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**STRESSES AND STRAINS IN THE HARDENED CEMENT PASTE -
WATER SYSTEM**

by J.J. Beaudoin and R.F. Feldman

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RÉSUMÉ

La théorie des variations de longueur proposée par Flood et Heyding pour les solides microporeux est appliquée à la pâte de ciment, en considérant l'effet de porosité et de compressibilité sur la phase solide. La théorie sert également à évaluer la dépendance du module d'élasticité vis-à-vis de l'humidité, et est en général en accord avec l'expérience. On arrive à mieux expliquer le changement microstructural et son effet sur la variation de longueur au moyen d'estimations d'un facteur de structure κ . Les valeurs de κ sont à peu près constantes pour des taux d'humidité allant jusqu'à 56%. Toutefois des changements de structure importants se produisent à des taux d'humidité plus élevés.

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STRESSES AND STRAINS IN THE HARDENED CEMENT PASTE - WATER SYSTEM

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ABSTRACT

The length change theory proposed by Flood and Heyding for microporous solids is applied to cement paste in considering the effect of porosity and compressibility on the solid phase. The theory is also used to estimate the dependence of modulus of elasticity on humidity and is in general agreement with experiment. Some insight into microstructural change and its effect on length change is provided by estimates of a structure factor, κ . For humidities up to 56%, values of κ are approximately constant, but major changes in structure occur at higher humidities.

Introduction

Hardened portland cement paste (HCP) - a term used to describe the rigid porous body, excluding any free or adsorbed water, formed when cement hydrates - is a multicomponent, microporous, moisture-sensitive material. Numerous studies have been conducted on the mechanical properties of HCP and the model proposed by Feldman and his co-workers (1,2) has been useful in explaining results, e.g., the dependence of modulus of elasticity (E) on humidity where increases in E with humidity were attributed to the stiffening effect of interlayer water.

Thermodynamic treatment of HCP length-change data is complicated because of irreversible processes that occur when the system is wetted. In addition to surface adsorption these processes include intercalation of water between sheets, swelling, agglomeration effects and possibly the effects of shear stresses in the solid material. Flood and Heyding used a thermodynamic approach (subsequently referred to as the F-H approach) to determine theoretically the length change isotherms for water vapor on carbon and for water vapor on porous glass (3). They derived a simple expression for length change as a function of porosity, compressibility of the solid, microstructure of the adsorbent, and amount of H_2O adsorbed. Their theory provides a possible means of assessing both irreversible effects on length changes of HCP and the assumption that these effects are due to exit and entry of interlayer water.

This paper describes the application of the F-H thermodynamic approach to the cement paste-water system and assesses the results based on the model for HCP developed by Feldman and his co-workers.

Length Change Isotherms

F-H Approach

Briefly, the F-H theory assumes that assemblies of volumes of pure adsorbable gas and assemblies of volumes of pure adsorbent can exist separately, in equilibrium with externally applied forces, in states thermodynamically identical to those in the adsorbent-adsorbate system. The conditions of reversibility and equilibrium lead to the following expression for the pressure of the pure adsorbate, p_a , in the pore volume V_a

$$p_a = \int_0^{p_1} \frac{\rho_a}{\rho_1} dp_1 = \left(\frac{\rho_a}{\rho_1} \right) \cdot p_1 = \alpha p_1$$

where ρ_a is the mean density of the substance in V_a , and p_1 and ρ_1 are the gas pressure and density of the gas surrounding the sample. The term, α , is the mean value of ρ_a/ρ_1 averaged over the pressure interval dp_1 .

If $\phi = V_a/V_s$, where V_s is the non-porous solid volume, it may be shown that $p_s = (1 + \phi - \alpha\phi)p_1$, which is the pressure on the solid adsorbent in equilibrium with the surrounding gas at pressure p_1 .

If the pressure on the solid adsorbent is uniform, the length change isotherm can be obtained from the equation

$$\frac{\delta l}{l} = \frac{1}{3} \beta (1 + \phi - \phi\alpha) dp_1 \quad (1)$$

where β is the compressibility of the porous body.

Where solid pressures are not constant, κ , a small numerical factor dependent upon the structure of the porous solid, is introduced into eq. (1), i.e., the term in brackets becomes $(1 + \phi\kappa - \phi\kappa\alpha)$. κ , the ratio of the linear average pressures to volumetric average pressures, is generally independent of the nature of the adsorbate, but is a characteristic of the structure of the adsorbent. Flood and Heyding determined values of κ for various ideal models of pore structure, e.g., $\kappa = 1.0$ for a system of continuous non-intersecting straight capillaries, and $\kappa = 5.6$ for a system of continuous intersecting straight capillaries (3). If the shape of the average pore is not statistically independent of the surface free energy of the solid enclosing the average micropore, then κ will become a function of p_1 . For large adsorptions $\alpha \gg 1$ and

$$\frac{\delta l}{l} = \frac{1}{3} \beta \phi \kappa dp_a \quad (2)$$

i.e., $\frac{\delta l}{l}$ becomes proportional to $\int_0^{p_1} \frac{\rho_a}{\rho_1} dp_1$

Porous Glass

The weight change isotherm for porous glass in the adsorption region is reversible and glass is considered to be relatively stable. Using the length

change data of Amberg and McIntosh (4), Flood and Heyding (3) were able to obtain good agreement between the calculated isotherm and experimental data, suggesting that eq. (2) is applicable to systems in which wetting and drying involve mainly reversible processes.

Hardened Cement Paste (HCP)

HCP-water isotherm. A brief comment on the HCP-water isotherm and on the assumptions made in using isotherm data to apply the F-H procedure follows. Along the adsorption branch of the HCP-water isotherm several reversible and irreversible effects occur. If relative humidity is reduced from a particular value on the adsorption curve, a scanning curve is obtained, for example, curves 1, 2, 3, Fig. 1. It has been argued that (to a first approximation) mainly reversible processes occur over a large part of the scanning curve.

A "reversible" isotherm can be constructed by appropriate summation of reversible portions of the scanning curves. Details of this procedure have been published (5). It is assumed that irreversible effects can thus be separated from reversible ones. In addition, it is recognized that the reversible adsorption processes operative along each scanning curve are acting on a material that has changed since the previous scanning curve, i.e., the material is different for each of curves 1, 2, 3, Fig. 1. Thus, in transferring from curves 1 to 2 to 3, irreversible processes are operative. Application of the F-H procedure to the reversible isotherm assumes, however, that the irreversible changes in the solid material (interlayer penetration, etc.) do not affect the nature of the reversible adsorption processes occurring on the surface of the layers, and that surface energy changes are acting on a different material with different properties when positions are changed on the isotherm. It is assumed, then, that a step-by-step application of the F-H procedure along the reversible adsorption path is valid, even where intercalation of the layered silicate hydrate occurs; i.e., since the scanning isotherm is reversible, the F-H procedure is applicable. If scanning isotherms are irreversible, then changes have occurred in the porous system and the F-H procedure cannot be applied. Thus, the procedure may not be applicable when major changes in pore structure occur.

Figure 1

Schematic of primary adsorption curve with scanning curves

Application of F-H procedure to HCP. To apply eq. (2) to the HCP system it

is necessary to evaluate the integral $\int_0^{P_1} \frac{\rho_a}{\rho_1} dp$. Consider the following:

For a cement paste with $w/c = 0.50$, porosity is approximately 26%. Therefore, $\phi = V_a/V_s = 0.351$. Assuming density of the non-porous solid = 2.2 g/cc, the mass/cc of the porous sample is $2.20 \times 0.74 = 1.63$ g/cc or 1 g of porous sample = $1/1.63 = 0.610$ cc.

Thus V_a/g of sample = $0.260 \times 0.610 = 0.160$ cc

$$\text{and } \rho_a = \frac{\Delta W/W}{V_a} = 6.26 \frac{\Delta W}{W} \quad (3)$$

where $\Delta W/W$ = weight change per unit weight of sample. The mass of the gas in the void volume, V_a , is negligible in relation to the mass of the adsorbed phase. The density of the gas (water vapor) ρ_1 is 18.34×10^{-6} g/cc at 21°C and 100% RH.

Data from weight and length change isotherms are taken from Feldman (5). Using scanning loops, these isotherms were separated into irreversible and reversible isotherms. The reversible isotherm is used in the following calculations:

$$\text{A plot of } \frac{\rho_a}{\rho_1} \text{ versus } p_1 \text{ is given in Fig. 2; and the integral } \int_0^{p_1} \frac{\rho_a}{\rho_1} dp_1 \text{ is}$$

evaluated graphically by determining the area under the curve. This provides a measure of $p_a = \alpha p_1$ = pressure of adsorbate. A curve of αp_1 versus p_1 (not presented) was constructed to assist in the calculations. Thus, eq. (2) can be fitted to the experimental length change data by assuming an appropriate value for $\beta\kappa$.

Figure 3 is a plot of length change versus vapor pressure, giving curves for eq. (2) and experimental values. A single average value of $\beta\kappa = 1.76 \times 10^{-4} \text{ MPa}^{-1}$ was chosen to give a close fit between the experimental length change data and eq. (2).

Although this value of $\beta\kappa$ gives an approximation of the experimental data, $\beta\kappa$ varies with p and a more exact fit can be obtained by calculating $\beta\kappa$ at each data point. Values of $\beta\kappa$ at different humidities along the adsorption curve were calculated from eq. (2) using experimental values of $\delta l/l$. These values are given in Table 1.

Values of $\beta\kappa$ were also calculated for an HCP-water isotherm scanning curve over the range 56 to 11% RH. $\beta\kappa$ was approximately constant over that portion of the scanning curve (56 - 40% RH) used to construct the reversible isotherm. This supports the assumption that material properties are constant on the segment of each scanning curve used to construct the reversible isotherm.

Figure 2

Ratio of adsorbate density to gas density versus gas pressure

TABLE 1

Calculation of compressibility and modulus of elasticity for HCP
from adsorption data

RH %	$\frac{\delta l}{l} \times 100$	αp_1 MPa	$\beta \kappa$ $\times 10^4 \text{ MPa}^{-1}$	β^* $\times 10^4 \text{ MPa}^{-1}$	E $\times 10^{-5} \text{ MPa}$
10.3	0.016	6.67	2.06	1.08	0.167
12.7	0.018	7.88	1.96	1.03	0.176
15.4	0.020	9.18	1.85	0.97	0.186
18.5	0.022	10.74	1.76	0.92	0.196
24.1	0.026	12.99	1.70	0.89	0.202
27.8	0.030	14.28	1.79	0.94	0.192
31.1	0.032	15.84	1.73	0.91	0.199
34.0	0.033	16.93	1.68	0.88	0.206
37.4	0.035	18.09	1.65	0.86	0.209
42.7	0.037	20.13	1.56	0.82	0.221
45.3	0.039	20.67	1.60	0.84	0.216
48.5	0.040	21.90	1.56	0.82	0.221
51.5	0.041	22.71	1.52	0.80	0.226
53.6	0.042	23.46	1.52	0.80	0.226
56.6	0.043	24.48	1.49	0.78	0.230
62.2	0.047	26.04	1.57	0.82	0.219
66.9	0.052	27.54	1.60	0.84	0.216
72.5	0.057	29.85	1.63	0.85	0.245
88.0	0.080	36.72	1.85	0.97	0.265

* Calculation made using $\kappa = 1.91$

Values of β are calculated from $\beta \kappa$ values, assuming $\kappa = 1.91$. Choice of this κ value gives an initial value of β comparable to β calculated from the relation $\beta = \frac{3}{E}(1 - 2\nu)$, where ν is Poissons ratio of 0.20, as well as β determined by other methods (6). (Calculations of $\beta \kappa$ were also made using length change data for the porous glass-water system, but these are not tabulated.)

Figure 3

"Reversible" length change isotherm for portland cement paste, w/c = 0.50, experimental and theoretical

Figure 4

Dependence of $\beta\kappa$ on relative humidity for cement paste and porous glass

Figure 5

Modulus of elasticity versus relative humidity for cement paste, $w/c = 0.50$

Figure 4 is a plot of $\beta\kappa$ for both HCP and porous glass. $\beta\kappa$ for HCP is dependent on RH, whereas for porous glass it is independent of RH. It would be expected that porous glass would be stable, i.e., not undergo a material change as RH increases. Thus, the relatively constant value of $\beta\kappa$ determined by the F-H procedure is appropriate. The dependence of $\beta\kappa$ on RH is expected for HCP since the hydrated calcium silicates are unstable, i.e., C-S-H solids change as RH increases.

Figure 5 is a plot of E versus RH for HCP. One of the curves is a plot of the calculated E (determined by F-H procedure using $\kappa = 1.91$).

Figure 6

- (a) Structure factor κ versus relative humidity
- (b) Density of HCP exposed to various relative humidities and returned to 11% RH

Another curve is a plot of experimental values of E (7). On adsorption up to 56% RH, the two curves have a maximum difference in E (at any RH) of only 0.01×10^5 MPa, and E increases with RH. At higher humidities use of the structure factor $\kappa = 1.91$ gives decreasing values of E to 68% RH, followed by another increase in E as RH increases further. By adjusting κ at each humidity above 56% RH, however, (and determining a new value of β from $\beta\kappa$), the calculated value of E increases monotonically as the dashed curve (Fig. 5) is extended from 56 to 88% RH. The extended curve also gives values of E close to those determined by experiment.

Figure 6a is a plot of κ versus RH for HCP and porous glass. κ is constant for HCP up to 56% RH and is humidity-dependent thereafter. κ for porous glass is constant over the whole humidity range. Several irreversible changes take place in HCP at higher humidities. It is known, for example, that rewetting a dried sample above 50% RH significantly increases creep and drying shrinkage. It is in the high humidity range that the microstructure, and hence pore shape and/or contiguity, may be altered; for example, in Fig. 6b it is shown that absolute density (measured on samples of HCP exposed to various RH's and dried to 11% RH) is constant to about 42% RH and decreases thereafter. Experiments have shown that after wetting HCP to 42% RH, He gas is able to penetrate fully spaces previously vacated by water (8). It is noteworthy that each point on the curve in Fig. 6b represents the density of HCP that has been conditioned along each different scanning curve of the isotherm, since the material on each is different. The change in density at higher humidities suggests that microstructural changes, in addition to those occurring at lower humidities, occur (changes at lower humidities are attributed mainly to interlayer penetration). These changes appear to be reflected in the changing value of κ at higher humidities.

Concluding Remarks

The Flood-Heyding length change theory for microporous adsorbents can be used to estimate the reversible length change isotherm for hardened cement paste and gives credence to the model of cement paste developed by Feldman and his co-workers. The theory is also in agreement with the observed humidity dependence of modulus of elasticity for the cement paste system. Although many of the irreversible microstructural changes resulting from wetting and drying of HCP are indeterminate, an appreciation of these effects can be obtained from estimates of the structure factor κ . Significant changes in the value of κ at humidities greater than 56% RH are concurrent with changes in the solid density of HCP.

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MECHANISM AND KINETICS OF HYDRATION
OF C_3A AND C_4AF , EXTRACTED FROM CEMENT.

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ABSTRACT The early hydration of $C_3A + C_4AF$ extracted from cement and mixes with quartz, gypsum and pulverised fuel ash (PFA) has been studied by x-ray diffraction. The investigation has shown that the hydration of both aluminates is essentially a mechanism which obeys a modified diffusion equation. The values obtained for the reaction rates show that the hydration of C_3A takes place at seven times the rate of hydration of C_4AF . PFA was shown to be a very effective retarder. A mechanism to explain retardation is also proposed.

Introduction

Addition of gypsum during the grinding process for the production of cement is the industrial accepted method for controlling flash setting which arises from the rapid hydration of cement. It is accepted that the main constituent of cement responsible for flash setting is C_3A , and that gypsum retards the hydration of this phase.

What is still a matter of controversy is the manner in which gypsum retards hydration; also there is very little information regarding the mechanism and kinetics of hydration of C_3A and C_4AF . The theories proposed to explain retardation of hydration can be broadly divided in two groups:

(a) The protective layer theory: researchers supporting this theory disagree mainly on the composition of the protective layer. Earlier work in the 1950's (1) advanced the idea that the protective layer consisted of a thin layer of ettringite formed around the aluminate particles. Later work (2,3,4) including the investigations of Collepardi et al (5) have supported this theory. Other investigators, notably Gupta, Chatterji and Jeffery (6) came to the conclusion that the impervious layer consists of C_4AH_n which is formed on the aluminate grains in the presence of CH and CSH_2 . They indicated that the thin C_4AH_n layer is overlaid with ettringite; when the ettringite cover becomes sufficiently thick, the mobility of the sulphate ion is restricted and thus the tetra-aluminate will be converted to monosulphate instead of ettringite.

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