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FRACTURE TOUGHNESS OF AUTOCLAVED PORTLAND CEMENT/SILICA MIXTURES

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ABSTRACT

Fracture toughness measurements made at 11% RH on autoclaved cement/silica mixtures having a wide range of silica contents and porosities yielded a series of curves for K_c versus porosity and K_c versus silica content. Those for preparations having low porosity and silica content were unique. Apparently αC_2S-hydrate, unreacted silica and pores having specific size distribution can act as crack arrestors. K_c versus hardness curves were similar to those for K_c versus porosity. Simple microhardness tests may be useful in predicting fracture toughness of autoclaved cementitious systems.

Introduction

Many industrial products, including concrete block, are formed by autoclaving portland cement/silica mixtures, variations in the cement/silica ratio producing a variety of cement matrices with different compositions and pore structures. These matrices are multi-component microporous systems.

The reactions that occur when cement/silica mixtures are autoclaved have been the subject of extensive study (1). Depending on initial proportions of cement and silica, the principal products are crystalline αC_2S-hydrate, 11 Å tobermorite, poorly crystallized tobermorite, and sometimes hillebrandite and xonotlite. At low silica contents formation of dense αC_2S-hydrate is known to occur. The low strength of autoclaved portland cement paste is attributed to the presence of αC_2S-hydrate, although when porosity is significantly reduced, e.g., by sulfur impregnation, these materials have greatly increased strength in proportion to the amount of αC_2S-hydrate (2). Mixtures having high silica contents (e.g., 50%) contain significant amounts of unreacted silica. Optimization of silica content for maximum strength has been well documented and the microstructure of the products at optimum silica content has several characteristics similar to those of C-S-H formed during normal hydration of portland cement, e.g., density, crystallinity, etc (3).

Traditional methods of studying and characterizing cement and cement/mineral systems include surface area, microscopy, X-ray diffraction, DTA, TGA, calorimetry and pore structure analysis. By comparison, fracture mechanics techniques and measurements using miniature test pieces under conditions of

equilibrium with respect to relative humidity have received little attention, although they provide additional means of characterizing multicomponent, moisture-sensitive cementitious systems.

Identification of microstructural features that affect toughness can assist concrete producers in designing the best concrete mixes for various requirements. This investigation was undertaken to determine the dependence of terms characterizing fracture on C-S-H composition and pore structure for a variety of calcium silicate systems. A second objective was to test whether inclusions of αC_2S-hydrate and unreacted silica can act as crack arrestors and toughen the matrix material. Another was to investigate the dependence of fracture toughness on microhardness for these cement systems in order to establish whether microhardness testing can provide a simple method of estimating fracture toughness.

Experimental

Materials

Type I cement with the following composition was used: SiO_2 = 20.78%; Al_2O_3 = 6.20%; Fe_2O_3 = 2.22%; CaO = 64.83%; MgO = 1.84%; SO_3 = 3.17%; Na_2O = 0.05%; K_2O = 0.40%; loss on ignition = 0.51%. The calculated Bogue compound composition was: C_4AF = 6.7%; C_3A = 12.7%; C_3S = 51.4%; C_2S = 20.3% and $CaSO_4$ = 5.4%.

Silica

Ottawa silica sand was ground and the fraction passing 100-mesh sieve was mixed with cement in the following amounts: 5, 10, 20, 30, 50 and 65 per cent by weight of solids.

Sample Preparation

Samples for autoclaving were prepared at water/solid ratios of 0.25, 0.30, 0.35, 0.40 and 0.45: at each water/solid ratio, six sets of samples, each set having a different silica content, for a total of 30 preparations. Samples were cast and moist cured for 24 h in moulds 1.2 × 7.5 × 20 cm, then autoclaved at 216°C (2 MPa) for 3 h. Test pieces were sliced from the autoclaved samples, and attempts were made to slice samples made with 0% SiO_2, but they were so fragile that the majority fractured during cutting. No tests, therefore, were carried out with 0% SiO_2. Test pieces were beams 1.2 cm deep × 0.127 cm thick × 7.5 cm long with a mid-span notch 0.025 cm wide × 0.6 cm deep. The details of fabrication have been published (4). The test pieces were maintained in desiccators at 11% RH until tested to minimize the risk of carbonation, further hydration, and excess volume change; this is a convenient reference state. A minimum of three test pieces for each preparation were tested.

Techniques

Microhardness. Microhardness was measured with a Leitz miniload tester in a conditioned box (11% RH) free of CO_2 using a Vickers pyramid indentor. Five determinations were performed on the surface of each sample.

Porosity. Porosity determinations were made using helium pycnometric methods (5), and pore size distributions were determined using an Aminco Mercury porosimeter capable of intrusion pressures up to 407 MPa.

Absolute Density. Densities of the various preparations were determined by dividing sample mass by solid volume, the latter by helium pycnometry.

Fracture Tests

An environmental chamber was mounted on the cross-head of an Instron

testing machine. Notched beam test pieces conditioned to 11% RH were simply supported in it and loaded at the mid-point. The mid-span deflection was measured using an LVDT with a readout accurate to 0.0001 mm. Cross-head speed was 0.005 mm/min. Load deflection curves were obtained from the Instron chart records; the 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).

Critical stress intensity factor, K_c, and work of fracture were determined from load-deflection records, but because the data have similar trends only the former is reported. K_c was determined using the following expression for mid-point loading of single, edge-notched, flexural specimens (6):

$$K_c = Y\ 3/2\ (P_{max}\ \ell\sqrt{a})/(b.d^2)$$

where

$$Y = 1.93 - 3.07\ a/d + 14.53\ (a/d)^2 - 25.11\ (a/d)^3 + 25.8\ (a/d)^4$$

P_{max} = maximum load

ℓ = length of beam

a = length of notch

b = beam width

d = beam depth.

Observations

Figure 1 is a plot of K_c versus silica content for test pieces prepared at water/solid ratios ranging from 0.25 to 0.45. With the exception of curve 1 (w/s = 0.25), K_c values generally increase to a maximum and then decrease with silica content. Curve 2 (w/s = 0.30) shows a small decrease in K_c between

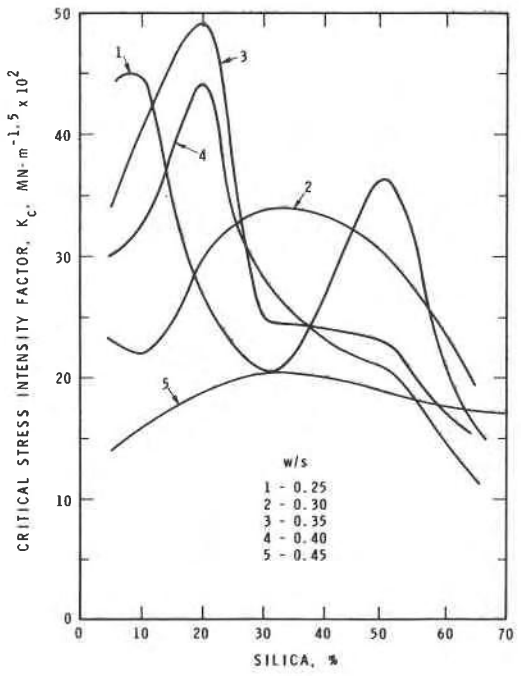


FIG. 1

Critical stress intensity factor, K_c, versus silica content for autoclaved cement/silica mixtures prepared at various water/solid ratios.

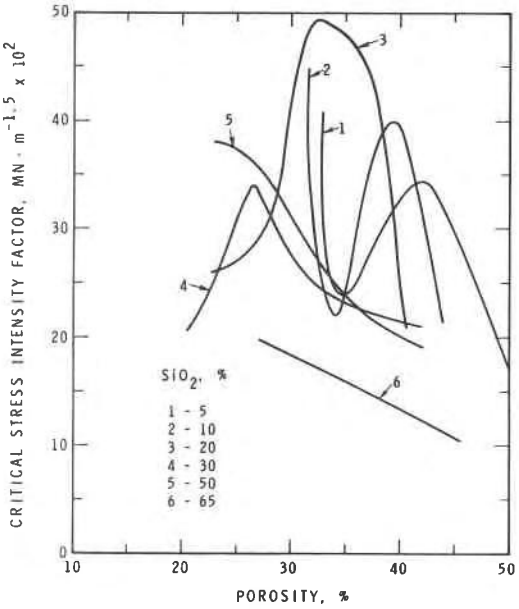


FIG. 2

Critical stress intensity factor, K_c, versus porosity for autoclaved cement/silica mixtures containing varying proportions of silica.

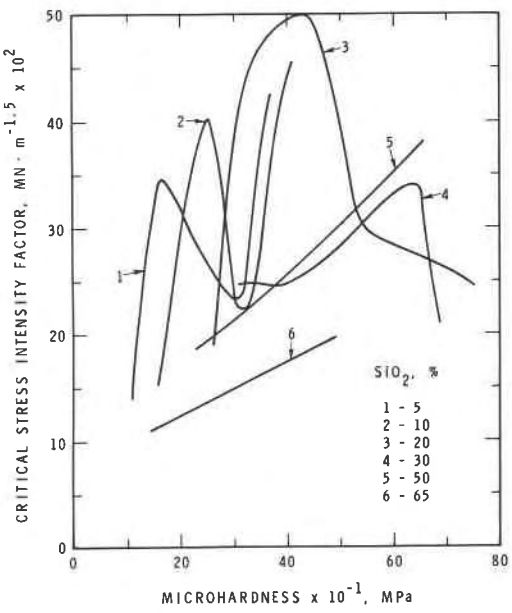


FIG. 3

Critical stress intensity factor versis microhardness for autoclaved cement/silica mixtures.

5 and 10% silica content, but the shape of the curve generally conforms to that of the others. Highest values of K_c for w/s = 0.25 occur at 5 and 10% silica content. This is followed by a decrease in K_c to a minimum at 30% silica content, a further increase to a maximum at 50% silica content and subsequent decrease.

Figure 2 is a plot of K_c versus porosity for preparations containing varying amounts of silica (5-65%). Curves for 5 and 10% silica have high values of K_c for low porosity preparations. The K_c values decrease to a minimum at about 34% porosity and then increase to a maximum (39 and 42% porosity), followed by further decrease. K_c values for 20 and 30% silica curves increase to a maximum (at 32.5 and 26% porosity, respectively,) and then decrease as porosity increases. K_c values for 50 and 65% silica curves decrease in approximately linear fashion as porosity increases.

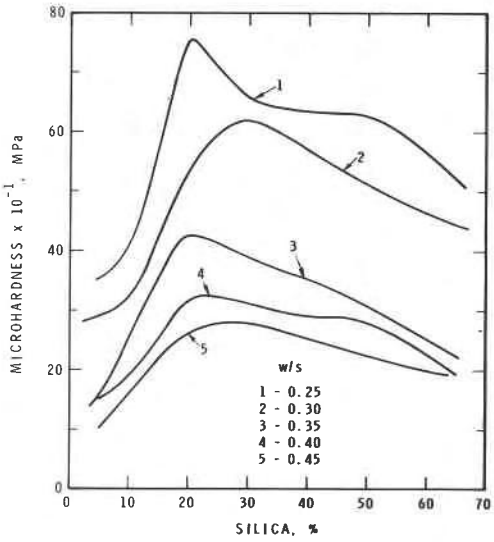
Figure 3 is a plot of K_c versus microhardness. The trends for the curves are similar to the K_c versus porosity curves (Fig. 2), considering that microhardness decreases as porosity increases (7).

Figure 4 is a plot of microhardness versus silica content. Microhardness increases to a maximum and then decreases as SiO_2 content increases. Similar results for compressive strength versus SiO_2 content have been reported (3,7).

It was thought that neither matrix effects alone nor total porosity could explain the differences between the behaviour of products formed at w/s = 0.25 and those formed at higher w/s ratios. Porosimetry studies were therefore

FIG. 4

Microhardness versus silica content for autoclaved cement/silica mixtures.



carried out. Pore size distribution data were used to calculate the ratio that would be an indicator of the relative amounts of small and large pores in the various preparations. An arbitrary pore diameter was chosen (0.1 μm) and the relative proportions of small to large pores (in terms of their total volume) determined with respect to this diameter. Values are given in Table 1.

TABLE 1

Ratio of Pore Volume Having Pores Less than 0.1 μm to Pore Volume Having Pores Greater than 0.1 μm.

SiO_2, %	Water/Solid Ratio				
	0.25	0.30	0.35	0.40	0.45
5	7.2	0.86	0.55	0.46	0.89
10	6.0	2.84	1.03	0.95	1.08
20	34.0	47.00	1.48	2.00	4.92
30	42.0	∞	7.56	6.20	13.80
50	∞*	∞	∞	12.30	2.43
65	∞	6.90	8.57	3.45	1.85

* ∞ means no pores greater than 0.1 μm detected

This pore size ratio for preparations at each w/s ratio generally increases to a maximum and then decreases as SiO_2 content increases. At w/s ratios = 0.45 the maximum value of the ratio is at 30% SiO_2. For other w/s ratios the maximum value of the pore size ratio occurs at SiO_2 contents greater than 30%. At constant SiO_2 content the pore size ratio decreases to a minimum as w/s ratio increases to 0.35 - 0.40. At SiO_2 contents of 50 and 65%, the minimum value of the ratio occurs at w/s = 0.45.

Absolute densities of the various preparations are given in Table 2. For preparations at each w/s ratio they generally decrease as SiO_2 content increases. The absolute density values, however, increase as SiO_2 increases from 50 to 65%. At constant silica content the largest changes in absolute density with respect to the value at w/s = 0.25 are 1.8, 3.3, 2.5, 10.0, 5.7 and 3.8% for SiO_2 contents of 5, 10, 20, 30, 50 and 65%, respectively. With the exception of preparations with 30% SiO_2 content the difference in absolute density for the various water/solid ratios are all less than 6% and

TABLE 2

Absolute Densities of Autoclaved Cement/Silica Preparations (g/cc)

SiO_2, %	Water/Solid Ratio				
	0.25	0.30	0.35	0.40	0.45
5	2.72	2.71	2.72	2.70	2.67
10	2.70	2.68	2.67	2.64	2.61
20	2.41	2.47	2.44	2.46	2.46
30	2.29	2.38	2.39	2.42	2.52
50	2.28	2.39	2.36	2.39	2.41
65	2.39	2.47	2.43	2.46	2.48

the differences in absolute density for the 5, 10 and 20% SiO_2 preparations are $\leq$3.3%.

Total porosities for the various preparations are given in Table 3. That at each SiO_2 content increases with water/solid ratio. In general, the lowest total porosity at a given water/solid ratio occurs for 20 or 30% SiO_2.

As chemical composition of the hydrated products varies with silica content, references in the text to "low" or "high" porosity preparations are made with respect to a particular SiO_2 content. For the purposes of this paper, therefore, low porosity refers to preparations having the lowest porosity at a given SiO_2 content. All occur at w/s = 0.25. High porosity generally refers to preparations having w/s = 0.40 or 0.45 for a given SiO_2 content. It is apparent that the terms low and high are relative with respect to porosity and dependent on the particular cement system studied.

Discussion

The evidence presented in this study is insufficient to corroborate any particular crack growth mechanism in autoclaved cement/silica systems. The data, however, and information from the literature tend to indicate the relative roles of various factors that influence fracture toughness. Inclusions (the primary matrix phase is poorly crystalline C-S-H) may act as crack arrestors in ceramic and cementitious sytems (4,8). Of particular interest in autoclaved cement/silica systems are particles of αC_2S-hydrate, unreacted SiO_2, and porosity. In previous work it was found that porous

TABLE 3

Total Porosities of Autoclaved Cement/Silica Preparations (%)

SiO_2, %	Water/Solid Ratio				
	0.25	0.30	0.35	0.40	0.45
5	33.1	34.7	42.2	44.8	50.7
10	32.5	34.0	39.8	43.2	44.8
20	23.2	28.4	32.3	37.0	40.3
30	20.8	26.6	32.7	37.9	41.9
50	22.7	30.3	34.6	40.1	42.7
65	30.3	34.1	39.8	41.9	45.8

bodies containing dense second-phase inclusions are usually weak (e.g., C_3AH_6 particles in aluminous cement systems), but they can be strong at low porosity (8). Discussion of the data in Fig. 1 is divided into two parts: preparations having w/s = 0.25, and preparations having w/s > 0.25.

Preparations having w/s = 0.25

The highest K_c values for samples obtained with 5 and 10% SiO_2 occur at w/s = 0.25. These samples contain significant amounts of dense αC_2S-hydrate (note high solid densities, Table 2); this has been verified by X-ray diffraction and other techniques (1). It has been concluded that formation of dense, second-phase products in confined space enhances the "intimacy" of interparticle contact, resulting in formation of strong bodies (9). The porosity of the w/s = 0.25 samples with 5 and 10% SiO_2 (33 and 32%, respectively) is not low enough to give highest microhardness values (Fig. 4). It is, however, sufficiently low to give relatively high fracture toughness values. It may be seen, for w/s = 0.25, that the 5 and 10% SiO_2 samples have the lowest small pore/large pore ratio (Table 1) and that the w/s = 0.25 samples in general have lower total porosity when compared with higher w/s ratio samples. It is suggested that for these preparations αC_2S-hydrate particles may act as crack arrestors.

As SiO_2 content increases, the amount of αC_2S-hydrate decreases and formation of poorly crystalline C-S-H increases. It is argued that the decrease in K_c as SiO_2 increases to 30% is due, in part, to the decrease in amount of αC_2 S-hydrate. The subsequent increase in K_c with increase in SiO_2 content to 50% may be due to crack-arresting properties of unreacted SiO_2 particles, although there is no direct evidence of this. Further decrease in K_c with SiO_2 content is probably due to increased porosity and weak interparticle contacts.

Preparations having w/s > 0.25

As shown in Fig. 1 (curves for w/s ratio > 0.25), K_c increases to a maximum and then decreases as SiO_2 increases. K_c is also low at low SiO_2 contents, in spite of the fact that αC_2S-hydrate is present. This suggests that other factors controlling toughness predominate. For these preparations the maximum for each w/s ratio occurs in the general range of silica content corresponding to lowest total porosity, and the poorly crystalline C-S-H phase, which is predominant, may exert a significant influence on fracture behaviour.

The K_c versus porosity curves (Fig. 2) provide additional information on the fracture behavior of the systems studied. The 5 and 10% SiO_2 preparations that contain significant amounts of αC_2S-hydrate have high values at low porosity (w/s = 0.25). The K_c values decrease as porosity (and w/s ratio) increases and then increase to a maximum. This maximum corresponds to a low value of the small/large pore ratio (0.55) relative to the value for the w/s = 0.25 preparation (7.2). The K_c values for the 20 and 30% SiO_2 preparations increase to a maximum and then decrease as porosity increases. The porosity values where maximum values of K_c occur correspond to values of w/s ratio given in Table 3. The value of the maximum itself is also associated with composition. The reaction products in autoclaved cement/silica mixtures contain proportionately more poorly crystalline C-S-H and less αC_2S-hydrate as silica content increases. The 20% SiO_2 preparation has the highest value of K_c for any of the samples, and it appears that this composition contributes to maximum toughness. For 50 and 65% SiO_2 preparations that contain significant amounts of unreacted silica the highest values of K_c occur at lowest porosity. All K_c values decrease as porosity increases. The small/large pore ratio decreases as porosity increases

(Table 1). The additional phase (unreacted silica) makes it difficult, however, to draw any conclusion about the effect of pore size distribution on fracture toughness.

The K_c versus microhardness curves (Fig. 3) are similar to the K_c versus porosity curves. Microhardness generally decreases as porosity increases. Fracture toughness, however, increases at intermediate porosities for many of the preparations studied. This behavior, observed for several ceramic, portland and alumina cement systems, has been attributed, in part, to crack-arresting properties of pores (4,8,10).

Silica contents for maximum values of microhardness are the same for every water/solid ratio (20%) except w/s = 0.30 preparations (30%). Silica contents for maximum values of K_c are within the range of 20 to 30% except for low porosity, w/s = 0.25, preparations. An optimum mixture of αC_2S-hydrate and C-S-H for maximum K_c and microhardness may exist at these silica contents.

Conclusions

1. Fracture mechanics is a useful tool that complements traditional techniques for studying the effect of microstructural changes on performance and behavior of cement systems.
2. There is an optimum silica content for maximum toughness in the systems studied when water/solid ratio is greater than 0.25. The maximum toughness for each water/solid ratio generally occurs at lowest total porosity.
3. Maximum toughness is dependent on composition. The largest value is obtained for 20% silica preparations that contain mixtures of poorly crystallized C-S-H and αC_2S-hydrate.
4. Dependence of critical stress intensity factor on SiO_2 content and porosity for low water/solid ratio preparations, e.g., w/s = 0.25, are unlike those for high water/solid ratios. The influence of αC_2S-hydrate and unreacted SiO_2 particles on fracture toughness appears to be greater at low water/solid ratio.
5. There is a maximum in the dependence of fracture toughness on porosity that depends on silica content.
6. Porosity and pore size distribution appear to play a role in the resultant fracture toughness of cement/silica systems and may be one of the factors responsible for increases in fracture toughness.
7. Microhardness measurements can be used to predict fracture toughness of autoclaved cement/silica mixtures.

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