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THE MICROSTRUCTURE OF PORTLAND CEMENT-BASED MATERIALS: COMPUTER SIMULATION AND PERCOLATION THEORY

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ABSTRACT

Portland cement-based materials are usually composites, where the matrix consists of portland cement paste. Cement paste is a material formed from the hydration reaction of portland cement, usually a calcium silicate material, 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 evolving microstructure in terms of the three percolation thresholds that are of importance in the cement paste microstructure: the set point, capillary porosity percolation, and the percolation of the C-S-H phase.

INTRODUCTION

Percolation theory plays an important role in interpreting and understanding the microstructure of cement-based materials in general. 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.

Cement paste, formed from the reaction of portland cement in water, has more percolation thresholds of importance in it than any other material of which we are aware. There are three percolation thresholds of significance in this material. These all play an important role in relating the microstructure to properties. To understand the significance of these thresholds, one must first know something about percolation concepts, and then something about cement paste 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 random 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 amount of phase present at this point is usually given as the value of the percolation threshold.

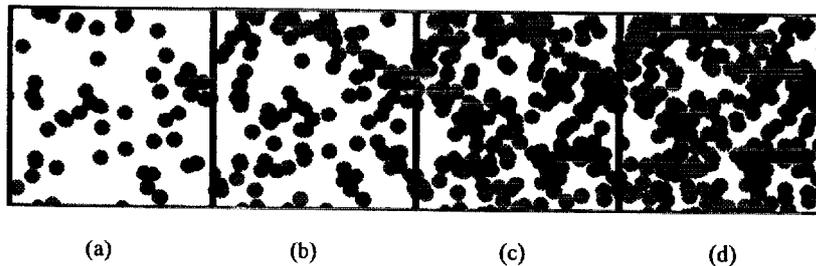


Figure 1: Showing four cases of monosize circles (gray) randomly placed on a plane (white), with different area fractions: (a) gray = 0.22, white = 0.78, (b) gray = 0.39, white = 0.61, (c) gray = 0.60, white = 0.40, (d) gray = 0.70, white = 0.30.

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].

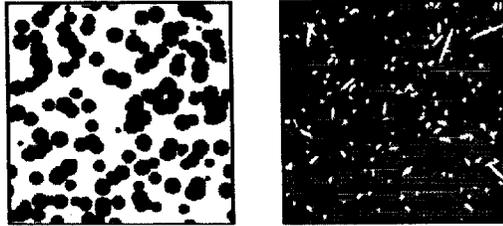


Figure 2: Showing: (a) a slice through a 3-D system of 40% by volume randomly placed monosize spheres, and (b) a slice through a 3-D system of 7% by volume randomly placed prolate (10:1 aspect ratio) ellipsoids of revolution. In 3-D, both sets of objects are percolated, while in the 2-D slices, they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

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 below 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.

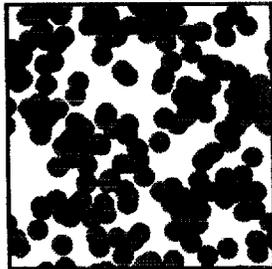


Figure 3: Area fractions: gray = 0.60, white = 0.30. Black line encloses a region of white phase that is isolated from the rest of the continuous white phase.

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 oriented in either the x or the y directions. The right-hand image in each set shows the ellipses that are accessible from the top in 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.

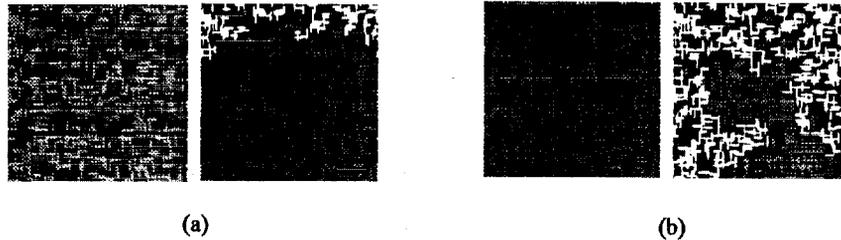


Figure 4: Showing ellipses (gray) randomly placed on a black background. The right-hand image in each pair shows how much of the ellipse phase is accessible (white) from the top down: (a) 40% ellipses, (b) 47.5% ellipses. In (b), the fraction connected of the ellipse phase is about 0.60.

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. The cement clinker is manufactured by firing carefully proportioned and interground mixtures of limestone, clay, and iron ore, or other sources of CaO , SiO_2 , Al_2O_3 , and Fe_2O_3 . After grinding, the cement powder consists of multi-size, multi-phase, irregularly shaped particles generally ranging in size from less than $1 \mu\text{m}$ to about $100 \mu\text{m}$, with an average diameter of about $15\text{-}20 \mu\text{m}$.

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-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 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.

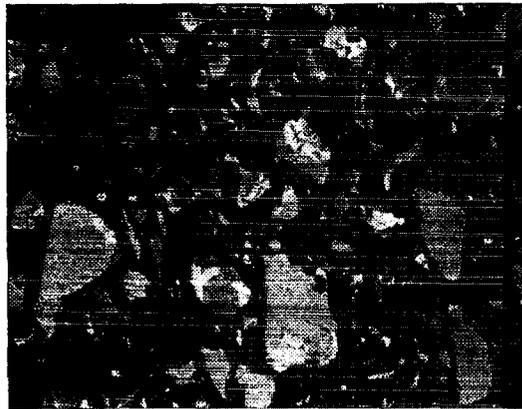


Figure 5: Back-scattered scanning electron micrograph of a portland cement powder embedded in epoxy. The gray scales show the random mineral composition of the grains. The main phase is calcium tri-silicate = C_3S .

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.

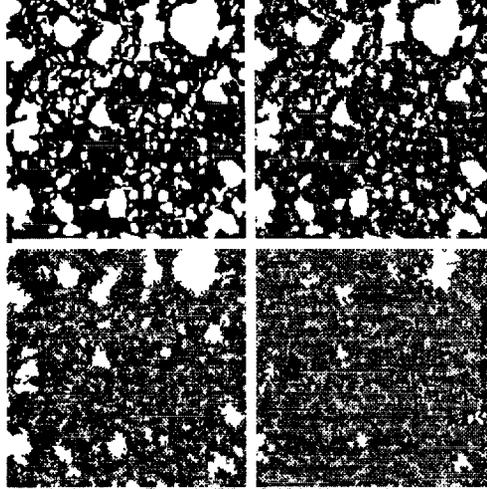


Figure 6: Four stages of hydration in a microstructural model of C_3S hydration. The degrees of hydration are: top left—0, top right—20 %, bottom left—50%, bottom right—87%. White = unreacted cement, light gray = CH, dark gray = C-S-H, and black = porosity.

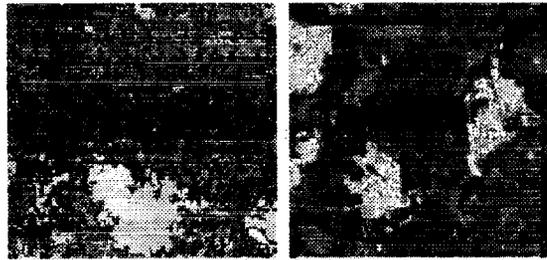


Figure 7: Qualitative comparison between: (right) backscattered scanning electron micrograph of real cement paste and (left) model version with realistic gray scale.

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 experiment is 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.

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 [8], turns into a viscoelastic solid, with a finite long-time shear modulus. 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 product, 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. 8. 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 [8,9]. 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 $\alpha = 0.02-0.08$ [8]. This has been successfully predicted by the cement paste microstructure model [9].

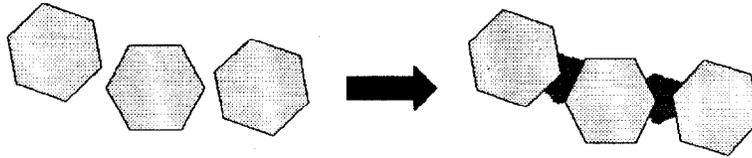
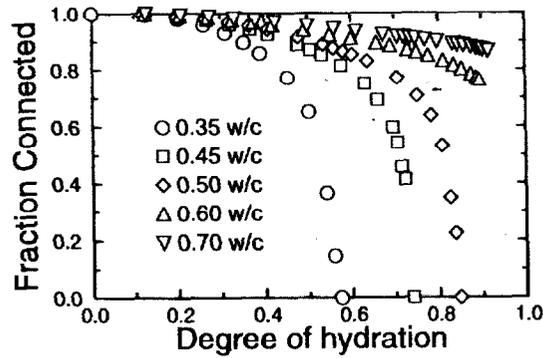


Figure 8: Schematic illustration of the setting process for cement paste. The light gray grains are cement, the dark material linking the cement grains is C-S-H, and the dark arrow shows the elapse of time, usually about 3-6 hours at ordinary temperatures using typical cements.

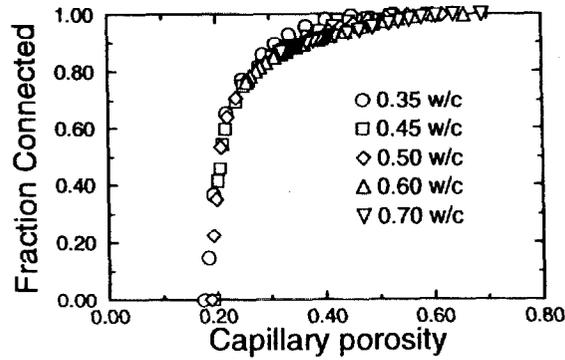
Capillary porosity percolation and transport phenomena

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 [10,11], and theoretically using the cement paste microstructure model [12]. Figure 9 shows the model results for the connectivity of the capillary pore space for a variety of w/c ratios, for pure C_3S cement pastes. Figure 9a 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 9b 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 have a small dependence on cement particle size distribution and cement chemical type, and ranges from 0.18-0.22 volume fraction.



(a)



(b)

Figure 9: Fraction connected for capillary porosity for various w/c ratio cement pastes: (a) plotted vs. degree of hydration, and (b) plotted vs. capillary porosity.

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 10 shows a schematic view of this process.

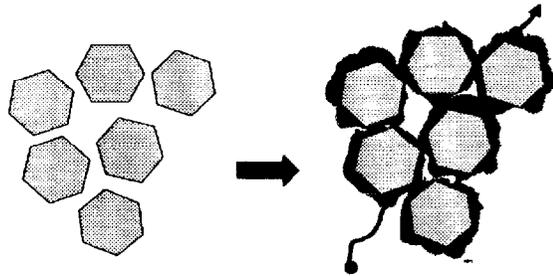


Figure 10: Schematic illustration of the C-S-H percolation process (light gray = cement, dark gray = C-S-H, arrow indicates the elapse of time, about 12-24 hours, and the curved arrow shows continuity of the C-S-H phase).

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 [13]. In an electrical conductivity experiment, there is only conduction through the sample when the C-S-H phase is continuous. Figure 11 shows the results of such measurements, for two different w/c ratios and for model predictions and experiments [13]. 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, 13].

DISCUSSION AND CONCLUSIONS

Cement paste, a micrometer scale material, has the most percolation thresholds of significance of any material that we know. These are three in number, and include the set point, the C-S-H percolation threshold, and the capillary porosity percolation threshold.

If one goes down in length scale, to the nanometer length scale, one sees the structure of C-S-H, which is itself a nanoporous material. There does not seem to be any percolation phenomena at this length scale. These nano-scale pores seem to be always connected and allow transport.

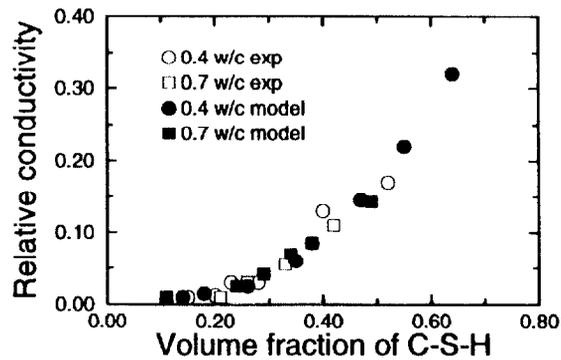


Figure 11: Showing the conductivity of the cement paste (at 40°C) relative to the conductivity of C-S-H, plotted vs. the volume fraction of C-S-H.

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. There is a percolation phenomenon of importance at this length scale. Because of the particulate nature of cement paste, at first mixing 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 [14]. 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

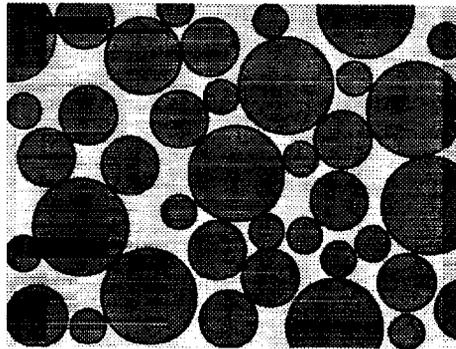


Figure 12: Schematic picture of many sand and rock grains (dark gray) packed into a cement paste matrix (light gray), each surrounded by interfacial transition zones (black).

paste. Figure 12 shows a 2-D schematic picture of how these regions look in a concrete. In Fig. 12, the ITZ regions do 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 [15]. 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 [16].

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. 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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