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Polymer Impregnated Hardened Cement Pastes and Mortars

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Contents

Polymer Impregnated Hardened Cement Pastes and Mortars

James R. Clifton, James E. Fearn, and Erik D. Anderson

Polymer impregnated hardened cement pastes and mortars have been prepared and their properties compared to those of unimpregnated specimens. Specimens were made by impregnating, under pressure, dried and evacuated precast hardened cement pastes and mortars with methyl methacrylate, which was subsequently thermally polymerized. The effects of the microstructure of the cement pastes and mortars on the performance of polymer impregnated cement pastes and mortars were investigated using specimens with a wide range of porosities which were prepared by varying the water to cement ratio and the curing times prior to impregnation.

The properties of impregnated and unimpregnated specimens were investigated by: scanning electron microscopy; porosity determinations; fracture mechanics studies; and strength determinations. The polymer impregnated mortars had compressive and flexural strengths and fracture toughnesses which were substantially higher than unimpregnated mortars.

Key words: Cement; compressive strength; flexural strength; fracture mechanics; mortar; polymer impregnation; polymer impregnated cement; polymer impregnated mortar; porosity; scanning electron microscopy.

1. Introduction

1.1. Background

A cooperative program was initiated in 1967 by the Brookhaven National Laboratory (BNL), Office of Saline Water (OSW), and the U.S. Department of the Interior's Bureau of Reclamation (USBR), to improve the properties of portland cement mortars and concretes by developing concrete-polymer composite materials [1][1]. Three distinct types of materials were investigated: (1) polymer-cement concrete (PCC), a premixed mixture of water, portland cement, and aggregate to which monomer or resin is added during mixing and subsequently polymerized; (2) polymer-concrete (PC), consisting of an aggregate mixed with a monomer or resin which is subsequently polymerized; and (3) polymer-impregnated concrete (PIC), which consists of a hardened precast portland cement concrete impregnated with a monomer system which is polymerized in situ. To date, the most successful approach to improving the strength and durability properties of a portland cement concrete has been with PIC [1–5].

Remarkable improvements in many of the strength and durability properties of portland cement mortars and concretes have been obtained when their pores have been filled with polymers. For example, the compressive strength of a control concrete was increased from 5,270 psi (36.3 MN/m^2) to 20,260 psi (139.7 MN/m^2) when the concrete was fully impregnated with ca. 6 percent by weight of poly[methyl methacrylate] (PMMA) [6]. Similar improvements were measured in tensile strengths of the concrete. The durabilities of PIC when exposed to freeze-thaw cycling, acids and corrosive salts were also substantially improved compared to the control concretes.

The promise of PIC for building and other construction was soon recognized and a number of government agencies are now collaborating with BNL and USBR in investigating specific applications such as bridge decks [7–10], underwater structures [11], concrete sewer pipe [5], improving underground support in mines [12], and prefabricated housing [13]. Since the issuance of a patent on March 2, 1971, to BNL for the PIC process [14], other countries have commenced its commercial application and are developing a variety of products [15]. Polymer impregnated mortars and concretes appear to have great potential for use as building materials and in other areas of civil engineering [16–17], and are potential substitutes for possibly more expensive building materials, such as steel, glass, aluminum, wood and brick.

Most of the previous studies have been directed towards improving the strength and durability of PIC by optimizing the impregnation and polymerization processes, and by using different polymer systems. Only a few studies on the effects of the microstructure of the inorganic matrix on the performance of the composites have been reported [18–21]. These studies emphasized the relationship between porosity and strength. This is an area of great importance as the microstructural characteristics of the matrix could have a strong influence on the ultimate properties of the composite.

1.2. Project Objectives

The objectives of this project are to identify the important microstructural properties which affect the mechanical properties of polymer impregnated hardened cement pastes and mortars and to investigate models for interpreting the relationship observed. The results of this project are intended to contribute to the knowledge of polymer impregnated mortars and concretes.

1.3. Approach to Fulfill Objectives

A range of hardened cement pastes (HCP) and mortars was prepared which represents a wide range

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[1] Figures in brackets indicate literature references at the end of the paper.

of microstructural features. The microstructural features which were varied intentionally were the phase composition and phase distribution of the hydrated cement component and the porosity and pore size distribution of the matrix. Control materials, which were not impregnated, were characterized by their microstructural features and by selected mechanical properties. The same properties of companion specimens modified by being impregnated with selected polymers were determined.

2. Materials and Procedures

2.1. Cement

Two portland cements, both meeting the ASTM specifications for Type 1 portland cement [22], obtained from the NBS Cement and Concrete Reference Laboratory (CCRL) have been used. The portland cement identified as No. I, (CCRL samples No. 30), was used in the early portion of the study but, due to limited supply, it was replaced by cement No. II (CCRL sample No. 34). The chemical and compound compositions of the cements are given in table 1. Tricalcium silicate was obtained from an industrial cement research laboratory.

TABLE 1. *Chemical analysis of portland cements*

Constituent	Cement No. I Percent	Cement No. II Percent
SiO_2	20.9	20.9
Al_2O_3	5.0	6.1
Fe_2O_3	2.9	2.3
CaO	63.1	65.0
MgO	2.9	1.1
SO_3	2.9	2.6
Loss[a]	1.6	1.5
Insol.[b]	0.3	0.3
Na_2O	0.15	0.08
K_2O	0.67	0.38
Compound Composition[c]		
$3\,CaO \cdot SiO_2$	52.0	54.1
$2\,CaO \cdot SiO_2$	20.7	19.1
$3\,CaO \cdot Al_2O_3$	8.3	12.3
$4\,CaO \cdot Al_2O_3 \cdot Fe_2O_3$	8.8	7.0

[a] Ignition loss.

[b] Insoluble residue.

[c] Calculated by methods in standard specification for Portland Cement ASTM Designation C150–68 [22].

2.2. Sand

The sand was a natural Ottawa silica sand conforming to the requirements of ASTM Designation C109 [23].

2.3. Cement Paste and Mortar

The cement pastes and mortars were prepared by following the methods given in ASTM Designation C305 [24], (except that the mixing times were slightly varied to obtain homogeneously dispersed mixes for mortars with a water to cement ratio of 0.4) using an epicylic type (0.47m^3) mixer. All mortars were prepared with a cement to sand ratio of 1:2.75 (by weight). Specimens were removed from their molds after 24 hours, and cured under lime water (water saturated with calcium oxide) until tested or impregnated.

2.4. Monomer and Catalysts

Methyl methacrylate (MMA), inhibited with one ppm hydroquinone was mixed before use with a catalyst consisting of either one percent (by weight) 2.2′ azobis [2-methyl-propionitrile] (AMN) or one percent benzoyl peroxide (BPO). The catalysts were stored in a refrigerator until used.

2.5. Polymer Impregnated Cements and Mortars

The impregnation process usually consisted of the following sequence: (1) Specimens were dried at 160 °C for 18 hours; (2) the dried specimens were evacuated for 4 hours in a stainless steel reaction vessel (height of 5 inches, O.D. of 5 inches and wall thickness of 0.5 inches (12.7 × 12.7 × 1.27 cm) (fig. 1); (3) the specimens were soaked in MMA at ambient temperature under a pressure of 30 psi (0.21 MN/m^2) of $N_2(g)$ (the MMA was transferred to the reaction vessel without breaking the vacuum and then $N_2(g)$ was admitted) for 16 hours; when the specimens were removed from the MMA, (4) they were quickly wrapped in aluminum foil enclosed in plastic bags; and (5) placed in a water bath at 81 °C (to thermally polymerize the MMA) for 18 hours.

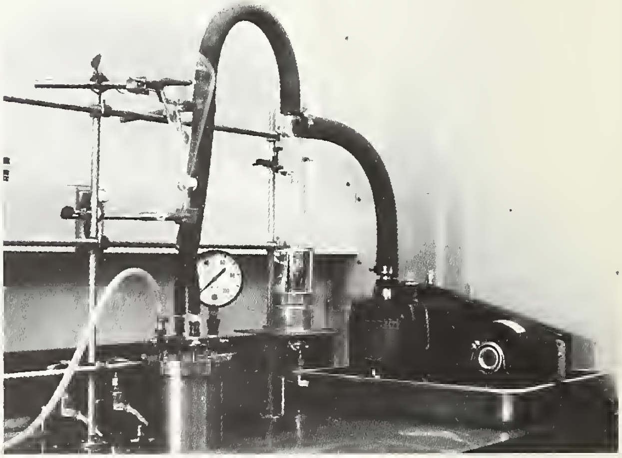

FIGURE 1. *Impregnation vessel and evacuation apparatus.*

Early in the study it was found that thermal polymerization of MMA with BPO was not complete at 81 °C., whereas apparent complete polymerization was achieved at 81 °C, using AMN as the catalyst. Strong odors of unpolymerized MMA were detected when specimens of hardened cement paste with supposedly polymerized MMA, using BPO as catalyst, were fractured or cut. These specimens also lost weight corresponding to about 50 percent of the amount of intruded MMA, when heated to 70 °C for several hours. These findings are in agreement with the observations of Auskern of BNL [25].

Difficulties were encountered in producing polymer impregnated hardened cement paste test specimens of suitable test size for many of the tests. When heated to remove evaporable water, the hardened cement paste specimens cracked badly and, therefore, only a limited number of studies were performed on polymer impregnated hardened cement pastes. In contrast, excellent polymer impregnated mortar specimens were producd by the above described impregnation process.

3. Experimental Methods and Results

The mechanical properties, fracture characteristics and porosities of polymer impregnated specimens were measured and compared with those of the unimpregnated (control) materials to determine the changes in properties attributable to filling the pores with a polymer. The experimental methods and experimental results are given in this section.

3.1. Porosity Determinations

A knowledge of the open pore volumes of unimpregnated hardened cement pastes and mortars is important because it is this volume that is available for polymer intrusion. By measuring the porosity of the polymer impregnated cements and mortars, the effectiveness of the polymer impregnation process in filling the pores can be ascertained.

Two standard methods were used to estimate porosities, (1) mercury porosimetry and (2) nitrogen capillary condensation.

3.1.1. Mercury Porosimeter Method

A mercury porosimeter capable of achieving pressures up to 60,000 psi (414 MN/m^2) was used. Pore diameters from 100 to 0.003 μm can be measured with this type of instrument. The pore diameters were calculated by the Washburn [26] equation for cylindrical pores

$$P = \frac{-4\ \gamma\ \mathrm{Cos}\theta}{d} \qquad (1)$$

where:
P is the applied pressure, γ is the surface tension of mercury, θ is the contact angle between mercury and the solid, and d is the smallest diameter of pore through which mercury will advance at pressure P. A value of 473 dynes per cm was used for γ, and θ was assumed to be 130 degree [27]. Introducing these values into eq 1, and rearranging, the following relationship is obtained [28]:

$$d\ (\mu\mathrm{m}) = \frac{175}{P\ (\mathrm{psi})} \qquad (2)$$

or

$$d\ (\mu\mathrm{m}) = \frac{12.1 \times 10^5}{P(\mathrm{N/m^2})}$$

which was used in this study.

Broken fragments, from 1 to 2 grams, of normal and impregnated cements and mortars were used for the porosity measurements. A specimen of PMMA 1½-inches (3.7 cm) long and ⅜ inch (1.0 cm) in diameter weighing 3.12 grams was also used for the porosity study.

The normal cements and mortars received the same cure treatments and heat treatments as the impregnated specimens. The specimens were cured under lime water prior to being treated.

Corrections for the compressibility of the porosimeter system were made by running blanks.

Both pressurization and depressurization studies were performed. In the pressurization study, the applied pressure was increased incrementally and the cumulative volume of intruded mercury was measured at each incremental increase in pressure (in this context, cumulative volume denotes the summation of the volumes of mercury intruded in all preceeding and the present pressure-increase step). On the basis of these data, intruded pore volume versus pore diameter diagrams are constructed, which in turn give an indication of the total volume of mercury intruded, the pore volume in any pore range, and the mode pore diameter (the range of pore diameters corresponding to the region of steepest slope of the pore volume-pore diameter curves). In the depressurization studies, the pressure is released and the mercury ejection volume is measured. For a pore structure without bottlenecks, all the mercury should be ejected. The fraction of mercury retained in the specimen after the pressure has been reduced to atmospheric pressure is termed the retention factor. High retention factors are indicative of a pore system with a significant number of constructions.

3.1.2. Nitrogen Capillary Condensation Method

A commercial nitrogen absorption instrument was used for the capillary condensation studies. The capillary condensation method is essentially limited to measuring pore diameters between 0.06 to 0.003 μm, for the reasons discussed in reference [29].

The pore size distribution information was obtained using a computer program based on the method of Barrett, Joyner, and Halenda [29].

The pore size distributions of the unimpregnated and impregnated hardened cement pastes with water to cement ratio of 0.6 were determined by the nitrogen condensation method. These specimens were taken from the same sample that had been fractured to obtain specimens for the mercury porosimetry study.

3.1.3. Results

Intruded volume-pore size distribution curves of impregnated and unimpregnated hardened cement pastes and mortars, based on the mercury penetration method, are shown in figures 2 and 3. Pressurization and depressurization curves of mortars and hardened cement pastes with water to cement ratios of 0.6 are compared in figure 4. The measured porosity of PMMA shown in figure 5, is probably due to its compressibility, because nitrogen absorption studies on polymer impregnated mortars indicated that poly [methyl methacrylate] was pore free. The adsorption-pore size distribution curve obtained with the nitrogen condensation study is shown in figure 6 for the unimpregnated hardened cement paste, with a water to cement ratio of 0.6. The adsorption-pore size distribution curve for the impregnated hardened cement paste is not shown because the nitrogen condensation method indicated that all the accessible pores of the impregnated hardened cement paste were filled with PMMA

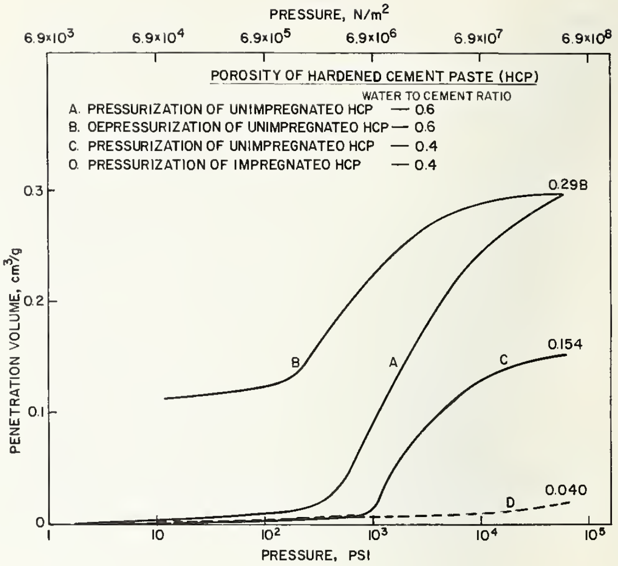

Figure 2. *Penetration volume curves of impregnated and unimpregnated hardened cement paste, cured for 28 days, measured by the mercury porosimetry method.*

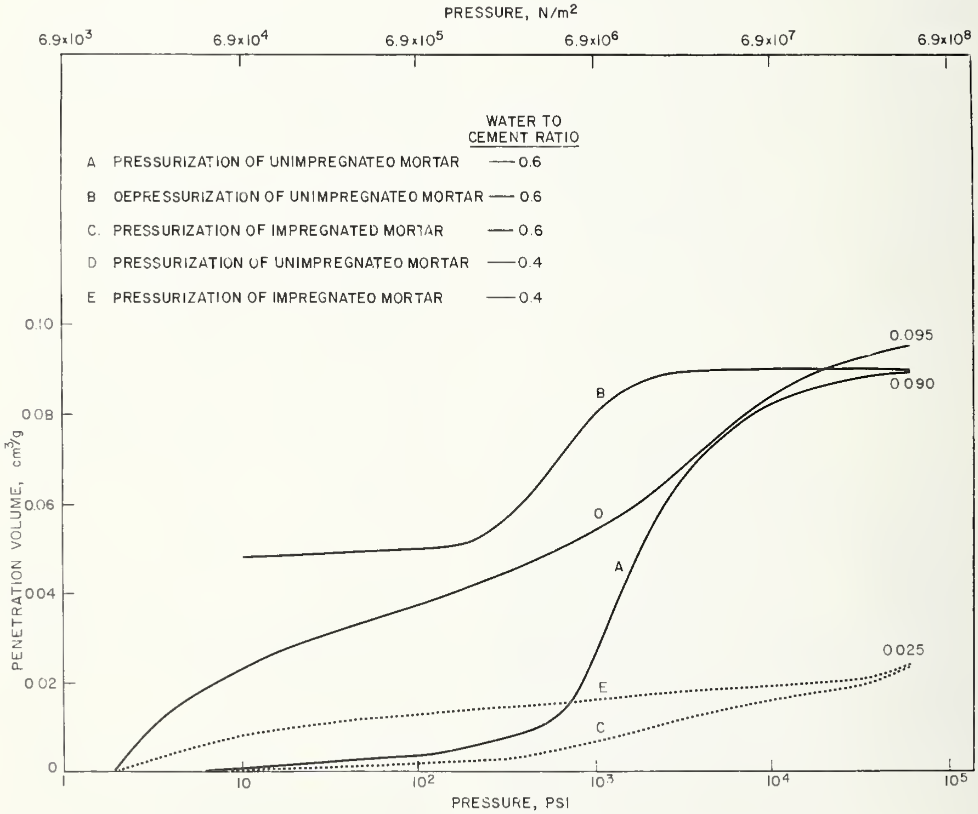

Figure 3. *Penetration pore volume curves of impregnated and unimpregnated mortars, cured for 28 days, determined by the mercury porosimetry method.*

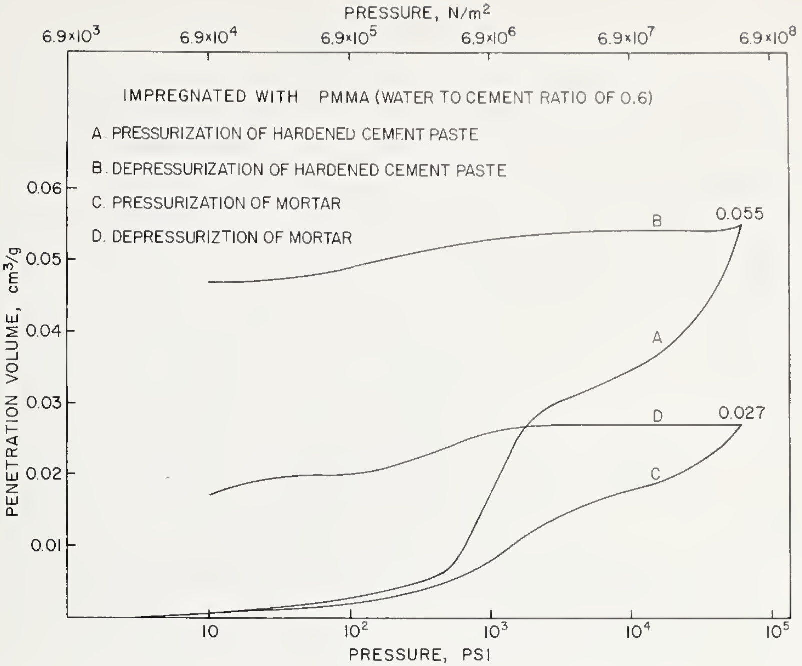

FIGURE 4. *Mercury porosimetry pressurization and depressurization curves for polymer-impregnated mortars and hardened cement pastes, cured for 28 days.*

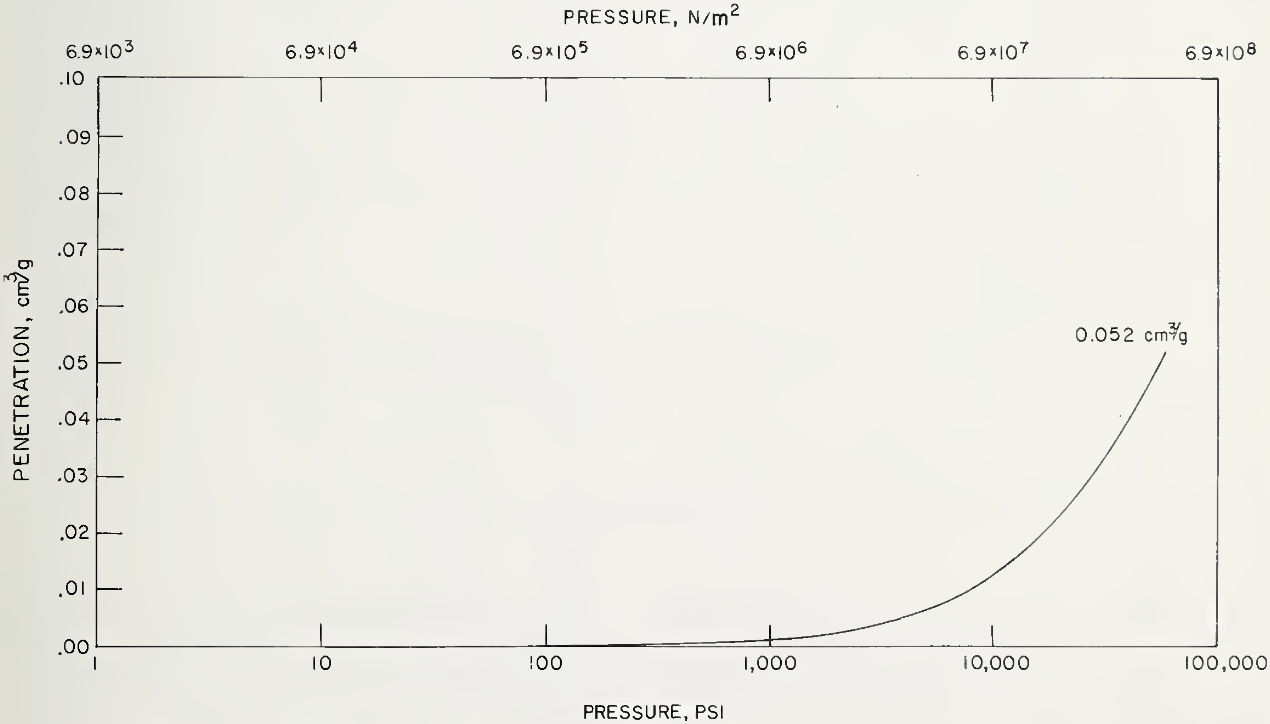

FIGURE 5. *Apparent porosity or compressibility of PMMA, determined by the mercury porosimetry method.*

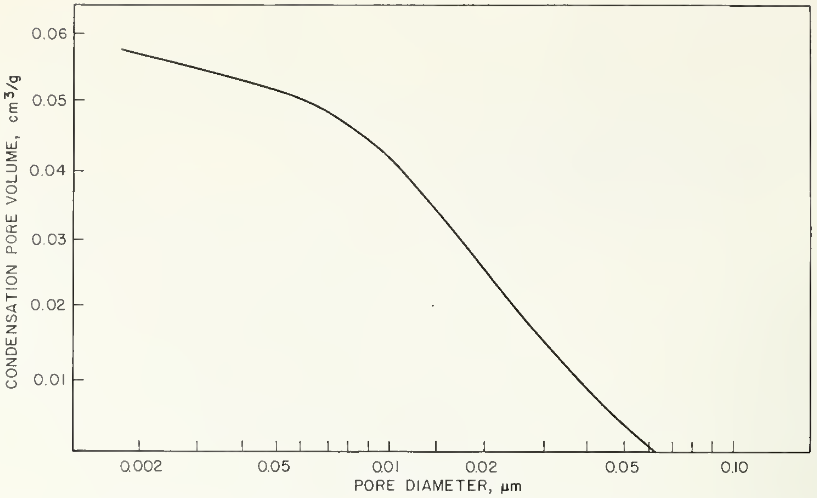

Figure 6. *Cumulative pore size distribution curve for hardened cement paste with water to cerment ratio of 0.6, determined by the nitrogen condensation method.*

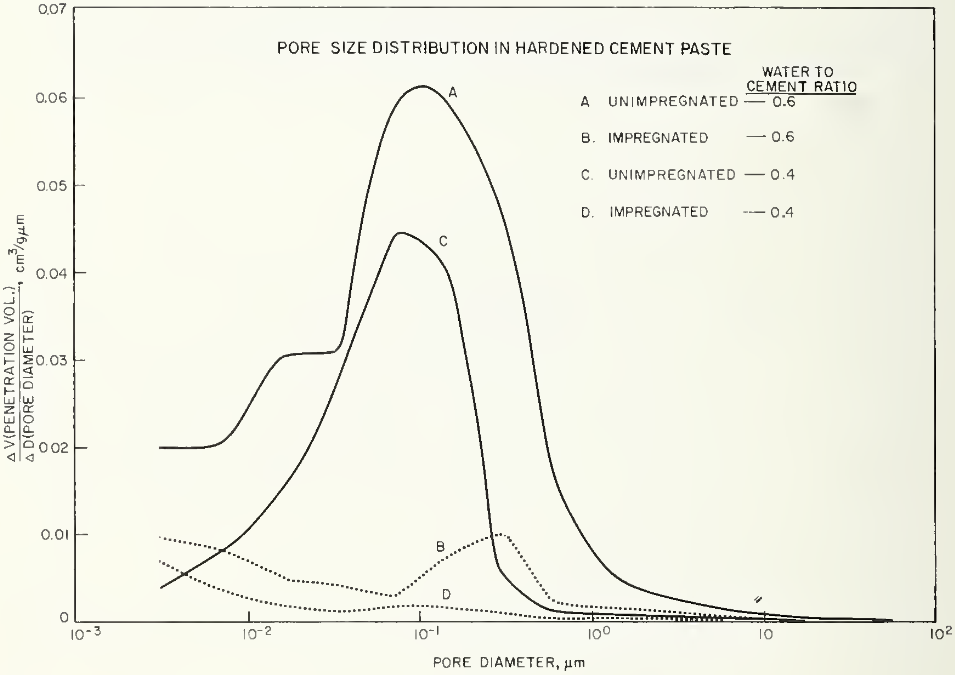

Figure 7. *Comparison of pore distribution of hardened cement paste (based on the curves in figs. 2 and 4).*

in the region of 0.06 to 0.003 μm. Differential pore size distributions, based on the mercury intrusion curves, corrected for the apparent porosity of PMMA, of the cements and mortars are presented in figures 7 and 8. The results of the mercury porosimeter study are compiled in table 2.

The intruded volume-pore size distribution curves (fig. 2 and 3) for the two unimpregnated hardened cement pastes are similar to those previously reported [30]. The measured porosity (table 2) of the hardened cement paste with a water to cement ratio of 0.4 was 0.154 cm³/g as compared to 0.298 cm³/g for a water to cement ratio of 0.6 (fig. 2). The main difference in capillary pore structure of the two pastes lies in the region of large pores; the paste with the water to cement ratio of 0.6 having more pores

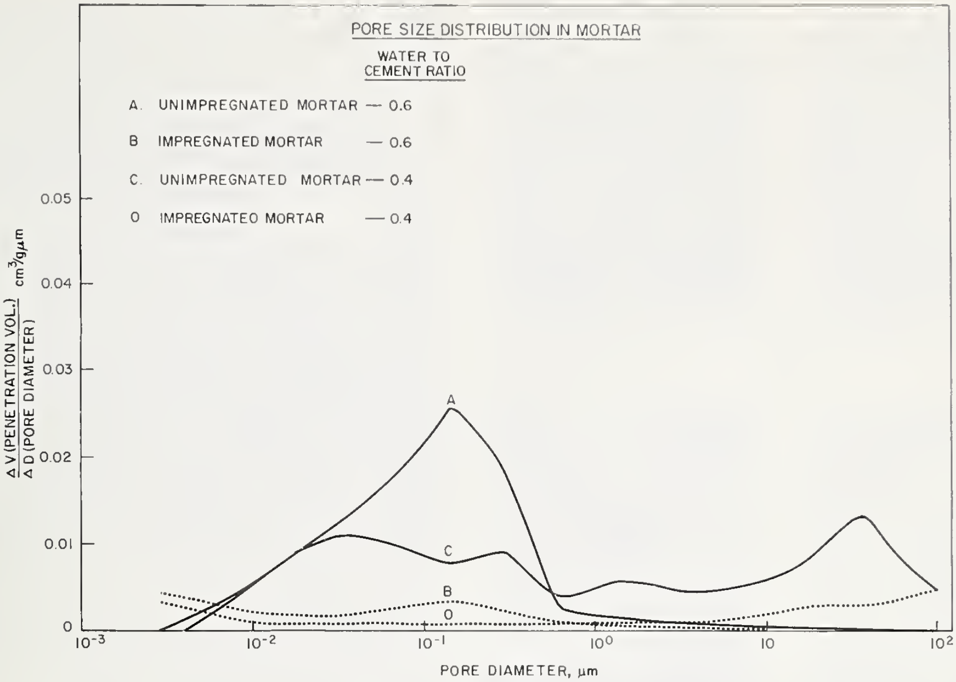

Figure 8. *Comparison of pore distribution of mortars (based on the curves in fig. 3).*

larger than 0.1 μm than the paste with the water to cement ratio of 0.4. These findings are in agreement with the study of Powers and Brownyard [31] on the water adsorption of pastes with different water to cement ratios. Consistent with a greater total porosity, the polymer loading for the hardened cement paste with a water to cement ratio of 0.6 was 25.6 percent, by weight, compared with a polymer loading of 15.6 percent, by weight, for the paste with the 0.4 water to cement ratio. The porosities of the two pastes were reduced by about 86 percent when impregnated.

Table 2. *Mercury porosimetry studies of specimens cured for 28 days*

Specimen W/C	Ratio	Percent loading PMMA	Porosity (cm³/g)	Retention factor [a]
HCP[b]	0.4	—	0.154	—
	.4	15.6	.040	—
Mortar[c]	0.4	—	0.095	—
	.4	8.6	.025	—
HCP	0.6	—	0.298	0.54
	.6	25.6	.055	.88
Mortar	0.6	—	0.090	0.40
	.6	7.4	.027	.67

[a] Ratio of volume of mercury remaining in the pores of atmospheric pressure to the volume intruded at 60,000 psi (414 MN/m^2).

[b] Hardened cement paste.

[c] Mortars prepared wth cement to sand ratio of 1:2.75, by weight.

The total porosities of the two mortars (fig. 3) were both close to 0.09 cm^3/g, in contrast to the larger differences in porosity for the pastes. However, the pore size distributions of the two mortars were significantly different from each other (fig. 8); the pore size distribution plot for the mortar with a water to cement ratio of 0.4 was relatively uniform in the range of 100 to 0.01 μm, while the pores of the mortar with a water to cement ratio of 0.6 were concentrated in the range of 0.01 to 0.8 μm, and tailed-off from either side. Possibly, the closeness in total porosity of the two mortars can be attributed to observed water bleeding which could reduce the porosity of the mortar with the higher water content. The polymer loadings of the mortars were 8.6 percent for the mortar with the water to cement ratio of 0.4, and 7.4 percent for the mortar with the 0.6 water to cement ratio and the reductions in porosity were about 75 percent.

Depressurization studies were performed, following pressurization to 60,000 psi (414 MN/m^2), on the hardened cement paste and mortar with 0.6 water to cement ratios (fig. 2–4 and table 2). The retention ratios (ratio of volume to mercury remaining in the pores at atmospheric pressure to the volume intruded at 60,000 psi (414 MN/m^2)) were 0.54 for the unimpregnated hardened cement paste and 0.40 for the unimpregnated mortar. Small retention values are indicative of pores with relatively uniform cross sections and large values indicate pores with constrictions [32], e.g., bottle-shaped pores with narrow necks [33]. The retention values for the impregnated hardened cement paste and mortar were 0.88 and 0.67, respectively, suggesting that the polymer is increasing the constrictions, i.e., decreasing the pore openings and not completely filling the pores. Studies at Brookhaven have suggested [3] that the MMA monomer fills only about 80 percent of the total cement pore volume available to the MMA and that on polymerization, there is about a 20 percent shrinkage in volume so only about 64 percent of the pore volume is actually filled with PMMA. The reduction in porosity measured in the present study was between 75 to 88 percent suggesting that a number of pores are sealed-off by a film of PMMA. Such a film could be either deformed or penetrated at the high pressure applied in the mercury porosimeter technique. PMMA is readily compressed or deformed at high pressures, as is shown in figure 5.

It is evident that the results of mercury porosimetery studies on polymer impregnated materials must be carefully analyzed. An example of contradictory information from the two porosity techniques (mercury intrusion and nitrogen absorption) concerns the pores smaller than 0.06 μm; the presence of a considerable volume of pores having diameters below 0.06 μm in the impregnated hardened cement paste (water to cement ratio of 0.6), is suggested by the porosimetry study (fig. 7); however, the total porosity of this impregnated hardened cement paste measured by the nitrogen condensation method was infinitesimal.

The nitrogen condensation study also resulted in a different pore size distribution curve (fig. 6) than the mercury porosimetry study (fig. 2) for the unimpregnated hardened cement paste with a water to cement ratio of 0.6. The high retention values measured in this study indicates that the mercury intrusion curves are probably biased in favor of small pores [32], which possibly accounts for this discrepancy. Diamond [34] has also noted that discrepancies exist between the pore size distributions based on the two methods.

3.2. Scanning Electron Microscopy

One of the most sensitive microscopic techniques available for the study of the microstructural features of hydrated cements and mortars is the use of the scanning electron microscope (SEM). This technique was used in the present study to ascertain differences in the fracture modes of unimpregnated and impregnated hardened cement pastes and mortars, and to examine the structures of these materials.

3.2.1. Experimental Procedures

A commercial scanning electron microscope, equipped with a camera and cathode ray tube, was used to obtain the scanning electron micrographs.

The general method of preparing specimens for the SEM study was to fracture a specimen and, soon as possible (usually within 10 min.), evaporate a gold or platinum-palladium film on the fresh fracture surface. Most of the specimens were formed in a special mold similar to those designed by Williamson [35]. These molds can be opened to expose a fresh fracture surface and the molds can be placed directly into the SEM.

3.2.2. Results

Scanning electron micrographs of unimpregnated and impregnated mortars and of hydrated tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$) pastes are shown in figures 9 to 15.

The fracture surface of unimpregnated mortars usually passes through the cement paste matrix and, as shown in figure 9, the sand grains remain covered with a layer of cement paste. A few craters observed in the fracture surface were caused by sand grains being pulled loose from the cement paste matrix, but these sand grains were also observed to be covered with a layer of paste. An uncoated sand grain was never observed in the analysis of over 50 micrographs of the fracture surfaces of mortars. Therefore, the weaker component in the unimpregnated mortar is the cement paste matrix. In contrast, the fracture surface of the companion polymer impregnated mortar frequently passed through the sand grains (fig. 10). Based on the observation of the fractured sand grains in the micrograph, it is evident that the strength of the cement paste matrix was increased to at least the range of strengths of the sand grains. The compressive strength of the unimpregnated mortar was 2450 psi (16.9 MN/m^2) and was increased to 19,600 psi (135 MN/m^2) when impregnated with 9.2 percent by weight, PMMA.

A typical interface between a sand grain and cement paste in an impregnated specimen is shown in figure 11 at a high magnification. The sand grain has been fractured and two small cracks extend perpendicularly to the sand-cement interface. Little, if any, polymer is observable at the sand-cement paste interface.

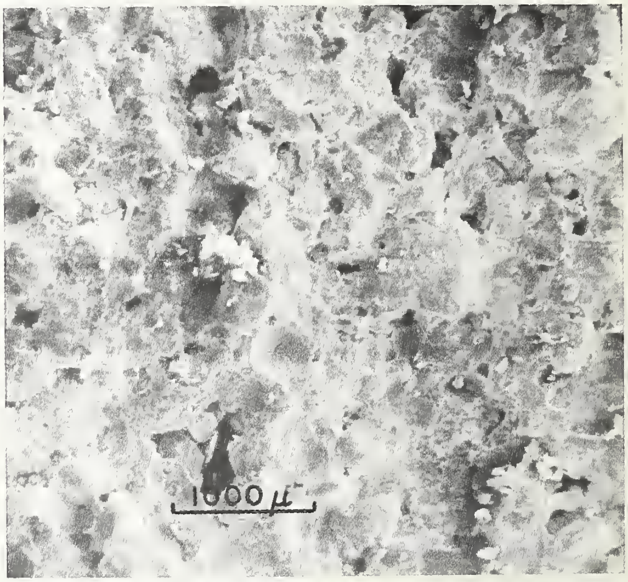

Figure 9. *Scanning electron micrograph of fracture surface of unimpregnated mortar with water to cement ratio of 0.6 and cured for 14 days.*

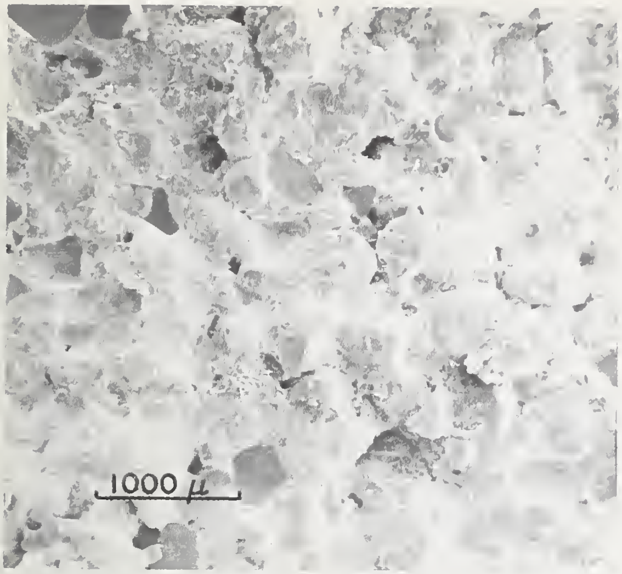

FIGURE 10. *Scanning electron micrograph of fracture surface of impregnated mortar with water to cement ratio of 0.6, cured for 14 days, loaded with 9.2 percent PMMA (on a weight basis).*

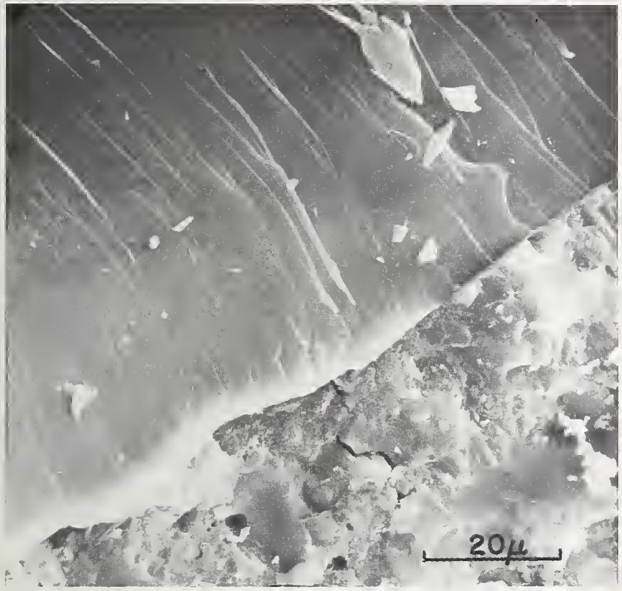

FIGURE 11. *Scanning electron micrograph of interface between sand grain and cement paste matrix of polymer impregnated mortar (water to cement ratio of 0.5, cured for 28 days, 9.6 percent PMMA on a weight basis).*

Hydrated tricalcium silicate pastes were studied to obtain a basic knowledge of the behavior of the most important cementitious constituent of portland cement. This was done because micrographs of the hydrated tricalcium silicate system are easier to interpret than those of portland cements which have 4 major components besides varying degrees of impurities [36].

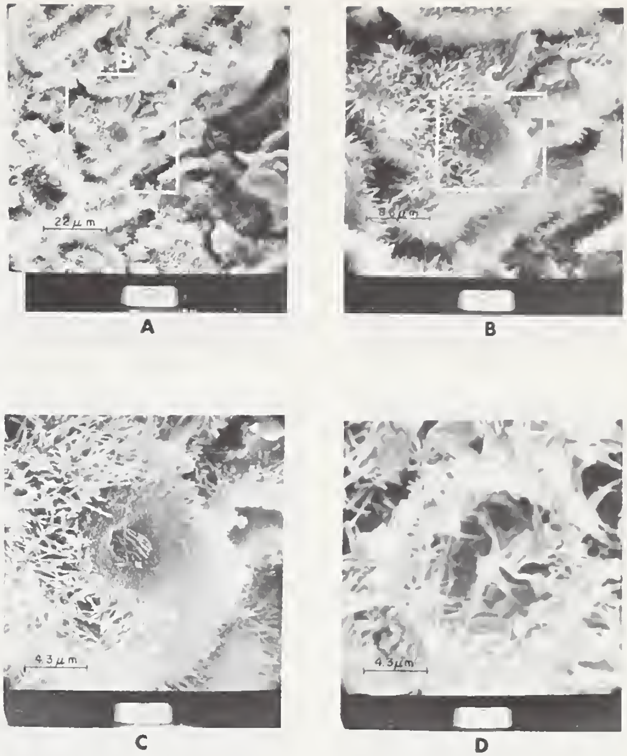

FIGURE 12. *Scanning electron micrographs of fracture surface of tricalcium silicate paste (water to cement ratio of 0.5 cured for 28 days).*

A. Hydration products and some tricalcium silicate. B. Enlargement of central portion of A. C. Enlargement of unhydrated material in B. D. Micrograph of another area of the specimen showing hydrated material having a foil-like appearance.

The micrograph of tricalcium silicate paste, water to cement ratio of 0.5 and cured under lime water for 28 days, is shown in figure 12 where B and C are enlargements of the central portion of A, and D is an enlargement of an area in the upper left side of A. The presence of an unhydrated core of $3CaO \cdot SiO_2$ which has been uncovered is evident in figures 12B and C. This unhydrated core is encircled by a ring of inner hydration product, the outer boundary of which is in contact with the outer product columnar zone (the basis for this interpretation is given in reference [35]). The needle-like structure present in figures 12B and C are crystals of hydration products of $3CaO \cdot SiO_2$ and this structure forms the spiny network of the hydrating paste [37]. The structure in the center of figure 12D was previously observed in the present studies and it has a foil-like appearance.

Micrographs of tricalcium silicate paste, water to cement ratio of 0.5 and cured for 56 days, are shown in figure 13. The spiny network has interlocked and the hydrated products are more clearly visible than at 28 days.

The large blocks of solid material in figure 13B and D are probably calcium hydroxide crystals.

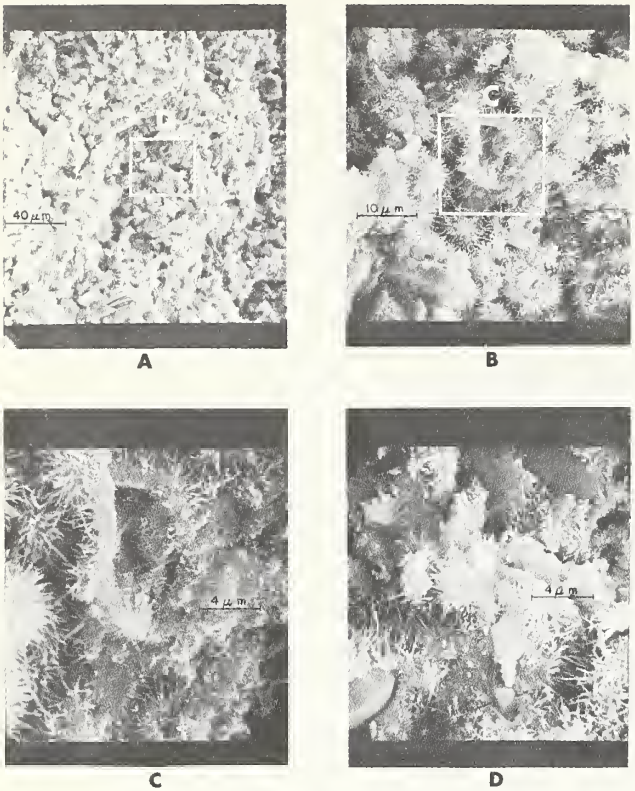

FIGURE 13. *Scanning electron micrographs of fracture surface of tricalcium silicate cured for 56 days (water to cement ratio of 0.5).*

A. Hydrated tricalcium silicate. B. Enlargement of central area of A, with well-defined spiny network. C. Enlargement of B, showing the outer hydration products of tricalcium silicate. D. Mixture of hydrated tricalcium silicate and calcium hydroxide crystals.

Micrographs of the 56 day old tricalcium silicate paste impregnated with PMMA are shown in figures 14 and 15, with the micrographs taken at high magnifications being area enlargements of figure 14A. The growth of crystals of portlandite ($Ca(OH)_2$) in small cavities can be seen in figures 14B, C, and D. These crystals are identified as portlandite by their size and fracture pattern and on the basis of the analysis of Williamson [35]. It has been observed in many micrographs that the polymer seems to obscure the spiny network of the hydrated paste, for example as in figure 15A and D. A cavity partially filled with PMMA is present in figures 15B and C. The polymer appears to line the walls of the cavity, thereby reducing its volume but not completely filling it.

3.3. Fracture Studies

Fracture studies of unimpregnated and impregnated mortars were performed by making subcritical, crack-growth-rate measurements. These measurements can lead to an understanding of the mechanisms causing slow crack growth [38], thereby giving an insight to means of predicting or improving the material's resistance to fracture. Estimates of life times of materials can also be obtained by fracture mechanics studies [39]. While the fracture toughness of cement paste has been measured by several investigators [40–43] and the critical stress intensity factor of PIC has been briefly studied [43–44], measurements of the subcritical, slow crack growth properties of polymer impregnated cement pastes, or related systems have not been previously reported.

A brief description of the fracture mechanics terms used in this paper is presented herein. For a crack to grow under static loading, two conditions must be fulfilled: (1) the stress must be sufficiently high to initiate fracture; and (2) the energy released by crack growth must be at least as much as that required to form the new fracture surfaces. The stress field near the crack then will be proportional to the product of the stress in the material times the square root of the crack length. This stress field is termed the stress Intensity Factor, K_I, i.e.,

$$K_I \propto \sigma_s \sqrt{a} \qquad (3)$$

where σ_s is the stress in the material near the crack and a is the crack length. Usually K_I is related to the stress applied at a boundary, σ_a, by the equation,

$$K_I = \sigma_a Y \sqrt{a} \qquad (4)$$

where Y is a dimensionless constant which depends on the geometry of the loading and the crack configuration. Different terminology is used for K, depending on the value obtained for the crack velocity; if the crack velocity is less than 10^{-1} m/s the stress intensity factor, K_I, is used, but if the velocity is greater than 10^{-1} m/s then the term "critical stress Intensity Factor", K_{IC}, is used. (The higher velocity indicates that the cracks have grown to the critical size which results in catastrophic failure).

In the present study, the double torsion method described by Williams and Evans [45], was used to measure the stress intensity factor (K_I) and the crack velocity (V). Evans [46] has shown that the stress intensity factor is uniquely related to crack velocity for brittle materials, and, therefore, the K_I versus V plot is a material property (i.e., the same K_I versus V plot would be obtained regardless of the specimen size or the loading techniques).

3.3.1. Experimental Procedures

The test specimens were 4⅛-inches long, 2¼-inches wide and approximately ¼-inch thick (10.5 × 5.7 × 0.63 cm). They were grooved along their length with a thin diamond saw to about half their thickness, and then notched at one end of the groove to help initiate the crack (fig. 16). The load was applied at two points spaced at equal distances from the crack initiating notch, using an electromechanical testing machine. Both K_I and V were measured by the load-relaxation method [45]. A value of 0.22 was assumed for Poisson's ratio of both the unimpreg-

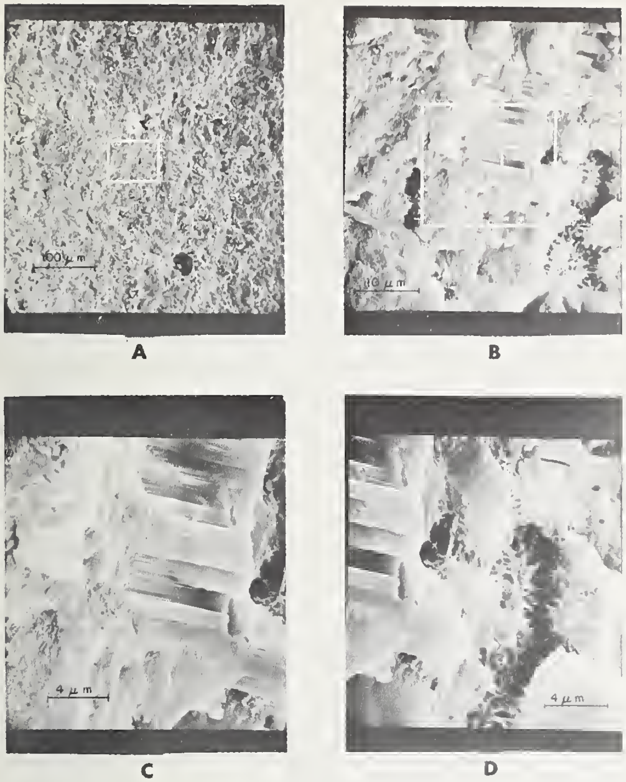

Figure 14. *Scanning electron micrographs of the fracture surface of polymer impregnated tricalcium silicate (water to cement ratio of 0.5, cured for 56 days).*

A. Low magnification micrograph of surface. B. Area enlargement of A, showing fractured crystals, probably calcium hydroxide crystals. The spiny network, shown in figure 13B, is apparently obscured by the PMMA. C and D are close-ups of the fractured crystals observed in B. Note lack of detail of the hydration products of tricalcium silicate as compared to figure 13.

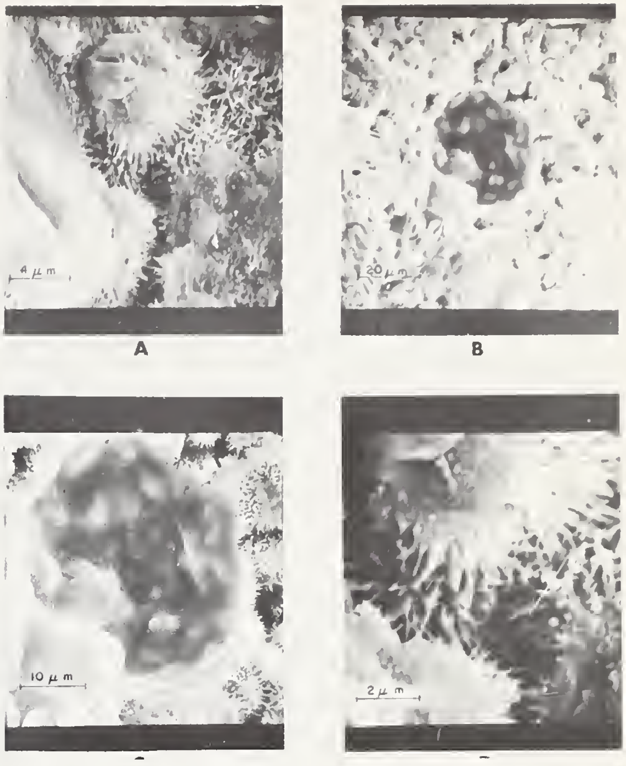

Figure 15. *Enlargements of sectors shown in micrograph of figure 14A.*

A. Hydrated tricalcium silicate particles apparently covered with PMMA. B. Cavity partially filled with PMMA. C. Enlargement of cavity in B, indicating that the polymer seems to line the walls of the cavity. D. Close-up of A, showing PMMA deposited on the spiny network.

nated and impregnated mortars on the basis of the work at Brookhaven National Laboratory [5], and the value of E calculated from resonance frequency measurements (ASTM Designation C215 [47]) were used.

3.3.2. Results

Data of V versus K_I are plotted in figures 17–19, for unimpregnated and impregnated mortars with water to cement ratios of 0.4, 0.5, and 0.6, cured for either 14 or 28 days. Compared to other studies, the variability in data for the unimpregnated specimens from the same mix was small. The data for the impregnated mortars were more scattered, possibly due to differences in the internal distribution of the polymer between supposedly identical specimens.

The unimpregnated mortars all have K_I values below 1.0 MN/m$^{3/2}$, compared to the impregnated mortars which have much higher values of K_I. This indicates that the latter are much tougher materials and will withstand greater stresses before failing. This conclusion is consistent with the higher K_{IC} value measured in this study for the impregnated mortars (table 3), than for the unimpregnated mortars. Cer-

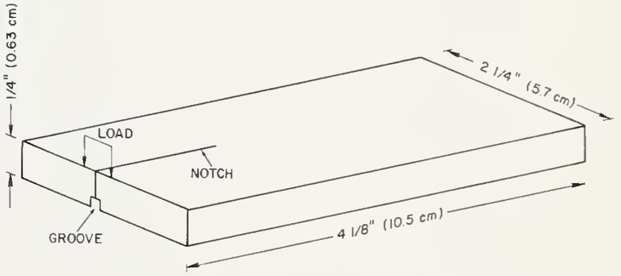

Figure 16. *Double torsion specimen for fracture mechanics measurement.*

Table 3. *Critical stress intensity factor, K_{IC}, for motars*[a]

w/c Ratio	Age (days)	Percent polymer loading [b]	K_{IC} (MN/m$^{3/2}$)
0.4	28	0	0.83
0.5	28	11.2	2.56
0.6	14	10.1	2.49

[a] Cement to sand ratio of 1:2.75, by weight.
[b] Percent by weight.

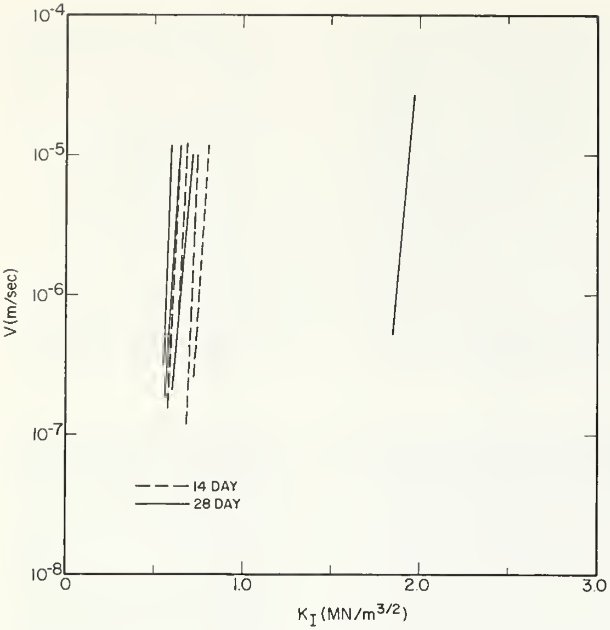

Figure 17. *Subcritical crack-growth data for unimpregnated and impregnated mortars of water to cement ratio of 0.4.*

K_I values below 1.0 MN/m$^{3/2}$ are for the unimpregnated mortar.

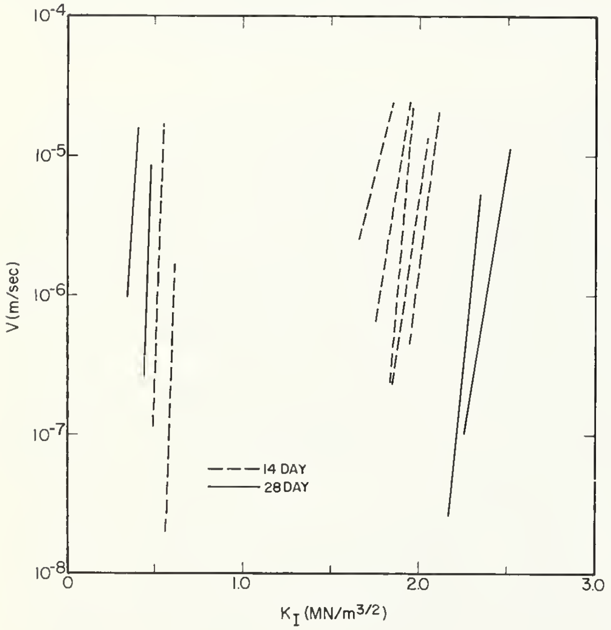

Figure 18. *Subcritical crack-growth data for unimpregnated and impregnated mortars of water to cement ratio of 0.5.*

K_I values below 1.0 MN/m$^{3/2}$ are for the unimpregnated mortar.

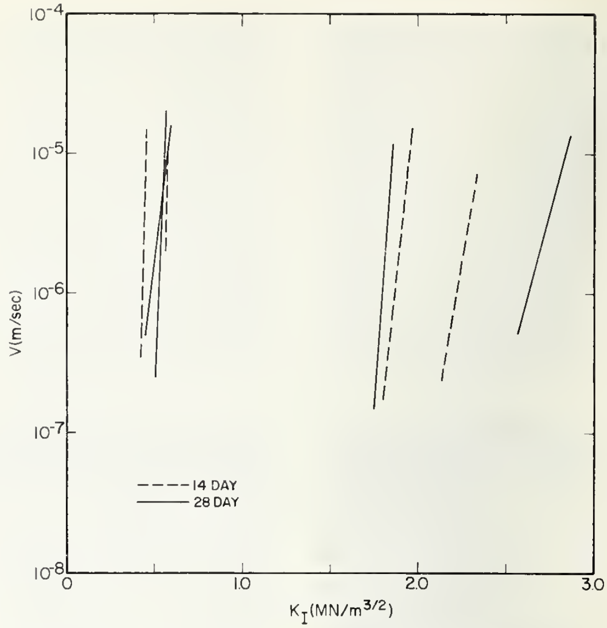

Figure 19. *Subcritical crack-growth data for unimpregnated and impregnated mortars with water to cement ratio of 0.6.*

K_I values below 1.0 MN/m$^{3/2}$ are for the unimpregnated mortar.

tainly, at identical stress levels, the polymer impregnated mortars will resist failure for much longer times than the unimpregnated mortars.

Changes in either the water to cement ratio or the curing age did not have a significant effect on the fracture properties of the unimpregnated and impregnated mortars. Possibly the cement to sand ratio of the mortars and the strength of the sand are more important variables and should be investigated.

3.4. Strength Properties

The compressive, tensile-splitting, and flexural strengths of unimpregnated and impregnated mortars and hardened cement pastes were measured by the appropriate ASTM methods for two purposes: (1) to serve as a rapid means of monitoring the efficiency of the impregnation process; and (2) to determine the effects of changes in microstructural features on these mechanical properties. Filling the pores of the cement matrix with PMMA can be expected to result in substantially increased compressive strengths [48], and an approximately three-fold increase in strength is quite reasonable in the case of mortars [49].

3.4.1. Experimental Procedures

The compressive and splitting-tensile strengths of 2 inch cubes (5.1 cm cubes) were measured by following the methods outlined in ASTM Designation C109 [23] and ASTM Designation C496 [501], respectively.

Flexural strengths of 1.58 × 1.58 × 6.3 inch (4.0 × 4.0 × 16 cm) bars were measured using a 3-point loading arrangement by the method outlined in ASTM Designation C348 [51].

3.4.2. Results

Values of the measured strength properties are listed in table 4 for unimpregnated and impregnated materials. The standard deviation in percent polymer loadings was about 0.6 percent within each series of impregnated specimens. The coefficient of variation of the strength values for the unimpregnated specimens was about 10 percent of the listed averages, and about 5 percent of the listed averages for the impregnated specimens. The average ratios of the strengths of the impregnated specimens compared to the unimpregnated specimens were: compressive strength, 4.0, and flexural strength, 5.8.

Changes in the compressive strengths of the polymer impregnated mortars (table 5) did not appear to be closely related to changes in water to cement ratios and curing ages. However, two interesting trends developed when considering the flexural and splitting tensile strengths of the impregnated specimens, which were: the flexural strengths at a given water to cement ratio decreased as the curing age increased; and also the splitting tensile strengths for the mortar with a water to cement ratio of 0.5 decreased as the age increased. These trends are possibly associated with different amounts of MMA intruded into the pores of the mortars because of changes in the porosity of the cement paste matrices, and indicate that increased amounts of intruded MMA increase the flexural and tensile strengths of the composites.

Table 4. *Strength properties of impregnated*[a] *and unimpregnated mortars and hardened cement paste*

Laboratory designations of specimens[b]	Cement No.	w/c[c]	Age (days)	*Percent loading*[d]	Compressive strength[e]		Splitting tensile strength[f]		Flexural strength[g]	
				PMMA	psi	(MN/m^2)	psi	(MN/m^2)	PSI	(MN/m^2)
20–M	I	0.4	47	10.0[12][h]	18300[2]	(126)	3450[2]	(23.8)	—	—
		.4	47	none	6900[2]	(47.5)	—	—	—	—
30–HCP	I	0.5	35	17.7[10]	18900[3]	(130)	2460[1]	(16.9)	—	—
		.5	35	none	7100[2]	(48.8)	850[1]	(5.86)	—	—
35–M	I	0.6	14	9.2[11]	19600[2]	(135)	—	—	—	—
		.6	14	none	2450[2]	(16.9)	—	—	—	—
36–M	II	0.5	7	9.5[13]	25480[5]	(176)	3068[5]	(21.1)	—	—
		.5	14	9.4[12]	24500[5]	(170)	3020[5]	(20.8)	4560[2]	(31.4)
		.5	14	none	3120[3]	(21.5)	—	—	781[4]	(5.38)
		.5	28	8.3[14]	24300[1]	(167)	2420[5]	(16.9)	4041[2]	(28.5)
		.5	28	none	5250[2]	(36.1)	—	—	792[5]	(5.46)
37–M	II	0.6	14	9.1[13]	22960[3]	(158)	—	—	4768[4]	(32.8)
		.6	14	none	3900[3]	(26.9)	—	—	831[5]	(5.72)
		.6	28	8.0[12]	22650[3]	(156)	—	—	3866[5]	(26.6)
		.6	28	none	5110[3]	(35.2)	—	—	828[5]	(5.70)
38–M	II	0.4	14	9.0[13]	22600[2]	(156)	—	—	4842[1]	(33.4)
		.4	28	none	3470[2]	(23.9)	—	—	885[4]	(6.10)
		.4	28	7.8[8]	24140[5]	(166)	—	—	4253[3]	(29.3)

[a] Impregnated under pressure of 30 psi (0.21 MN/m^2) of $N_2(g)$.

[b] M indicates mortar specimens, while HCP identifies hardened cement paste specimens.

[c] Water to cement ratio.

[d] Percent by weight.

[e] ASTM Designation C109 [23].

[f] ASTM Designation C496 [50].

[g] ASTM Designation C348 [51].

[h] Numbers in brackets give the number of specimens tested.

TABLE 5. *Effect of water to cement ratio and curng ages on mechanical properties of polymer impregnated mortars*

w/c Ratio [a]	Age (days)	Polymer (percent MAA) [b]	Compressive strength [c]		Flexural strength [d]		Splitting tensile strength [e]	
			Psi	(MN/m^2)	Psi	(MN/m^2)	Psi	(MN/m^2)
0.4	14	9.0	22600	(156)	4842	(33.4)	—	—
	28	7.8	24140	(166)	4253	(29.3)	—	—
0.5	7	9.5	25480	(176)	—	—	3068	(21.1)
	14	9.4	24500	(170)	4560	(31.4)	3020	(20.8)
	28	8.3	24300	(167)	4041	(27.8)	2450	(16.9)
0.6	14	9.1	22960	(158)	4768	(32.8)	—	—
	28	8.0	22650	(156)	3866	(26.6)	—	—

[a] Water to cement ratio.
[b] Percent by weight.
[c] ASTM Designation C109 [23].
[d] ASTM Designation C496 [50].
[e] ASTM Designation C348 [51].

4. Discussion

Polymer impregnated mortars and concretes are a new class of materials which require further study to delineate the relationships between material composition and structure, and performance. In this context, strength improvements, areas for future studies and test methods are discussed in the following.

4.1. Improvements in Mechanical Properties

The fracture toughness (sec. 3.3) and strength properties, (sec. 3.4) of mortars have been found in this study to be increased by over 300 percent by the incorporation of PMMA. A model has been developed by Auskern [52] to explain the improvements in the mechanical properties of mortars and concretes when their pores are filled with a polymer. He related the improvements to a decrease in porosity of the cement matrix and to increased bonding between the cement matrix and aggregate. The present study confirmed that the porosity of the cement matrix is substantially reduced by more than a factor of three (table 2), by the incorporation of PMMA. However, no evidence for increased bonding between the cement matrix and aggregate was obtained from scanning electron microscopic studies of fractured surfaces (sec. 3.2). Failure of the unimpregnated mortars took place by fracturing of the cement matrix; the sand grains were left loaded with a layer of cement paste indicating that the matrix aggregate bond was not the source of failure. The fracture surface of the impregnated mortar passed through both the cement matrix and sand grains. Based on these findings, it can only be concluded that the strength of the cement matrix was increased to the strength level of the sand grains by the impregnation with, and the subsequent polymerization of MMA.

The effect of the polymer on the mechanical properties of mortars and concretes can also be rationalized by consideration based on the fracture mechanics approach of Griffith [53]. In this approach when cracks in a brittle material reach a critical size catastrophic failure takes place. The polymer, by filling the pores of the cement matrix as well as voids and microcracks, reduces the size and numbers of cracks and flaws, etc., which can grow to critical size under stress. This results in an increase in the stress required to induce failure. Therefore, larger stresses are required to cause the failure of polymer impregnated materials than the unimpregnated materials.

4.2. Test Methods for Polymer Impregnated Mortars and Concretes

Polymer impregnated mortars and concretes will probably have two main uses for which different test methods are possibly applicable: (1) where high strength/weight ratios are important; and (2) where durability to aggressive environments is required. These different uses will require different test methods.

The strength properties of mortars and concretes most often measured, and upon which criteria are established, are the compressive and tensile strengths. It is apparent that properly prepared polymer-impregnated mortars and concretes will have strength properties many times higher (3 to 6 fold improvement) than the unimpregnated materials. Possibly the fracture mechanics approach can be used as a supplement to the conventional strength measuring techniques and, therefore, should be more thoroughly investigated.

When polymer impregnated materials are used because of the increased resistance to aggressive environments, the relationships between durability and the microstructure of the material should be investigated. Possibly, the traditional type of long-term durability testing (i.e., freeze-thaw cycling, resistance, weather exposure, etc.) can be partially supplanted by porosity determinations, once the relationships between pore structure and durability are determined.

5. Summary and Conclusions

The objectives of this project were to identify the important microstructural properties which possibly could affect the mechanical properties of polymer impregnated hardened cement pastes and mortars, and to identify models to interpret the relationships observed.

Results of this study indicate that the microstructural properties such as porosity and phase composition, of the mortars, prior to impregnation, have little effect on the compressive strength and fracture mechanic properties of the polymer impregnated mortar. However, when the porosity of a mortar of a specific water to cement ratio was decreased by increasing the curing times, then a definite decrease was measured for the flexural and tensile strengths of the polymer impregnated mortar specimens. These strength decreases can be attributed to a decreased amount of intruded MMA into the specimens. If the highest attainable flexural or tensile strengths are desired, the specimens should be impregnated at early ages.

The porosities of hardened cement paste and mortars were reduced by at least a factor of three by impregnation with MMA. Mercury intrusion studies of polymer impregnated hardened cement paste and mortars are difficult to interpret because of the apparent compressibility of PMMA at high intrusion pressures. However, high mercury retention factors indicate that the residual pores in the impregnated materials have constricted entrances, i.e., bottle neck or ink spot shapes.

The fracture characteristics of mortars changed when they were impregnated with MMA. Unimpregnated mortar specimens failed by fracture through the cement paste matrix, with the sand grains left covered with a layer of cement. The fracture surface of the impregnated specimens pass through both the cement paste matrix and sand grains. No evidence for increased bonding between the cement paste matrix and aggregate, often attributed to polymer impregnation of mortars and concretes, was obtained in this study.

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16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

Polymer impregnated hardened cement pastes and mortars have been prepared and their properties compared to those of control specimens. Specimens were made by impregnating dried and evacuated precast hardened cement pastes and mortars with methyl methacrylate, under pressure, which was thermally polymerized. The effects of the microstructure of the cement pastes and mortars on the performance of polymer impregnated mortars were determined by preparing specimens with a wide range of porosities by varying the water to cement ratio and the curing times prior to impregnation.

The properties of impregnated and control specimens were investigated by: scanning electron microscopy; porosity determinations; fracture mechanics studies; and strength determinations. The polymer impregnated materials had compressive and flexural strengths, moduli of elasticity, and fracture toughnesses which were substantially higher than unimpregnated materials.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)* Cement; compressive strength; flexural strength; fracture mechanics; polymer impregnated cement; polymer impregnated mortar; porosity; scanning electron microscopy

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