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Effect of Water and Other Dielectrics on Subcritical Crack Growth in Portland Cement Paste

by J.J. Beaudoin

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RÉSUMÉ

En étudiant l'effet de l'eau et d'une série d'alcools aliphatiques sur la croissance subcritique des fissures dans la pâte de ciment, on a obtenu, au moyen d'une technique double torsion, des courbes vitesse de fissuration (à l'échelle logarithmique)/facteur intensité des contraintes. On a constaté que la position relative des courbes dépendait de la constante diélectrique des médiums d'essai. La résistance en flexion de la pâte de ciment saturée dans des liquides organiques est également fonction de la constante diélectrique. On a cru observer un mécanisme de corrosion due aux contraintes, les liaisons Si-O de la pâte de ciment étant attaquées chimiquement.

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EFFECT OF WATER AND OTHER DIELECTRICS ON SUBCRITICAL
CRACK GROWTH IN PORTLAND CEMENT PASTE

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ABSTRACT

In studying the effect of water and a series of aliphatic alcohols on subcritical crack growth in cement paste, log crack velocity-stress intensity factor curves were obtained by means of a double-torsion technique. The relative position of the curves was found to be dependent on the dielectric constant of the test media. Flexural strength of cement paste saturated in organic fluids is also dependent on the dielectric constant. Stress corrosion processes involving chemical attack of Si-O bonds in cement paste appear to be operative.

Introduction

Fracture mechanics studies of the portland cement paste system have shown that subcritical crack growth is dependent on relative humidity and drying history (1). Evidence for the existence of a stress corrosion mechanism involving hydroxyl ion attack of the silicate network in cement paste has also been found (2).

Porous silica glass has been used to model the behaviour of portland cement paste in durability studies (3). In the presence of water and organic liquids, rupture of Si-O bonds in silica glass systems was modelled as a fission reaction in which Si-O bonds strained by crack-tip stresses are severed by the chemical environment (4). Dependence of crack growth on the dielectric constant of the test media was observed. The applied stress necessary for a given crack growth rate decreased as the dielectric constant increased.

Understanding of the factors affecting crack growth in cement paste can provide a basis for understanding cracking phenomena in concrete. The factors that control the service life of concrete can be determined by crack growth studies. Further elucidation of the processes influencing crack growth have been obtained from tests performed on silica glass in an alcohol media (4). It is therefore of more than passing interest to determine the effect of water and other dielectrics, specifically a series of aliphatic alcohols, on crack growth in portland cement paste.

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Experimental

Materials

Portland cement: Composition was as follows: $\text{SiO}_2 = 20.78\%$; $\text{Al}_2\text{O}_3 = 6.20\%$; $\text{Fe}_2\text{O}_3 = 2.23\%$; $\text{CaO} = 64.83\%$; $\text{MgO} = 1.84\%$; $\text{SO}_3 = 3.17\%$; $\text{Na}_2\text{O} = 0.05\%$; $\text{K}_2\text{O} = 0.40\%$. Blaine fineness was $300 \text{ m}^2/\text{kg}$, and calculated Bogue compound composition was $\text{C}_4\text{AF} = 6.7\%$; $\text{C}_3\text{A} = 12.7\%$; $\text{C}_3\text{S} = 51.4\%$; $\text{C}_2\text{S} = 20.3\%$ and $\text{CaSO}_4 = 5.4\%$.

Alcohols: Reagent grade methyl, ethyl, butyl, amyl, hexyl, octyl and decyl alcohol were used in the experimental work.

Mixes and Specimen Preparation

Cement paste mixes were made at water/cement ratios of 0.30, 0.35 and 0.40; double torsion (DT) specimens $38 \times 76 \times 1 \text{ mm}$ thick were fabricated (1) with a $1.5 \times 0.5\text{-mm}$ deep centrally-located guide groove running along the length. Starter cracks were notched in each specimen with a thin diamond blade (0.36 mm thick) to produce the final test specimen (Figure 1). Three specimens for each test were moist cured for approximately 12 months before testing.

FIG. 1
Double-torsion specimen geometry

Another set of cement paste mixes was made at water/cement ratios of 0.25, 0.35 and 0.45 for use in determining flexural strength. Beams were made as follows: mixes were cast in moulds $50 \times 80 \times 6.5 \text{ mm}$; specimens were demoulded after 24 h and sliced at 1-mm intervals to produce mini-beams $50 \times 6.5 \times 1 \text{ mm}$ thick; these were moist cured in lime water for 30 days before testing.

Fracture Mechanics Testing

An environmental chamber with a rectangular, thermostatically controlled perspex bath within it was mounted on the cross-head of an Instron testing machine. Tests in lime-saturated water or alcohol were conducted in the bath, which was maintained at $21^\circ\text{C} \pm 0.5^\circ\text{C}$. For those in alcohol media, the air in the chamber was kept dry by circulating it over magnesium

perchlorate. In addition, molecular sieves were placed in the perspex bath as a further precaution against any uptake of moisture by the alcohol.

The DT specimens were placed on a small reaction frame located within the bath. The test procedure has been described in detail (1). A load relaxation technique was used to determine the log crack velocity-stress intensity factor ($\log V-K_I$) curves for portland cement paste (5). An initial cross-head speed of $8.35 \times 10^{-5} \text{ mm} \cdot \text{s}^{-1}$ was used. Crack velocity was determined from the relaxation curves and the following relation:

$$V = da/dt = (P_i/P^2)(a_i + A/B)dP/dt \quad (1)$$

Subscript i refers to the initial crack length, i.e., P_i is the load at the initial crack length, a_i . A and B are the intercept and slope of the compliance-crack length curve. Compliance-crack length curves were obtained for each w/c ratio in each liquid. They are numerous and not presented because the ratio A/B determined from them is usually $\ll a_i$ and can be neglected. Values of the derivative dP/dt are obtained from the load-relaxation curve.

An expression given by Williams and Evans (5) was used to compute K_I :

$$K_I = P W_m (3(1+\nu)/W t_n^3) \quad (2)$$

where P is load, ν is Poisson's ratio, and the other terms are dimensions depicted in Figure 1 that are dependent on the geometry of the test piece and loading configuration.

Flexural Strength Testing

Flexural strength testing was performed on the mini-beams by means of a miniature loading device. Specimens were tested in three-point bending, and load was applied at mid-span by controlling the flow of water from a pipette into a vessel resting on the loading pan of the test apparatus. Loading rate was $4.35 \times 10^{-4} \text{ kg} \cdot \text{s}^{-1}$. Flexural strengths were determined using simple beam theory. The mini-beams were tested dry and saturated in the test fluids.

Results and Discussion

Subcritical Crack Growth

Log crack velocity-stress intensity factor ($\log V-K_I$) curves for portland cement paste saturated in water and several alcohols are presented in Figure 2(a-c). All curves have an initial linear region. Some exhibit a subsequent non-linear region, e.g., curves for amyl alcohol (w/c = 0.30 and 0.35); hexanol, methanol and octanol (w/c = 0.35); methanol and decanol (w/c = 0.40). Curves for amyl alcohol (w/c = 0.30 and 0.35) exhibit a second linear region.

Three regions in the $\log V-K_I$ curves for cement paste have been observed (1). Their significance for soda-lime glass has been discussed in detail by Wiederhorn et al. (4). The first linear region was described as reaction-rate dependent. In the subsequent non-linear region crack velocity is controlled by the rate of transport of the fluid to the crack tip. The second linear region has been described as environment (usually gaseous) independent, although experiments with glass in alcohol media indicate that crack velocity here is dependent on the dielectric constant of the test fluid (4).

Crack velocity data for glass tested in alcohol indicate that the position of the first linear region of the $\log V-K_I$ curve with respect to K_I is dependent on the dielectric constant of the medium (4,6). Wiederhorn et al. employed elementary solvation theory to explain this dependence and

SUBCRITICAL CRACK GROWTH, ALCOHOLS, WATER, Si-O BONDS

FIG. 2

Crack propagation of cement paste in water and various alcohols: M(methanol); E(ethanol); B(butanol); A(amyalcohol); H(hexanol); O(octanol); D(decanol)

assumed that the oxygen and silicon atoms of the Si-O pair become fully charged as a result of a fission process. The free energy of formation of each charged atom was shown to be inversely proportional to the sum of the dielectric constants of the liquid and glass.

Crack velocity data for cement paste also indicate that there is a dependence of crack velocity on the dielectric constant of the test fluid. For example, in Figure 2(b) (with the exception of the curves for hexanol and butanol) the $\log V-K_I$ curves for $w/c = 0.35$ specimens are displaced with respect to K_I in order of decreasing dielectric constant of the test fluid. The position of the curves for hexanol and butanol ($w/c = 0.30$ and 0.40) with respect to K_I are out of the sequence that would be expected if crack velocity were dependent on dielectric constant. The reason is not clear.

The median value of stress intensity factor, $K_{I,*}$ for each $\log V-K_I$ curve is plotted against the dielectric constant of the test fluid in Figure 3. There is a non-linear dependence of $K_{I,*}$ on the dielectric constant for all three water/cement ratio preparations. (Data points for $w/c = 0.35$ specimens tested in hexanol and butanol are not included.) Changes in the value of $K_{I,*}$ as dielectric constant increases are much smaller for the $w/c = 0.40$ specimens. These have the highest porosity of the specimens tested and it is suggested that porosity may be the controlling factor determining $K_{I,*}$ for higher w/c ratio preparations. The curve for $w/c = 0.30$ specimens is higher than the curve for $w/c = 0.35$ specimens. Lower w/c ratio pastes generally have higher flexural strength and this property may be the determining factor for the relative values of $K_{I,*}$ (for these preparations).

*As the $\log V-K_I$ curves are steep for cement paste specimens, it is convenient to discuss the relative displacement of the curves along the K_I axis in terms of the median value of K_I for each curve.

**Specimens are dried by heating under vacuum at 110°C and tested at a humidity determined by the vapor pressure of magnesium perchlorate.

FIG. 3
Median stress-intensity factor versus dielectric constant of the test fluid (M etc. as above)

FIG. 4
Crack growth curves for cement paste and soda-lime glass tested in octanol, decanol, and dry condition. O(octanol); D(decanol)

The logV-K_I curves for octanol and decanol (w/c = 0.30 and 0.35) have significantly higher K_I values than those of specimens tested dry** (Fig. 4). Results obtained by Wiederhorn et al. (4) show that the logV-K_I curve for soda-lime silica glass tested in decanol also shifts to higher values of K_I

than that for glass tested in a dry N_2 atmosphere. No explanation was given. One possibility is that octanol and decanol interact with the matrix material in both cement paste and glass to change the radius of curvature of the crack tip. No direct evidence (for example, evidence obtained by microscopic examination of crack tips) of a crack-blunting mechanism was obtained. For $w/c = 0.40$ specimens, the $\log V-K_I$ curve for the dry specimen has the highest value of K_{Ic} . It is suggested that any modification of the crack tip (e.g., by decanol) responsible for increasing K_{Ic} is secondary to the effect of higher total porosity at $w/c = 0.40$.

Flexural Strength Testing

Flexural strength determinations were carried out on specimens saturated in water and in the alcohols used in the crack growth studies. The ratio of saturated strength to dry strength is plotted against the dielectric constant of the test fluid in Figure 5. The ratio decreases non-linearly with increase in dielectric constant. The dependence of the ratio on dielectric constant is stronger if the data points for decanol ($w/c = 0.35$) and butanol ($w/c = 0.45$) are considered as outliers.

It is suggested that the electrostatic model (4), which predicts a dependence of Si-O bond fission energy on dielectric constant of the test fluid, offers a possible explanation for the effect of the alcohols on flexural strength of portland cement paste.

Compressive strength results for portland cement paste saturated in methanol, ethanol, propanol and butanol were obtained by Robertson and Mills (7,8), who also found a weakening effect when originally dry specimens were tested in water and alcohols.

Conclusions

1. Subcritical crack growth in cement paste is dependent on the applied stress-intensity factor and the dielectric constant of the media in which tests are performed.

FIG. 5

Ratio of saturated flexural strength to dry strength versus dielectric constant of test fluid. (Legend as above)

2. In alcohol medias processes affecting Si-O bonds in the hydrated silicate structures of portland cement paste may influence subcritical crack growth.
3. Flexural strength of cement paste is dependent on the dielectric constant of the test fluid. Chemical attack of Si-O bond may weaken cement paste.

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