The Effect of Intermolecular Forces on the Preparation of the Organic Waster-Cement Pastes*

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Abstract: Organic wasters can be treated with cement to become useful materials. The effect of organic materials on the hydration of cement is discussed in this study. A water film fluid flow model was proposed to describe the transfer of water within the paste. It is supposed that water films exist within the partial dried hydrated cement particles. Water transfers within the water film and diffuses into the cement particles through the porous amorphous medium. For a water film with the film thickness less than 100nm, the disjoining or the conjoining pressure dominates the direction of water flow. The disjoining or the conjoining pressure is produced due to the overlapping of interfacial regions. Simulation results showed that the local water available for hydration reaction is $Q = -A_{sh}/6\pi$. The replacement of hydrated cement particles with organic particles would change the Hamaker constant of the water film and therefore reduce the transfer rate of water. When the Hamaker constant is positive, the conjoining pressure makes the film unstable and inhabits the transfer of water to supply the need of cement hydration. The uncompleted hydration of cement will reduce the compressive strength of the final products.

Key words: organic waster; disjoining pressure; wetting film
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1 Introduction

Plastics and rubbers are important organic materials used. The treatment of plastics with cement has been conducted for a long time. In this paper the treatment of waste rubber with cement is theoretical studied. Because there are a large number of waste tires are discarded all over the world every year, and only a small proportion is either retreated or burned for energy recovery. Most of the waste rubbers are land filled or stockpiled. Since the waste rubber is not easily biodegradable even after a long period of land-fill, this is not only an environmental problem but also a waste of natural resources.

The use of granular rubber as an aggregate or additive to concrete is a possible solution to solve the above problems and has been studied for a long time[1-7, 9, 11, 14, 15, 17-22]. Previous research results showed the aggregating rubber could increase concrete's flexibility, elasticity, and capacity to absorb energy. It is suggested that the rubberized concrete can be used, for example, in highway constructions as a shock absorber, or in sound barrier as sound absorber, or in building as earthquake shock wave absorber, or in impact prevention structure such as Jersey barriers. It is believed that such concrete can also be used in the soil and water conservation construction materials.

Even amount of studies have been conducted, there are many inconsistent results should be studied, for example, the influence rubber granules' size on the compressive strength of the concrete. Topcus[18], Eldin and Senoucis[5] showed that the coarse grading of rubber granules lowered the compressive strength more than that of the finer grading. However, Alie et al[1] indicated the opposite. The reduction of the compressive strength is mainly attributed to the week adhesion between the interface of cement and rubber grains. To know the inconsistent results, some authors tried to modify the surface properties of the rubber particle to enhance its adhesion to cement paste. The modified agents used in literatures were sodium hydroxide solution[17], carbon tetrachloride, and latex admixture[6] etc. However, the effect of rubber grains on the transfer of water is never mentioned. In this study the cracklings of the surface of the rubberized pastes were observed with a microscopy. For a suitably pretreated rubber grains the crackling did not occur in the interface of the cement and the rubber grains but in the bulk cement regions. It is be-

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lieved that with the addition of the rubber particles, the transfer of water within the pores will be inhabited and then affect the hydration of the cement. A water film flux model is proposed to explain the influence of rubber grains on the transfer of water within the cement pastes.

2 Model development

Water within the newly prepared cement paste is consumed by both evaporation and cement hydration reaction. With the decrease of water content, thin liquid film is developed as shown in figure 1[8]. Water within the partially dried porous medium will transfer mainly through the thin liquid film and through the vapor phase. In this study only one dimension film flow with constant density (ρ) and viscosity (μ) is considered.

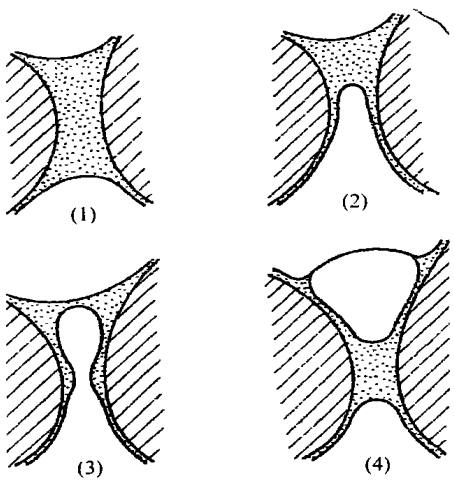


Fig 1　Pore level view of wetting film generation within the newly-prepared cement mortar

Figure 2 shows the film flow near the wall of the capillary. At steady state and neglecting the inertia term and gravity.

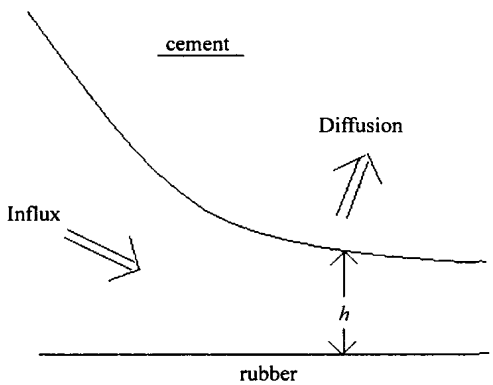


Fig 2　Water film flux model

$$\frac{\partial P_1}{\partial x} = \mu \frac{\partial^2 U}{\partial y^2} \tag{1}$$

The velocity profile in equation (1) is determining by imposing the boundary condition of no-slip at the solid wall and no-stress at the gas-liquid interface.

$$U(y) = \frac{1}{\mu}\left(\frac{dP_1}{dx}\right)\left(\frac{y^2}{2} - hy\right) \tag{2}$$

The mass flow rate per unit width of the film is

$$\Gamma = \rho_l \int_0^h U(y)\mathrm{d}y = \frac{-h^3}{3\nu}\frac{\mathrm{d}P_l}{\mathrm{d}x} \tag{3}$$

Where $\nu = \mu/\rho$,

According to Derjaguin and Churaev (1978)

$$\mathrm{d}P_1 = -\mathrm{d}P_d + \mathrm{d}(K\sigma) \tag{4}$$

K: curvature

σ: surface tension of the liquid

P_d: disjoining pressure

If the surface tension is constant and the curvature is neglected,

$$\Gamma = \frac{h^3}{3\nu}\frac{\mathrm{d}p_d}{\mathrm{d}x} \tag{5}$$

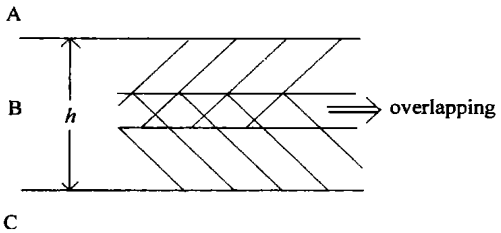
Paul Scovazzo and Paul Todd (2001) showed that the disjoining pressure for a submicrometer liquid-filled cylindrical geometries is

$$P_d = P_{dm} + P_{de} + P_{ds} = \frac{-A_{132}}{6\pi h^3} + D\exp(-Kh) + \frac{2C_\infty A_0}{\nu(h-\delta)^3} \tag{6}$$

Where P_{dm} is the London/van der Waals interactions component of disjoining pressure. P_{de} is the electrostatics interaction component of disjoining pressure and P_{ds} is the steric component of disjoining pressure. $D = (64nkT)\tanh^2[ze\Psi/4kT]$. $\kappa = (8\pi nz^2e^2/\varepsilon kT)^{0.5}$ is the Debye-Huckel reciprocal length. C_∞ is the bulk solute concentration. A_0 is the solute/water interaction constant. V is molar volume. δ is the minimum solute approach distance. n is the ion number density. K is the Boltzmann constant. z is the solute charge density (valence). e is electron charge. Ψ is the electrostatic surface potential. ε is the absolute permittivity.

With the large concentration of salts (about 300 mM) in the water of our system, Therefore in our system $P_d = \frac{-A_{132}}{6\pi h^3}$ is considered only.

The Hamaker constant, A_{132}, of the London/van der Waals interaction component of the wetting film as depicted in figure 3 can be evaluated by the following equation (3)



$P_{(h)}=P_1-P_0$

P_1=pressure in thin liquid film

P_0=pressure in bulk liquid

P_1=disjoining pressure

Fig 3 Illustration of disjoining pressure

From equation (5)

$$\Gamma=\frac{h^3}{3v}\frac{\mathrm{d}}{\mathrm{d}x}\left(-\frac{A_{132}}{6\pi h^3}\right) \tag{7}$$

$$\Gamma=\frac{-A_{slv}h}{6\pi v}\frac{h'}{h} \tag{8}$$

Assuming a triangle as an approximate shape for the curve film as discussed by Wanyer[24], the minimum possible area under the film per unit width is h/h'. Therefore the available maximum fluid in this region can be expressed as

$$Q=\frac{-A_{slv}}{6\pi v} \tag{9}$$

Equation (9) shows that the mass flow rate in the wetting film strongly depends on the Hamaker constant. Derjaguin[3] showed that the stability of the wetting film depends on $\mathrm{d}P_d/\mathrm{d}h$. In case $\mathrm{d}P_d/\mathrm{d}h>0$, the film is unstable, otherwise it is stable. Therefore the film is unstable if $A_{slv}>0$ and the flow in the wetting film will be inhibited. If $A_{slv}<0$ the film is stable and equation (9) can be used to predict the mass flow rate.

2.1 Evaluation of Hamaker constant

The Hamaker constant can be approximately calculated by the following equation[12]:

$$A_{132}=\frac{3}{4}kT\left(\frac{\varepsilon_1-\varepsilon_3}{\varepsilon_1+\varepsilon_3}\right)\left(\frac{\varepsilon_2-\varepsilon_3}{\varepsilon_2+\varepsilon_3}\right)+\frac{3h}{4\pi}\int_{\nu_1}^{\infty}\left(\frac{\varepsilon_1(i\nu)-\varepsilon_3(i\nu)}{\varepsilon_1(i\nu)+\varepsilon_3(i\nu)}\right)\left(\frac{\varepsilon_2(i\nu)-\varepsilon_3(i\nu)}{\varepsilon_2(i\nu)+\varepsilon_3(i\nu)}\right)\mathrm{d}\nu \tag{10}$$

Where ε_1, ε_2 and ε_3 are the static dielectric constants of the three media, $\varepsilon(i\nu)$ are the imaginary frequencies. The first term in Eq. (10) gives the zero-frequency energy of van der Waals interaction and includes the Keesom and Debye contributions. The second term gives the dispersion energy and includes the London energy contribution. The above approach may be used to calculate the van der Waals interaction between a small particle 1 in medium 3 with the surface of medium 2. In Eq. (10) The imaginary part of dielectric constant can be expressed as

$$\varepsilon(i\nu)=1+\frac{(\varepsilon-n^3)}{(1+\nu/\nu_{rot})}+\frac{(n^2-1)}{(1+\nu^2/\nu_e^2)} \tag{11}$$

Where r_{rot} is the rotational relaxation frequency typically at microwave and lower frequency. ν_e is the main electronic absorption frequency in the UV typically around 3×10^{15} and n is the refractive index of the medium in the visible [i.e. $n^2=\varepsilon_{vis}(\nu)$]. Since ν_1 is about $4\times10^{13}\ \mathrm{s}^{-1}>>\nu_{rot}$ (less than $10^{12}\ \mathrm{s}^{-1}$), the dispersion contribution is determined solely by the electronic absorption. We may therefore reduce Eq. (10) as

$$\varepsilon(i\nu)=1+\frac{(n^2-1)}{(1+\nu^2/\nu_e^2)} \tag{12}$$

If the absorption frequencies of all the three media are assumed to be at the same ν_e, we obtain the following approximate expression for the retarded dispersion contribution to the Hamaker constant

$$A_{132}=\frac{3h\nu_e(n_1^2-n_3^2)(n_2^2-n_3^2)}{8\sqrt{2}(n_1^2+n_3^2)^{1/2}(n_2^2+n_3^2)^{1/2}+\{(n_1^2+n_3^2)^{1/2}+(n_2^2+n_3^2)^{1/2}\}} \tag{13}$$

In this Eq. (13) is used to approximately predicted the Hamaker constant. Table 1 gives some Hamaker constants where the subscript 1 is solid substrate, 2 is air and 3 is water film.

3 Results and Discussions

In our previous works[2] the surface structure of the cement paste at time 85 and 90 minutes were shown as figure 4 and figure 5 show. Rubber particles used in this

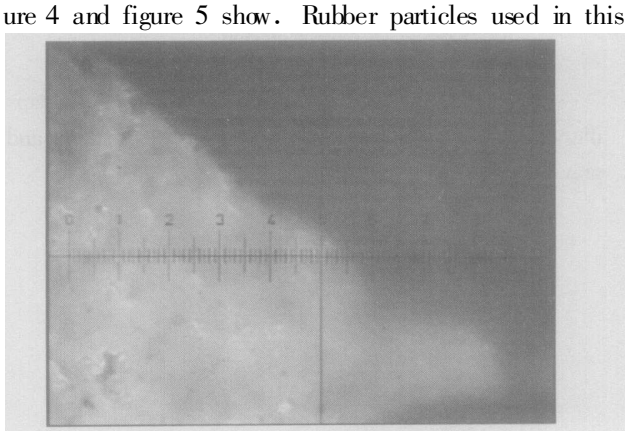


Fig 4 Rubber+ cement (85min)

specimen were as received without any surface modification treatment. The pictures give the evidence that the paste cracked at the time about 85—90 minutes. However, the cracking is not in the interface of cement and rubber. The result is interesting and is worthwhile further study. It is believed that the cracking of the paste will affect the mechanical properties seriously. The crystals and some amorphous materials surround rubber particles.

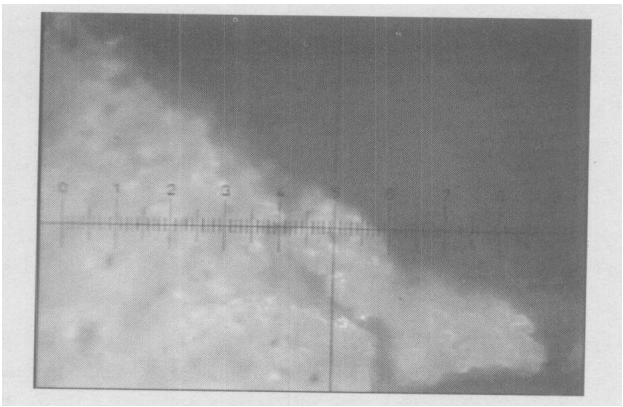


Fig 5　Rubber + cement (90min)

Huynh and Raghavan[11] showed that the hydration of Portland cement occurred within a few minutes and the reactions can be simplified as the following:

$Ca_3SiO_5 + 5.3H_2O \rightarrow 1.7CaO.SiO_2.4H_2O + 1.3Ca(OH)_2$

$Ca_2SiO_4 + 4.3H_2O \rightarrow 1.7CaO.SiO_2.4H_2O + 0.3Ca(OH)_2$

Water diffuses into the inner of the cement particle through these crystals and amorphous materials and hydrating continuously. The diffusion rate affects the rate of the hydration reaction and eventually the physical and mechanical properties of the concrete. Initially, abundant water makes the hydration reaction occur quickly. However with the crystals surrounding outsides the cement particle, the rate of diffusion of water is limited. The rate of hydration reaction changes from the reaction control to diffusion control. It is believed that continuous and quick supply of water into the cement particles is the most important point to be considered. Figure 5 shows no cracking occurs. The hydration products of cement adhere to rubber particles tightly. It is expected that concrete made of this type of rubber particles will have better mechanical performance than that of the as-received rubber particles.

A water film fluid flow model is proposed to explain the experimental results depicted above. It is supposed that there is a water film between the cement particle and the rubber surface. Small contact angle makes water wet the rubber surface easily. Water flows within the water film. Water diffuses into the cement particle through the porous amorphous medium. The direction of water flow depends on the pressure gradient within the water film. For a water film with the film thickness less than 100nm, the disjoining or conjoining pressure dominates it. The disjoining or the conjoining pressure is produced due to the overlapping of interfacial regions. More detail information can be found in references[3, 10]. Pe and Pm constitute the famous DLVO theory. Yang et al[25] discussed the interaction between cement particle with DLVO theory. Pc was experimentally proved to be important for concrete with chemical admixtures by Uchikawa et al[23] and Neubauer et al[16].

Hunter[10] provided the approximate values for water films in silica oxide and isoprene with equation (9) as the followings:

$$A_{slv}\left(\begin{array}{c} water \\ \diagup \\ isoprene \end{array}\right) = -0.836 \times 10^{-20}\ \mathrm{J}$$

$$A_{slv}\left(\begin{array}{c} water \\ \diagup \\ isoprene \end{array}\right) = -(1.0 \sim 5.32 \times 10^{-20})\ \mathrm{J}$$

As shown above, the substitution of cement hydrated products (usually silica oxide or metal oxide) by rubbers (isoprene) will reduce the absolute values of the Hamaker constant. The change of the disjoining may reduce the water flux to the cement particles as shown in equation (9). Hydration reaction of cement may be incomplete and the compressive strength of the concrete will decrease.

The modification of rubber surface will change the surface charge and therefore electrostatic component of disjoining will change. The change of the disjoining or conjoining pressure may induce the instability of the liquid and reduce water diffusion into the cement particles. Hydration reaction of cement may be inhibited in such condition and the performance of the concrete will decrease.

4　Conclusions

A simplified film flow model was developed to explain the previous experimental results. The existence of rubber particles will change the component of the disjoining pressure induced by the London/van der Waals force. Theoretical analysis showed that the decrease of the absolute value of the Hamaker constant would reduce the water flow rate within the water film. With the reduction the film flow rate, the hydration of cement may be incomplete and the performance of the concrete will decrease.

Nomenclatures

A　Hamaker constant, J
A_0　solute/water interaction constant, Jm^3
C_∞　bulk solute concentration, mol/m^3
D　$(64nkT)\tanh^2(ze\Psi/4kT)$, Pa
Q　Mass flux; Kg/s
e　lectron charge, C
h　film thickness, m
K　curvature
k　Boltzmann constant, J/K
m　ion number density, $ions/m^3$
n　refractive index
P　pressure, Pa
T　absolute temperature, K
U　velocity, m/s
V　volume of solvent molecules, m^3/mol
x　x-coordinate, m
y　y-coordinate, m
z　solvent charge number, valence

Greek symbol

δ minimum solvent approach distance, m
ε absolvent permittivity, C^2/Jm
μ Viscosity, kg/m sec
φ potential energy per unit mass due to surface forces, J/kg
ν dynamic viscosity, m^2/s
κ Debye-Huckel reciprocal length $=(8\pi nz^2e^2/\varepsilon kT)^{-0.5}$, m^{-1}
Γ mass flux, kg/m^2
η characteristic frequency, 1/s
ρ density, kg/m^3
σ surface tension, J/m^2
Ψ electrostatic surface potential, V

Subscript

s solid phase
l liquid phase
υ vapor phase
o bulk phase
d disjoining

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分子间作用力对制备含有机废弃之水泥浆体影响研究

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摘　要：研究以水泥处理固体有机物时，有机物对水泥水化的影响。以膜流模式说明水份在水泥浆体内传输的现象。水膜存在半干之水泥浆体，其厚度小于 100 nm，膜流由离分压所驱动，而离分压来自分子间作用力。膜拟结果发现，水泥浆体内局部位置可用以进行水化之水量为 $Q=-A_{sh}/6\pi$。当有机物添加在水泥浆体内时，会影响 Hamaker 常数，A_{sh}，因此可能使膜流不稳定或完全抑制膜流，因而使水泥浆体内局部缺水，影响水化进行，造成成品强度降低，影响品质。

关键词：有机废弃物；离分压；液膜
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