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# Mechanisms of Subcritical Crack Growth in Portland Cement Paste

by J.J. Beaudoin

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RÉSUMÉ

Les données concernant la propagation des fissures dans les échantillons de pâte de ciment Portland obtenues dans diverses conditions d'essai indiquent que les facteurs intervenant dans ce processus sont : l'humidité, la température, la rupture des ménisques, le vieillissement, les variations d'énergie de surface, la concentration d'ions hydroxyles dans l'eau interstitielle et le potentiel chimique des solutions interstitielles. L'auteur étudie la propagation des fissures causées par l'action possible de mécanismes d'attaque des liaisons Si-O à l'extrémité de ces fissures. L'étude démontre l'influence des alcools aliphatiques sur la modification de la structure C-S-H et conclut à l'influence de la corrosion sous contraintes sur la propagation des fissures dans la pâte de ciment.

*Fracture Toughness and Fracture Energy of Concrete*, edited by F. H. Wittmann
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# MECHANISMS OF SUBCRITICAL CRACK GROWTH IN PORTLAND CEMENT PASTE

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## ABSTRACT

Crack growth data for portland cement paste specimens obtained under a variety of environmental conditions indicate that influential factors include humidity, temperature, meniscus rupture events, aging, surface energy changes, hydroxyl ion concentration of pore water, and chemical potential of pore solutions. Possible mechanisms of crack growth involving attack of Si-O bonds at crack tips are discussed. Evidence is presented of modification of C-S-H structure by aliphatic alcohols and arguments are advanced for the existence of stress corrosion processes during crack growth in cement paste.

## INTRODUCTION

In recent years research on fracture mechanics of concrete has increased significantly, and several international symposia and a book based on the efforts of RILEM Technical Committee (50-FMC) have been published (refs. 1,2). The majority of the papers deal with fracture of concrete. Only a few deal with the cement paste binder. As it plays an important role in cracking of concrete (refs. 3,4), an understanding of the factors that influence crack initiation and propagation in paste could provide insight into concrete behaviour.

It is recognized that porosity, pore structure, calcium hydroxide and other microstructural features influence crack growth (refs. 5,6). Results of studies designed to assess the influence of environmental factors on crack growth are discussed with respect to possible subcritical crack growth mechanisms, including meniscus rupture, aging, and stress corrosion. Most of the discussion, however is confined to the role of calcium silicate hydrate (C-S-H) in the fracture process.

## EXPERIMENTAL

### Materials

Portland cement. Composition was as follows: $SiO_2$ = 20.78%; $Al_2O_3$ = 6.20%; $Fe_2O_3$ = 2.23%; CaO = 64.83%; MgO = 1.84%; $SO_3$ = 3.17%; $Na_2O$ = 0.05%; $K_2O$ = 0.40%. Blaine fineness was 300 $m^2/kg$, and calculated Bogue composition was $C_4AF$ = 6.7%; $C_3A$ = 12.7%; $C_3S$ = 51.4%; $C_2S$ = 20.3% and $CaSO_4$ = 5.4%.

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

C-S-H. The material was provided by Lafarge Coppée Recherche, France. It had a surface area of 56.6 $m^2/g$ and density of 2.05 g/mL.

## Mixes and specimen preparation

Cement paste mixes were made at water/cement ratios of 0.36 and 0.41; double torsion specimens 38 × 76 × 1 mm thick were fabricated with a 1.5 × 0.5 mm deep, centrally-located guide groove running along the length (ref. 7). Starter cracks in each specimen were notched with a thin diamond blade (0.36 mm thick) to produce the final test specimen.

## Fracture mechanics testing

An environmental chamber containing a rectangular, thermostatically-controlled perspex bath was mounted on the cross-head of an Instron testing machine. Additional details are available (ref. 8).

The double-torsion specimens were placed on a small reaction frame within the bath, and a load relaxation technique was used to determine the log crack-velocity vs stress-intensity factor curves for portland cement paste (ref. 9).

Specimens tested in alochol media were dried in vacuum at 110°C for 3 h prior to saturation in alcohol (they were stored in the alcohol for 48 h before testing).

## X-ray diffraction

X-ray powder diffraction data for selected samples were obtained with a Guinier-Hägg Powder Camera, Model XDC-700.

## RESULTS AND DISCUSSION

Log crack-velocity vs stress-intensity factor (log V-$K_I$) curves obtained under a variety of test conditions are presented in Fig. 1. Curves obtained for experiments designed to assess the effect of humdity, temperature (in lime-saturated water), and alcohol liquids on crack growth are given. Additional results have already been presented elsewhere (refs. 7,8,10). Each of these test conditions will be used in discussing factors that affect crack growth.

## Meniscus rupture events

It is apparent from the curves in Fig. 1(a) that the equilibrium moisture content at a particular humidity affects the applied stress required for a given crack velocity. For each curve the median value of the stress intensity

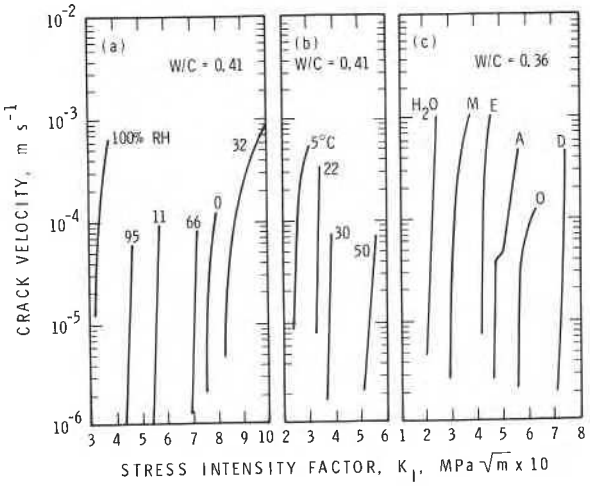


Fig. 1. Crack-velocity vs stress-intensity factor curves for portland cement paste tested: (a) at different humidities; (b) in lime-saturated water at different temperatures; (c) in aliphatic alcohols (M-methanol; E-ethanol; amyl alcohol; O-octanol; D-decanol)

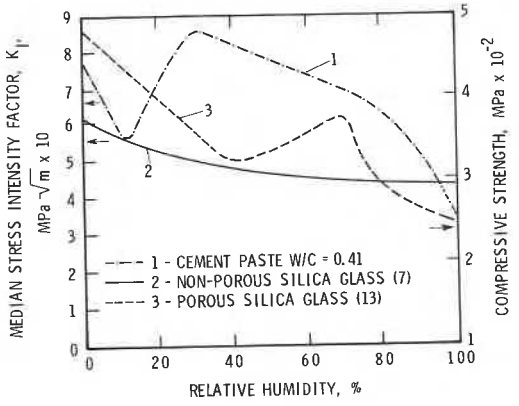


Fig. 2. Stress-intensity factor vs relative humidity for cement paste and non-porous glass; compressive strength vs relative humidity for porous glass

factor ($K_I$)* is plotted against relative humidity in Fig. 2. A similar curve is plotted for non-porous glass. In addition, compressive strength of porous glass versus relative humidity is shown. It has already been observed that for some

*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.

systems compressive strength and fracture energy terms have a similar dependence on material characteristics such as porosity (ref. 11). The curves for cement paste and porous glass have a maxima at about 30% and 70% RH, respectively. Adsorption isotherms for both systems exhibit primary hysteresis that terminates as humidities reach these values (refs. 12,13). Hysteresis has been associated with the formation of concave menisci on drying. It has been postulated that formation of concave menisci leads to contraction and strengthening of the porous solid (ref. 14). When the menisci rupture there is a weakening effect on the solid. If there were no effect of menisci forces on strength and stress intensity factor values these terms would be expected to decrease monotonically to the value reached at complete saturation, as is the case for non-porous glass.

Aging

In the present context aging of cement paste refers to time-dependent microstructural changes that occur on drying. Increased layering, or consolidation of C-S-H sheets that occurs on drying (ref. 15), is generally accompanied by physical changes such as decrease in nitrogen surface area. Major changes take place at low humidities between 11 and 0% RH, although the increase in median stress intensity factor may be partly due to aging phenomena. Strength increases in cement paste dried from 11 to 0% RH have been reported (ref. 16).

Surface energy changes

For adsorbents such as porous glass, strength reduction in the region of reversible adsorption has been attributed to a decrease in surface-free energy. Weakening effects due to stress corrosion have generally not been considered. Some authors have attributed a decrease in strength of cement paste on wetting to a decrease in surface-free energy, ignoring the large secondary hysteresis in the water adsorption isotherm of cement paste (ref. 12). Such free-energy calculations are incorrect and cast doubt on the validity of any conclusions based on them. The decrease in strength of porous glass in the adsorption region (see Fig. 2, 0 to 40% RH) is probably due to a reduction of surface-free energy that leads to a weakening of the solid. Other processes such as stress corrosion at crack tips may however be operative in cement paste. For example, the Bangham expression relating length change to free-energy change should be independent of the adsorbate. Calculations using water* and methanol adsorption isotherms obtained for cement paste (ref. 12) indicate that the length change,

*The water isotherm is separated into reversible and irreversible components. The reversible isotherm (ref. 11) is used for calculations.

free-energy relation is not independent of the adsorbate for this system (Fig. 3). The curve for methanol adsorption has a slope approximately three times that for water adsorption, implying that processes other than adsorption take place. Additional evidence of this possibility will be presented later.

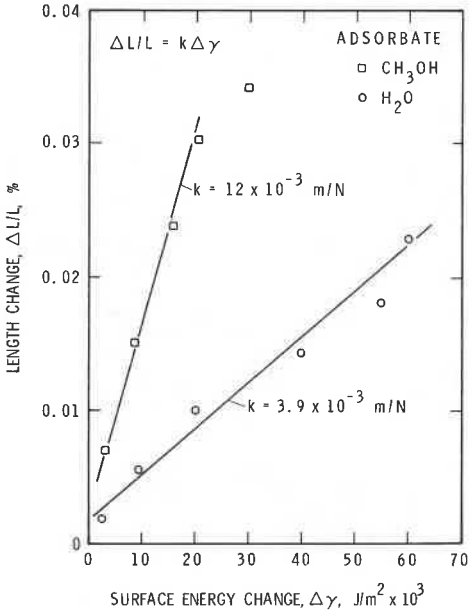


Fig. 3. Length change vs surface energy change curves determined from adsorption data of water and methanol on portland cement paste

Role of hydroxyl ion

An autocatalytic dissolution mechanism was proposed some time ago by Charles (ref. 17) to account for water corrosion in soda-lime glass. It includes the following two reaction steps: $-(\overset{'}{Si}-O-\overset{'}{Si})- + OH^- + -(\overset{'}{Si}-OH) + (\overset{'}{Si}O^-)$ and $-(\overset{'}{Si}O^-) + H_2O + (HO-\overset{'}{Si})- + OH^-$. Crack growth studies of cement paste indicate that the hydroxyl ion may play a role in fracture of pastes. Log V-$K_I$ curves for cement paste (Fig. 1b) and $C_3S$ paste (ref. 8) were obtained from tests performed in lime-saturated water at temperatures in the range of 5 to 50°C. The displacement of the curves with respect to $K_I$ is in a non-Arrhenius sense, i.e., as temperature decreases the applied stress required to produce a given crack velocity also decreases. Observed non-Arrhenius behaviour corresponds to an increase in hydroxyl ion concentration with decrease in temperature. How the hydroxyl ion interacts with C-S-H is not certain. A widely-accepted microstructural model for C-S-H (after Feldman (refs. 12,18)) is illustrated schematically in Fig. 4. It represents C-S-H as a layered

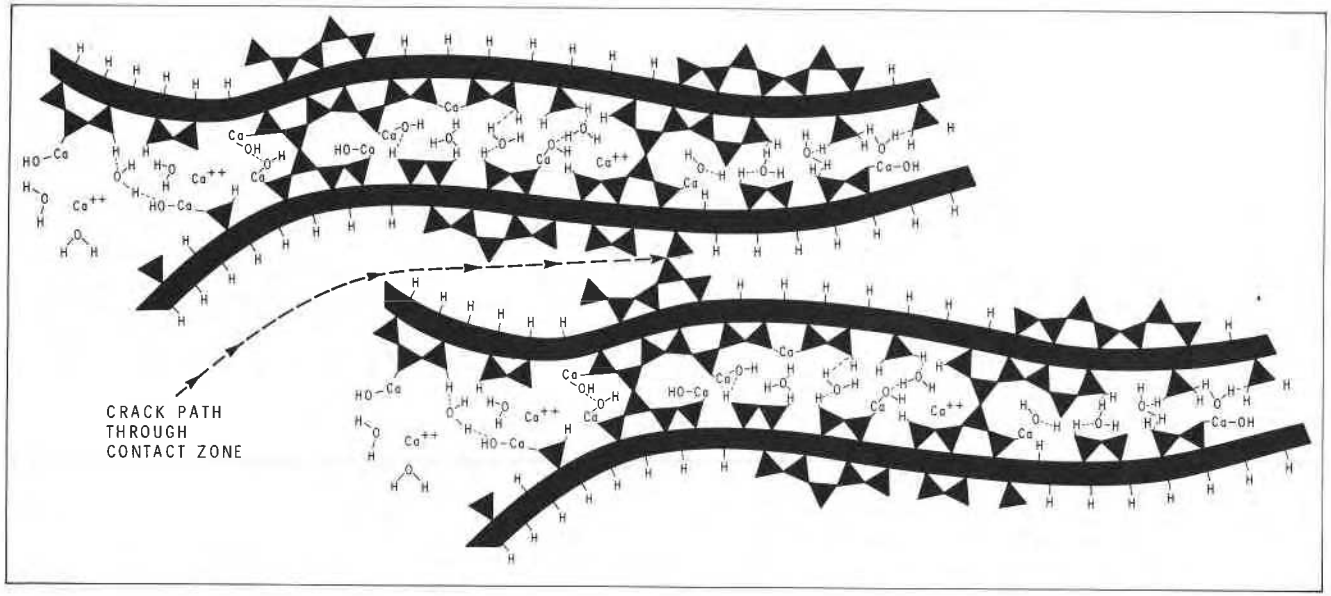


Fig. 4. Model of C-S-H (after Feldman, ref. 12,18) depicting possible crack path through points of contact between sheets. Triangles are silica tetrahedra

material; aggregations of layers meet at contact points containing Si-O bonds. The energy required to separate the C-S-H sheets themselves is larger than the energy required for a crack to propagate through points of contact. Although the population of Si-O bonds at points of contact is much less than that associated with the C-S-H sheets, it is postulated that the strength of the contact point bonds controls crack propagation. Weakening of these bonds by the action of hydroxyl ions influences crack growth.

Environmental factors

The log V-$K_I$ curves for cement paste tested in a series of aliphatic alcohols are displaced with respect to $K_I$ values (see Fig. 1(c)), which generally increase with decrease in dielectric constant of the test fluid (ref. 10). This dependence is not in itself a priori evidence that solvation processes assist the fission of Si-O bonds in cement paste, as has been postulated for the soda-lime glass system (ref. 19). X-ray diffraction evidence obtained in this study, however, indicates that aliphatic alcohols modify the C-S-H structure, e.g., the XRD densitometer traces (Fig. 5) reveal that methanol treatment of C-S-H modifies the structure. The peak at d = 0.279 nm adjacent to the main C-S-H peak at 0.303 nm is truncated for the methanol-treated sample. A similar observation is made for C-S-H samples treated with the other aliphatic alcohols (ref. 20). In addition, peaks at d = 0.139 and 0.166 nm are barely detectable after C-S-H treatment in methanol.

XRD also indicates that methanol reacts with bulk $Ca(OH)_2$ (a major constituent of portland cement paste) to form calcium methoxide (ref. 21). On the basis of these results it is suggested that, in addition to any surface-free energy effects, chemical modification of C-S-H and $Ca(OH)_2$ or stress corrosion

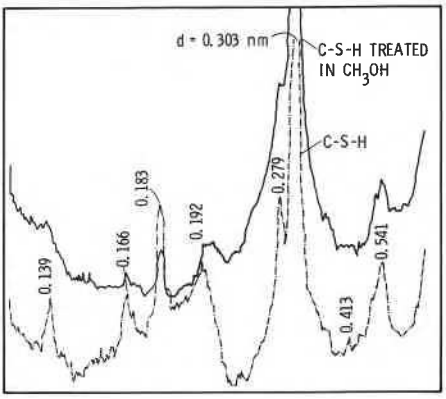


Fig. 5. X-ray diffraction densitometer traces for C-S-H and C-S-H treated in methanol

processes may influence crack propagation behaviour of cement paste tested in alochols.

## CONCLUSIONS

1. Crack growth of portland cement paste is dependent on relative humidity.
2. Hydroxyl ion concentration of pore water influences crack growth of cement systems. A crack growth mechanism involving hydroxyl ion attack on Si-O bonds at crack tips may operate. Si-O bonds at points of contact between agglomerations of C-S-H sheets probably have a strong influence on crack path.
3. Surface-free energy change in C-S-H due to adsorption of water and alcohols is not the sole mechanism responsible for weakening of the solid.
4. Alcohols interact with and modify C-S-H; methanol, in particular, reacts with $Ca(OH)_2$. It is concluded that chemical processes (stress corrosion) influence crack growth in cement paste.
5. Several factors influence crack growth in cement paste simultaneously; they include meniscus rupture in capillary pores, surface energy decrease of C-S-H solids, stress corrosion processes at crack tips involving hydroxyl ion attack of Si-O bonds, chemical modification of C-S-H in alcohol environment, and aging of C-S-H.

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