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Hydration and percolation at the setting point

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ABSTRACT

The setting of cement paste is widely understood to be caused by percolation of the links that are created by overlap of hydration products on the surfaces of reacting grains of clinker. Percolation theory predicts that the elastic modulus will increase with a certain functional form, but few attempts have been made to demonstrate this behavior quantitatively. We discuss the appropriate variables to use for this test of the theory, and show that the percolation probability is proportional to time only over a narrow time interval. We compare the measured and predicted degree of hydration at the percolation threshold, and show that the hard-core/soft-shell model strongly over-estimates the amount of hydration at the setting point. The discrepancy is attributed to agglomeration of particles in the paste, which reduces the amount of hydration needed to link the particles into an elastic network.

1. Introduction

The setting of cement paste is generally understood to be a percolation process in which the hydration products that form on the surface of clinker particles intersect, leading to the formation of clusters that eventually join into a continuous elastic network. The percolation of the solid and pore phases has been investigated using numerical simulations, the earliest of which was by Bentz and Garboczi, using CEMHYD [1]. That paper predicted a high degree of hydration at the percolation threshold, but later work produced lower, more realistic, values [2]; the difference apparently resulted from increasing the spatial resolution used in the simulation [3]. Similar studies have been done using HYMOSTRUC to predict the fraction of connected solids [4]. The connection between the percolation of solids and the rise in elastic modulus has also been examined by comparing various measures of rigidity, such as the Vicat test or sound velocity, with the degree of connectivity simulated with CEMHYD [5–7] or HYMOSTRUC [4,8]. Only a few studies have tried to quantify the change in properties near the setting point in terms of percolation theory, but each of those analyses has defects that will be discussed.

The purpose of this paper is to re-examine the use of percolation theory for interpreting the setting behavior of cement paste. The analysis will be demonstrated by using data for the ultrasonic pulse velocity and chemical shrinkage obtained in an earlier study [9]. We will then compare the observed threshold to the prediction of the hard-core/soft-shell (HCSS) percolation model developed by Torquato et al. [10, Ch. 10 of ref. 11], which is particularly relevant to setting of cement paste.

2. Percolation theory

2.1. Lattice and continuum percolation

In its simplest form, percolation theory describes the growth of clusters as particles are placed on the sites of a lattice, or as bonds are established between particles in an array. The probability of filling a site or forming a bond is p, and it is found that a continuous network (or, infinite cluster) is formed at a critical value, $p = p_C$, called the percolation threshold. In the vicinity of the threshold, many properties (P) of the network obey power-laws, such as

$$P \propto (p - p_C)^{\gamma} \tag{1}$$

where γ is called a critical exponent [12]. The value of p_C depends on the geometry of the lattice, but the critical exponents do not (for systems in which connections are made only between nearest neighbors [11]).

It has been demonstrated that the percolation threshold occurs at a fixed volume fraction of connected particles (or area fraction, in two-dimensional lattices) [12], which makes it practical to apply percolation theory to physical problems. This is called continuum percolation, because it assumes that the percolating objects are placed at random in continuous space, rather than on a lattice. The critical exponents for geometrical properties (such as the cluster size distribution) are identical for continuum and lattice percolation, but the exponents for transport properties may be different. For example, if

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equal-sized balls of glass and aluminum are randomly mixed, then the mixture will become electrically conducting when the volume fraction of aluminum particles, ϕ, exceeds $\phi_C \approx 16$ vol.%, which is the percolation threshold in 3-d [12]. In this case, the conductivity, σ, would vary as

$$\sigma \propto (\phi - \phi_C)^{\tau} \tag{2}$$

where the exponent $\tau \approx 1.6$–2 in 3-d (with more recent analyses favoring the higher value) (Ch. 9 of ref. 11[12]). In this example, the percolating objects are non-overlapping spheres, and they exhibit the same exponent as a lattice model. Feng et al. [13] showed that the conductivity exponent for overlapping spheres (what they call the "inverse Swiss-cheese model") is also the same as τ for a lattice model; however, if random spherical voids are placed in a conducting continuum, then the exponent rises by 0.5. The change in τ is attributed to the influence of very tenuous links that are created when two voids are close together; in contrast, all of the links in a lattice model have equal conductivity.

Models for the elastic behavior of percolating systems show a broad range of critical behavior. For a system described by an isotropic Born potential, in which relative displacements of particles in any direction generate the same force (a situation called *scalar*, or *isotropic*, *elasticity*), the shear modulus is expected to exhibit the same critical exponent as σ [14,15]; however, under purely central forces, a higher exponent (on the order of 3.4–4.4 [16]) and a higher percolation threshold are predicted to apply [14]. The Born potential is not rotationally invariant (i.e., it indicates that interparticle forces result from a rotation of the whole body), so it is not clear that it provides a correct representation for any physical system. Lattice models in which bonds resist both stretching and bending yield a critical exponent of $\gamma \approx 4$ for the elastic modulus [13], and continuum models with overlapping spheres are predicted to have $\gamma \approx 4.5$ in 3-dimensions.

Some experimental studies show the higher exponents, and some seem to indicate that there is a crossover from lower to higher values as the degree of connectivity increases [16]. On the other hand, studies of gelation of polymers usually indicate an exponent near 2 (e.g., [17]), as do studies of the setting of cement [18]. In general, the form of Eq. (1) applies only in the immediate vicinity of the percolation threshold, because it is only one term in a series expansion, and there is no way to anticipate its range of applicability a priori. It is possible that the theoretically predicted exponents only apply in a very narrow range of p–p_C that is not captured by the experiments. Well beyond the threshold, conventional composite models will apply, and these predict a nearly parabolic dependence on the volume fraction of solids [19,20]. A further complication is that hard spheres exhibit highly nonlinear elastic behavior, as they oppose being pushed together, but not being pulled apart [21]. In the case of an HCSS particle, the ratio of resistance to compression versus tension depends on the thickness of the shell and the magnitude of the strain.

The development of the modulus during setting of cement paste has been measured by rheometry e.g., [22] and acoustic methods [22–30]. In most cases, the increase in stiffness was correlated with the degree of connectivity calculated from a numerical simulation [4,5,8,27,31]. In one case [31], the calculated amount of connected solids was used together with an assumed critical exponent of $\gamma = 1.53$ to find the constant of proportionality in Eq. (2); however, the modulus data were compromised by entrapped air in the sample, as explained in the next section. Another study [8] used a similar procedure, but applied Eq. (2) to data very far from the percolation threshold (>36 h of hydration), where the theory is not expected to apply. Boumiz et al. [18] analyzed acoustic data in terms of percolation theory by assuming that the progress of the percolation process could be approximated by replacing p–p_C with the elapsed time, t–t_C. This is valid if the rate of the process is constant in time, but that is an assumption that needs to be verified. We will demonstrate in Section 3 that it only applies in a very small time interval near the percolation threshold.

2.2. HCSS percolation

The standard version of continuum percolation theory clearly does not describe the setting of cement, where the volume fraction of solids is initially well above 16%. The particles in cement are not located randomly in space: they are dispersed in a liquid and, in the absence of aggregation,[1] it would be possible to put more than 60 vol.% particles into a slurry without forming a network. In the paste, the network forms as a result of the growth of hydration products on the surfaces of the clinker particles, so the quantity p–p_C must be related to the degree of hydration. This process is described by the HCSS model [11], where the hard core represents the unhydrated clinker and the soft shell represents the layer of hydration products. The shells overlap to link the particles into increasingly large clusters, leading to percolation. Although the geometry of this model is different from conventional continuum percolation, the same critical exponents apply [32]. The comparison of the HCSS model with data for Class H cement will be shown in Section 4.

3. Acoustic transmission

3.1. Slurries and networks

The velocity, V, of a longitudinal wave in a suspension is given approximately by [33]

$$K_M = \rho_M V^2 \tag{3}$$

where ρ_M and K_M are the mean density and bulk modulus of the suspension, which are defined by

$$\rho_M = \phi\rho_S + (1-\phi)\rho_F \tag{4}$$

and

$$\frac{1}{K_M} = \frac{\phi}{K_S} + \frac{1-\phi}{K_F} \tag{5}$$

where ρ_S and ρ_F are the densities, and K_S and K_F are the bulk moduli, of the suspended particles and the fluid medium, respectively; the mean density of a cement paste with w/c = 0.35 is $\rho_M \approx 2023$ kg/m^3. A more rigorous expression, which takes account of the frequency of the sound and the size of the suspended particles, was derived by Harker and Temple [33], and is discussed in Appendix 1. The effect of air on the velocity is shown in Fig. 1, where V drops below the speed of sound in air (~300 m/s) when the volume fraction of air exceeds ~0.1%; very similar results are obtained using Eq. (3). The impact of entrapped air was emphasized by Keating et al. [22], and the effect is clearly illustrated in Fig. 5 of Sant et al. [30]. In contrast, cement particles suspended in water are predicted to have a minor effect on V, as shown in Fig. 2. The particles cause some attenuation of the wave, but the effect is very small compared to that of air, as shown in Fig. 3.

[1] Throughout this paper, we use the term "aggregation" and "aggregate" to describe loose clusters of cement particles in the paste that have flocculated as a result of attractive van der Waals forces. These aggregates are to be distinguished from the rigid links created by overlapping hydration products, which lead to formation of an elastic network at the percolation threshold.