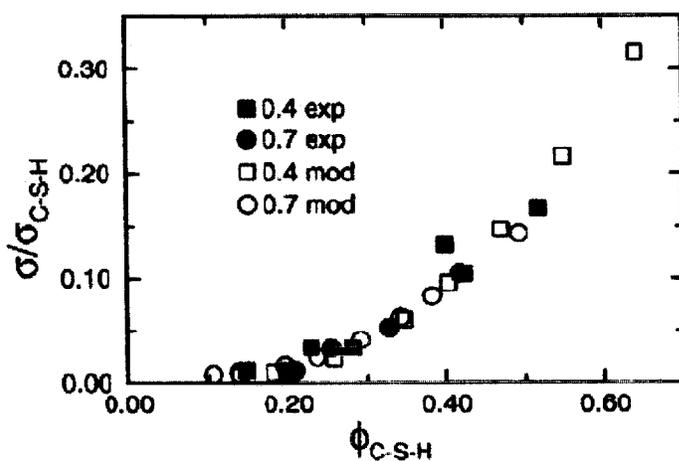


Fig. 13—Showing conductivity of cement paste (at 40 C) relative to conductivity of C-S-H plotted versus volume fraction of C-S-H.

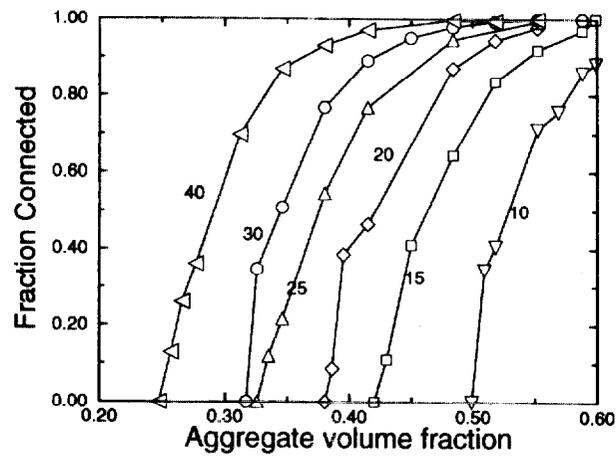


Fig. 14—Showing fraction connected for ITZ phase versus width taken for ITZ for mortar model.

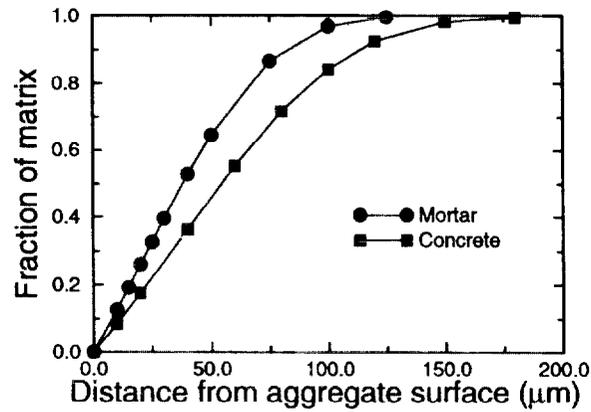


Fig. 15—Showing volume fraction of cement paste within distance d of aggregate surface for both mortar and concrete.