Effect of humidity and porosity on fracture of hardened Portland cement
Beaudoin, J. J.

Cement and Concrete Research, 12, November 6, pp. 705-716, 1982-11-01

https://doi.org/10.1016/0008-8846(82)90033-3

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at https://nrc-publications.canada.ca/eng/copyright

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L’accès à ce site Web et l’utilisation de son contenu sont assujettis aux conditions présentées dans le site https://nrc-publications.canada.ca/fra/droits

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D’UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n’arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.
EFFECT OF HUMIDITY AND POROSITY ON FRACTURE OF HARDENED PORTLAND CEMENT
by J.J. Beaudoin

Reprint from
Cement and Concrete Research
Vol. 12, No. 6, 1982
p. 705-716

DBR Paper No. 1057
Division of Building Research

Price $1.50

OTTAWA

NRCC 20677
EFFECT OF HUMIDITY AND POROSITY ON FRACTURE OF HARDENED PORTLAND CEMENT

J.J. Beaudoin
Building Materials Section, Division of Building Research, National Research Council of Canada, Ottawa, Canada K1A OR6

(Communicated by J. Skalny)
(Received March 19; in final form Aug. 2, 1982)

ABSTRACT
The dependence of fracture mechanics terms ($\gamma_T$, $K_c$, $G_c$ and $J_c$) on relative humidity and porosity is determined for hardened portland cement paste (HCP). The cardinal features of the fracture term/humidity curves and fracture term/porosity curves are discussed. Large hysteresis in fracture term/relative humidity curves is observed, the magnitude depending on the drying history of HCP. Meniscus effects, aging and moisture-assisted stress corrosion processes are thought to contribute to fracture of HCP. Unhydrated portland cement, Ca(OH)$_2$ particles, and pores with specific size distributions in the HCP system possibly act as crack arrestors.

Introduction
Traditional methods of studying cement and cement mineral systems include microscopy, X-ray diffraction, DTA, DSC, thermogravimetric analysis, calorimetry and pore structure analysis. Fracture mechanics techniques have provided additional tools for studying ceramic systems, giving insight into factors affecting strength development, fracture toughness, and durability. Such techniques are also useful for characterizing multicomponent, moisture sensitive, cementitious systems and have ultimately led to new developments in building materials.
Developments in concrete construction have included numerous cement-based composite products (1). Fibre-reinforced cement products are gaining acceptance since they generally have greater flexural strength and fracture toughness than conventional unreinforced cement products. The cement-based matrix and the reinforcing fibre both contribute to strength and toughness of the composite. The cement matrix is frequently hydrated portland cement paste (HCP), for which the majority of fracture mechanics studies have been conducted only in the last decade (2). Data are often conflicting and there is disagreement concerning the applicability of linear elastic fracture mechanics (LEFM) and the relative merits of test procedures and expressions describing fracture behaviour. There appears to be, however, a universal consensus that, whatever the extent of the validity of LEFM to brittle fracture, the information has been valuable in characterizing materials and providing input useful to concrete producers.

Numerous studies have demonstrated that hydrated portland cement paste is a moisture-sensitive material, i.e., that many of its physical, mechanical and chemical properties other than the hydration process itself are humidity dependent (3,4). Furthermore, aging phenomena, which include surface area decrease with time and time-dependent changes in solid volume, apparent volume, porosity and chemical changes (excluding hydration), influence some mechanical properties. Use of thin samples has been necessary to achieve moisture equilibrium within the pores of these systems.

The study was designed to measure fracture mechanics terms for HCP at various equilibrium values of relative humidity and to determine the porosity dependence of these terms at each humidity.

**EXPERIMENTAL**

Portland cement composition was as follows: SiO₂ = 20.78%; Al₂O₃ = 6.20%; Fe₂O₃ = 2.22%; CaO = 64.83%; MgO = 1.84%; SO₃ = 3.17%; Na₂O = 0.05%; K₂O = 0.40%. Blaine fineness was 300 m²/kg, and calculated Bogue compound composition was C₄AF = 6.7%; C₃A = 12.7%; C₃S = 51.4%; C₂S = 20.3% and CaSO₄ = 5.4%.

Samples were made at the following water/cement ratios: 0.25, 0.30, 0.35, 0.40, 0.45, 0.50 and 0.60. Mixes were cast in moulds (1.2 x 7.5 x 20 cm) fitted with metal shims (0.6 x 0.025 cm thick) running the length of each mould to provide a precast crack in the specimens. Samples were also made with no precast crack by removing the shims from the moulds. Those made at water/cement ratios of 0.50 and 0.60 were rotated in the moulds to prevent bleeding. All samples were removed from the moulds after 24 h and stored at 100% RH for approximately 18 months. After this hydration period they were sawn at 0.127 cm intervals along their length to produce final test specimens 1.2 cm deep x 0.127 cm thick x 7.5 cm long and with a mid-span notch 0.025 cm wide x 0.6 cm deep.

Test pieces were weighed and divided into three sets prior to conditioning; Fig. 1 outlines the conditioning sequence. The various humidities were obtained by conditioning the air over saturated salt solutions; a saturated CuSO₄·5H₂O solution was used for 97% RH. The
samples were dried by heating under vacuum at 105°C for 3 h. This procedure is nearly equivalent to drying samples to equilibrium with the vapor pressure of dry ice at -78°C and is referred to as d-drying (5). A minimum of one month was allowed for the sample to reach equilibrium at any particular humidity. All test pieces for each set were weighed again, prior to testing, in a gloved box conditioned to the humidity at which the test piece had been conditioned. A minimum of three test samples for every test condition were tested. At water/cement ratios of 0.50 and 0.60 notched samples were very fragile and it was not possible to test them for every condition of exposure.

Porosity Measurement

Porosity of cement paste samples was measured by helium pycnometry (6). Pore size distribution was determined using an Aminco Porosimeter capable of intrusion pressures up to 407 MPa.

Fracture Testing (See Appendices)

An environmental chamber (Fig. 2) was mounted on the cross-head of an Instron testing machine (10,000 kg capacity). Notched beam specimens conditioned in desiccators were transferred to the test chamber at the humidity at which they were conditioned. Specimens were simply supported and loaded at the mid-point. The mid-span deflection was measured using an LVDT with a read-out accurate to 0.0001 mm. Cross-head speed was 0.005 mm/min. Load-deflection curves were obtained from the Instron chart records; maximum loads were generally less than 1 kg (the stiffness of the Instron machine is extremely large in relation to the flexural stiffness of the test pieces). Testing was performed at approximately 21°C.

Fracture mechanics terms were determined from the load-deflection curves (Appendix A), which include the following:

- $K_C$, critical stress intensity factor;
- $G_C$, critical strain energy release rate;
- $J_C$, critical value of J-integral;
- $\gamma_T$, work of fracture.

Observations

Dependence of Fracture Terms on Humidity

Fracture terms, $\gamma_T$, $K_C$, $J_C$, and $G_C$, are plotted against relative humidity in Fig. 3 for cement paste samples prepared at a water/cement ratio of 0.30. The main features of the curves are summarized in Table I. Hysteresis is large over the full humidity range covering the first drying and wetting cycle for $\gamma_T$ versus RH. For $K_C$, $J_C$, and $G_C$ hysteresis is small between 0 and 11% RH.

Hysteresis in $\gamma_T$, $K_C$, $J_C$, $G_C$ versus RH curves covering second drying and wetting cycles occurs over most of the humidity range (97% - 11% RH), but is
Fracture terms $\gamma_T$, $K_C$, $J_C$ and $G_C$ versus relative humidity.

much less than that between the first drying and wetting curves. The extent of hysteresis between first drying and wetting, as expressed by differences in fracture terms, is given in Table II. Figure 4 is a plot of $K_C$ versus RH for HCP with various water/cement ratios. On first drying ($w/c = 0.25$ curve) there is no decrease in $K_C$ from $32 \rightarrow 11\%$ RH. Instead, there is a continual increase in $K_C$ from $100 \rightarrow 0\%$ RH and significant hysteresis on wetting. Values for $K_C$ on second drying are similar to those for first drying from $100 \rightarrow 32\%$ RH. With second drying, however, as relative humidity decreases from $32 \rightarrow 11\%$, there is a decrease in $K_C$ followed by an increase from $11 \rightarrow 0\%$ RH.

$K_C$ versus RH curves for HCP having water/cement ratios of 0.30 and 0.35 are as previously described. At higher water/cement ratios, e.g., $w/c = 0.45$, hysteresis between first drying and wetting is greatly reduced. On first drying, $K_C$ increases as RH decreases from $100 \rightarrow 84\%$ and then remains approximately constant from $84 \rightarrow 0\%$ RH. On wetting, $K_C$ decreases from $0 \rightarrow 11\%$ RH and then increases from $11 \rightarrow 32\%$ RH. No significant change occurs between $32 \rightarrow 84\%$ RH, but there is a decrease in $K_C$ as RH increases from $84 \rightarrow 97\%$ RH. The second drying curve parallels the first, except that the $K_C$ values are slightly smaller.

Dependence of Fracture Terms on Porosity

$\gamma_T$ and $K_C$ versus porosity curves for HCP conditioned at various humidities are plotted in Figs. 5 and 6. $J_C$ and $G_C$ versus porosity curves have similar features comparable to those of $\gamma_T$ and $K_C$ and are not presented. It is apparent that the values of the fracture terms are dependent on humidity and sample history in addition to porosity. As the curves are numerous, only a few general features will be described. The first drying curve in Fig. 5(a)
HUMIDITY, POROSITY, CEMENT PASTE, FRACTURE

TABLE I

Relevant Data Extracted from Fracture Term/Humidity Curves, Fig. 3

<table>
<thead>
<tr>
<th>Sample History</th>
<th>( \gamma_T )</th>
<th>( K_C )</th>
<th>( J_C )</th>
<th>( G_C )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>First drying</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 ( \rightarrow ) 32% RH &amp; 106% incr.* &amp; 120% incr. &amp; 167% incr. &amp; 300% incr.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32 ( \rightarrow ) 11% RH &amp; 16% decr. &amp; 30% decr. &amp; 47% decr. &amp; 52% decr.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11 ( \rightarrow ) 0% RH &amp; 9% incr. &amp; 1% incr. &amp; 12% incr. &amp; 55% incr.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Wetting</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 ( \rightarrow ) 11% RH &amp; 29% decr. &amp; 1% decr. &amp; 21% decr. &amp; 22% decr.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11 ( \rightarrow ) 32% RH &amp; 20% incr. &amp; 17% decr. &amp; 33% decr. &amp; 20% decr.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32 ( \rightarrow ) 97% RH &amp; 45% decr. &amp; 37% decr. &amp; 45% decr. &amp; 46% decr.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Second drying</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>97 ( \rightarrow ) 32% RH &amp; 93% incr. &amp; 91% incr. &amp; 150% incr. &amp; 230% incr.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32 ( \rightarrow ) 11% RH &amp; 13% decr. &amp; 7% decr. &amp; 32% decr. &amp; 3% incr.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11 ( \rightarrow ) 0% RH &amp; 24% incr. &amp; 15% incr. &amp; 19% incr. &amp; 32% incr.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Percentages refer to increases or decreases in fracture terms relative to values at starting RH in the interval.

TABLE II

Difference in Fracture Terms for First Drying and Wetting (\%)*

<table>
<thead>
<tr>
<th>RH, %</th>
<th>11</th>
<th>32</th>
<th>53</th>
<th>84</th>
<th>97</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma_T )</td>
<td>24.1</td>
<td>25.8</td>
<td>22.8</td>
<td>17.5</td>
<td>15.6</td>
</tr>
<tr>
<td>( K_C )</td>
<td>5.3</td>
<td>45.5</td>
<td>53.2</td>
<td>24.2</td>
<td>15.3</td>
</tr>
<tr>
<td>( J_C )</td>
<td>12.5</td>
<td>37.5</td>
<td>60.7</td>
<td>44.4</td>
<td>23.1</td>
</tr>
<tr>
<td>( G_C )</td>
<td>14.7</td>
<td>55.0</td>
<td>68.8</td>
<td>46.2</td>
<td>37.5</td>
</tr>
</tbody>
</table>

* Differences are expressed as \% of value on first drying.

FIG. 4

Stress intensity factor, \( K_C \), versus relative humidity for various water/cement ratios.

has some typical features. At low porosities the work of fracture, \( \gamma_T \), is high. This is followed by a decrease in the value of \( \gamma_T \) to a minimum, followed again by an increase to maximum and subsequent decrease at still higher porosities. Many of the curves exhibit minima and maxima as porosity increases (Table III). Maxima frequently occur at porosities of about 22.5\%; minima usually occur at porosities < 20\%. 
Weight change isotherms were determined to be quantitatively and qualitatively similar to those determined by Sereda, Feldman and Swenson (7) and are not presented here. Figure 7 is a plot of $K_c$ versus weight change, $\Delta w/w$, for HCP having $w/c = 0.30$. The characteristics of the curves are qualitatively similar to the $K_c$ versus RH curves in Fig. 3(b).
Discussion

Humidity Effects

Hydrated portland cement paste is a moisture sensitive, multi-component, microporous system containing crystalline, micocrystalline, poorly crystalline and amorphous phases. Models for the structure and the behaviour of C-S-H have been published and their merits debated (4). These models recognize that the state of water in the hydrated cement system plays a role in determining mechanical behaviour.

The contribution of the different types of water in C-S-H (interlayer, adsorbed, bulk) to the fracture process is difficult to assess. Interpretation of some of the features of the fracture term/RH curves is, however, assisted by current research results and concepts of the structure of C-S-H. First drying shrinkage versus weight loss curves for HCP have a characteristic plateau (change in shrinkage is negligible between approximately 35 and 20% RH). This has been attributed to rupture of the meniscus in capillary pores and release of the compressive stress on the solid due to meniscus forces (8). Meniscus rupture probably contributes to the large decrease in the values of $\gamma_T$, $K_C$, $J_C$ and $G_C$ on first drying from 32 + 11% RH.

Aging phenomena in the HCP system include large irreversible shrinkages on first drying, subsequent cycles of wetting and drying, and large changes in surface area, as detected by low-angle X-ray scattering (9). Aging is manifested by agglomeration or layering of C-S-H sheets and occurs, to a large
### TABLE III

Porosities at Maxima and Minima in $\gamma_T$ and $K_C$ versus Porosity Curves

<table>
<thead>
<tr>
<th>Fracture Term</th>
<th>Relative Humidity, %</th>
<th>Porosity, %</th>
<th>Sample History</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_T$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>84</td>
<td>22.5</td>
<td>16-17</td>
<td>first drying</td>
</tr>
<tr>
<td>97</td>
<td>22.5</td>
<td>18.5</td>
<td>second drying</td>
</tr>
<tr>
<td>32</td>
<td>20.0</td>
<td>14.0</td>
<td>first drying</td>
</tr>
<tr>
<td>11</td>
<td>22.5</td>
<td>17.0</td>
<td>wetting</td>
</tr>
<tr>
<td>0</td>
<td>23.5</td>
<td>20.0</td>
<td>second drying</td>
</tr>
<tr>
<td>$K_C$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>20.0</td>
<td>20.0</td>
<td>first drying</td>
</tr>
<tr>
<td>32</td>
<td>22.5</td>
<td>first drying</td>
<td></td>
</tr>
<tr>
<td>84</td>
<td>23.5</td>
<td>20.0</td>
<td>first drying</td>
</tr>
<tr>
<td>11</td>
<td>22.5</td>
<td>14.0-16.0</td>
<td>wetting</td>
</tr>
<tr>
<td>32</td>
<td>22.5</td>
<td>wetting</td>
<td></td>
</tr>
<tr>
<td>84</td>
<td>22.5</td>
<td>wetting</td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>30.0</td>
<td>14.0-16.0</td>
<td>wetting</td>
</tr>
<tr>
<td>D-dry</td>
<td>20.0</td>
<td>15.0</td>
<td>second drying</td>
</tr>
<tr>
<td>11% RH</td>
<td>22.5</td>
<td>19.0</td>
<td>second drying</td>
</tr>
<tr>
<td>32% RH</td>
<td>15-17.5</td>
<td>second drying</td>
<td></td>
</tr>
<tr>
<td>84</td>
<td>23.0-24.0</td>
<td>20.0</td>
<td>second drying</td>
</tr>
</tbody>
</table>

Extent, on first drying between 11 + 0% RH. Collapse of structure due to removal of interlayer water from C-S-H sheets (11 + 0% RH) has been demonstrated by helium diffusion experiments (10). It is probable that aging is a dominant factor responsible for increases in values of fracture terms on first drying (11 + 0% RH). Aging of C-S-H is greater on first drying than on wetting and second drying, and would be expected to be reflected in fracture behaviour.

Static fatigue has been defined as time-delayed fracture under sustained load, depending on applied stress and humidity. Many have argued that fracture due to static fatigue in the presence of moisture results from moisture-dependent stress corrosion processes at crack tips (11-13). Charles (13) proposed a sequence of reactions to explain stress corrosion of glass in a moist environment. These hypothetical reactions were adopted in part by Krokosky (14), who noted the possibility that the $OH^-$ concentration of HCP in pore water is sufficient to cause stress corrosion. Briefly, the hydroxyl ion attacks the silicate network according to the following reaction:

$$- Si - O - Si + OH^- + - Si - OH + - SiO^-$$

This is followed by the reaction

$$- SiO^- + H_2O \rightarrow HO - Si + OH^-$$
Feldman and Sereda (15) suggested a similar mechanism to account for decreased flexural strength on wetting. They noted that modulus of elasticity values, in contrast with strength values, increased on wetting, and suggested that a different mechanism is operating, i.e., that entry of interlayer water between C-S-H sheets causes the system to stiffen.

Loading in a fracture test is short term, but time to reach equilibrium at each humidity is long enough to permit hydroxyl ions in the crack tip regions to attack the silicate network. It is possible that stress corrosion processes at crack tips may contribute to decreases in fracture toughness on wetting.

Weight change for HCP is dependent on relative humidity. A relation should exist, therefore, between weight change and fracture terms. Weight change versus RH curves (not presented) have both primary and secondary hysteresis. Hysteresis effects have been ascribed to intercalation effects in C-S-H due to exit and entry of interlayer water. The fracture term/weight change curves (Fig. 7) are similar in shape to the fracture term/RH curves of Fig. 3. There is insufficient evidence to permit assessment of the role of interlayer water on fracture directly.

Effect of Inclusions

All normally hydrated cement pastes contain unhydrated cement particles and approximately 20-26% Ca(OH)\(_2\) by weight, more or less uniformly distributed throughout the matrix. The amount of unhydrated cement is generally greater for low water/cement ratio preparations, and estimates of as much as 40% for low water/cement ratio samples have been reported.

Several factors that influence fracture toughness of ceramic and cement bodies have recently been discussed (16-22), including the effect of second phase inclusions and microstructure, e.g., grain size and porosity. Increases in fracture toughness have been attributed to crack arresting properties of solid inclusions as well as pores.

Figure 8 is a simplified representation of some of the fracture toughness/porosity curves for HCP obtained at different humidities. It is used for descriptive purposes only and is not applicable to all cases. At A, fracture toughness of low porosity, low w/c ratio cement paste is high and the degree of hydration correspondingly low. The finely divided, uniformly dispersed cement particles may act as crack arrestors, and it is possible that Ca(OH)\(_2\)
crystals act in the same capacity. They are not, however, so hard as cement particles and should be less effective.

As porosity increases to B, the volume concentration of unhydrated cement decreases, the amount of Ca(OH)$_2$ increases, and fracture toughness decreases. It appears that the Ca(OH)$_2$ crystals are, indeed, less effective than unhydrated cement particles. As porosity increases to C, fracture toughness increases to a maximum. This is attributed to crack arresting properties of the pores. The maximum at C frequently occurred at a porosity of about 22.5%. At higher porosities, D, fracture toughness decreases as the number of interparticle contacts decreases; the probability that cracks and pores may become interconnected increases at very high porosities. The ratio of porosity between 0.1 and 0.01 μm to porosity between 0.01 and 0.003 μm was calculated from the pore size distributions. Values of this ratio for w/c ratios 0.25, 0.30, 0.35, 0.40, 0.45 and 0.50 were 0.77, 0.63, 0.71, 1.16, 2.46 and 2.50. The value of this ratio, corresponding to the maximum at C, is 1.16, suggesting that there is some optimum value in the volumetric ratio of large to small pores that optimizes the crack arresting capability of the pore system.

It is apparent that in multicomponent, composite systems such as HCP several simultaneously occurring, physical and chemical processes contribute to fracture behaviour. It is also apparent that the evidence provided in this study is insufficient to resolve conclusively the mechanisms that control fracture of HCP. Evidence obtained from establishing humidity and porosity dependence of fracture terms, considered in the light of existing knowledge, and research results describing fracture of porous ceramics, glass and other minerals does, however, provide some insight into these mechanisms for HCP.

Conclusions

1. Fracture mechanics studies contribute to understanding of the physical and mechanical behaviour of cement systems.
2. Fracture mechanics terms for HCP ($\gamma_T, K_C, J_C$ and $G_C$) are humidity and porosity dependent.
3. There is large hysteresis in fracture term/humidity curves for HCP between first drying and wetting; there is smaller but significant hysteresis between wetting and second drying curves.
4. There can be differences greater than 100% in the value of any fracture term, depending on relative humidity and drying history. It is therefore imperative to specify humidity and drying history when reporting results of fracture testing.
5. Meniscus rupture in capillary pores is suggested as a major factor in decreases of fracture term values on first drying from 32 ± 11% RH.
6. Aging and stress corrosion processes known to occur in HCP probably contribute to changes in the value of fracture terms with changes in humidity.
7. Unhydrated portland cement, Ca(OH)$_2$ particles, and pores in the HCP system possibly act as crack arrestors.
8. There appears to be an optimum ratio of large to small pores that contributes to maximum toughness.

Acknowledgement

The author wishes to acknowledge the fine technical assistance of J.J. Wood as well as the many fruitful discussions with his colleague, Dr. R.F. Feldman.
This paper is a contribution from the Division of Building Research, National Research Council of Canada, and is published with the approval of the Director of the Division.

References
Methods of determining the various fracture terms are outlined as follows:

1. **$K_c$**: critical stress intensity factor. For mid-point loading of single edge-notched flexural specimens:
   \[
   K_c = Y \frac{P_{\text{max}}^{1/2}}{(b.d^2)^{1/2}}
   \]
   where
   - $Y = 1.93 - 3.07 \frac{a}{d} + 14.53 \left(\frac{a}{d}\right)^2 - 25.11 \left(\frac{a}{d}\right)^3 + 25.8 \left(\frac{a}{d}\right)^4$
   - $P_{\text{max}}$ = maximum load; $b$ = beam width; $d$ = beam depth.

2. **$G_c$**: critical strain energy release rate. $G_c$ was calculated according to the following expression:
   \[
   G_c = \frac{P_{\text{max}}^2 (dC/da)}{2b}
   \]
   where
   - $P_{\text{max}}$ = maximum load; $C = $ compliance; $a = $ crack length; $b = $ beam width. Compliance was determined at each water/cement ratio and humidity according to procedures described elsewhere.

3. **$J_c$**: critical value of J-integral. This calculation requires load-deflection curves for both notched and unnotched samples:
   \[
   J_c = \frac{2}{b.d.} \left( A_n - A_u \right)
   \]
   where
   - $A_n$ = area under load-deflection curve up to maximum load, $P_{\text{max}}$ for notched sample;
   - $A_u$ = area under load-deflection curve of the unnotched sample up to maximum load, $P_{\text{max}}$, which was determined for the notched sample;
   - $b$ = specimen width.

4. **$Y_t$**: work of fracture. This term is determined by dividing the area under the total load-deflection curve by the area of the uncracked beam ligament ($b.(d-a)$).

**APPENDIX B**

Choice of specimen size, geometry and fracture testing procedure is subject to continuing debate. The minimum specimen depth to give valid fracture results is a moot point. In hydrated cement paste, inclusions in the vicinity of the crack tip tend to be only a few micrometers in diameter, and in this work the specimens are considered to be subject to requirements similar to those of fine grained ceramics. It is thought that specimen size is more than adequate. Thin samples (1.27 mm) are necessary to achieve hygral equilibrium. Thicker samples introduce the very real possibility of large errors due to moisture gradients.

Subcritical crack growth during testing of the specimens was minimal. Compliance-crack length curves obtained were too numerous to be presented. Change in compliance after reloading specimens that had previously been loaded to a high percentage of the failure load was marginal and was taken into account in the calculations. Direct observations of the notch root area in the SEM (sample preparation involves severe drying) did not reveal any significant microcracking.