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HIGH ALUMINA CEMENT-PHENOL RESIN COMPOSITE: WATER RESISTIVITY AND EFFECT OF POST HYDRATION OF UNREACTED CEMENT ON DURABILITY

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ABSTRACT

Phenol resin-high alumina cement composite, a high flexural strength cement based material is investigated here in view of its durability. It showed satisfactory durability performance for one year in water at 20°C and outdoor exposure. High durability is the specific property of high alumina cement—phenol resin composite but not of other cement/phenol resin composites or other fillers/phenol resin combinations. The strength loss after immersion in water at 20°C for one year is only 9%, and the elastic modulus remains almost unchanged. Linear expansion and weight increase of high alumina cement—phenol resin composite are 0.12% and 0.82%, respectively, under the same immersion condition. However, this composite contains a large amount of unhydrated cement because basic hardening takes place with a very small quantity of water which is released from the phenol resin during the polycondensation reaction to form a crosslinking structure. The present paper discusses the influence of unhydrated cement particles on durability based on the results of several immersion tests and some other experiments and suggests a method ("immunization") to improve the stability of the material. © *1997 Elsevier Science Ltd*

Introduction

Durability of very high flexural strength cementitious systems is a long felt desire of cement scientists from the landmark invention of Macro Defect Free (MDF) cement. With invention of MDF a research group of Imperial Chemical Industries introduced a series of water soluble polymers to the cement field (1). These water soluble polymers play an important role in improving flexural strength, but let the system water sensitive. Although several studies suggested several ways to improve water resistivity of PVA/high alumina cement system, those efforts are still not in a sufficient level (2–4). As we have understood, water resistivity of any particulate polymer matrix composite depends largely on:

TABLE 1
Mix Proportions

	Resin + solvent + modifier/ (parts by weight)	Mix proportions (parts by weight)						
		Solid substances						
Mix type		HAC	Al_2O_3	$Al(OH)_3$	Resin	Solvent	Modifier	Plasticizer
Standard	23	100			13.06	8.24	1.70	2.30
Comparison	23		66	40	13.06	8.24	1.70	2.30

- stability of polymer matrix in water
- stability of particulates in water
- resistivity of particle-matrix interface to water and water transportation.

As a matter of fact, substitution of water soluble polymer with water insoluble polymer is the immediate solution. We selected alcohol soluble phenol resin precursor which has certain advantages as given below.

- Phenol resin precursor forms an insoluble three dimensional network during heat curing.
- The resin expels water during heat curing which can be hydrated to the outermost surface of cement particles.
- The network resin is remarkably thermally stable compared to many other conventional polymers.

This innovation is directed to the cement composition that contains a hydraulic cement and a water insoluble polymer precursor that is substantially anhydrous but generates water during the heating process (5,6). However, the amount of generated water is limited to 6–7% of the nonvolatile component of the precursor and no additional free water is added to the composition in order to hydrate the cement. The nonvolatile content is rather dependent on commercially available phenol resin precursors and it was found to be 58 to 62% by weight of the precursor. Accordingly, the water utilized in hydration is nearly 1% by weight of the cement in the standard mix proportion of the present study. Such a small amount of water might be enough only for hydrating the surface of the cement particles, but not the inert body of the particles. Hence, this manner of hydration should leave a large part of the cement body unreacted.

Phenol resin-alumina cement composite demonstrated favorable stability in water, but post hydration of unreacted high alumina cement particles in the composite cast doubt on long term stability of the material. This paper aims to provide an extensive study of long term stability properties in water immersion and to suggest methods to improve their stability.

Materials and Mix Proportions

Mainly two types of mix proportions were used and these are given in Table 1. One is "standard," which consists of high alumina cement (HAC) and the other one is "comparison," in which cementitious components are not included but consists of equal volume fractions of Al_2O_3 and $Al(OH)_3$. High alumina cement (r.d. 3.01) used is composed of 54.3 wt% Al_2O_3, 37.0 wt% CaO, 4.5 wt% SiO_2 and 1.5 wt% Fe_2O_3. The main mineral constituent of high alumina cement is monocalcium aluminate (CA). Alumina powder (r.d. 3.95) contains 99.6 wt% Al_2O_3. Reagent grade pure $Al(OH)_3$, of which relative density is 2.42, was used. Commercially available resole type phenol resin precursor was used as the main binder. The precursor is essentially anhydrous and soluble in methanol, and contains 58 to 62 wt% of nonvolatile matter. Specific gravity is 1.09 and viscosity is 340 cps. N-methoxymethyl 6-nylon was incorporated to modify the phenol resin and to develop the plasticity of the paste. Glycerol was used as a plasticizer.

General Methods

Preparation of Specimens. The materials shown in Table 1 were processed by the methods described in related literature (5–7). Heat pressing after calendering was excluded for the present study. To prepare the test specimens, processed sheets were cut into strips, of 25 × 2.5 × 180 mm before heat curing. Mainly two types of specimens were used. One was prepared according to the "standard" mix proportion and the other according to the "comparison" (Preparation of wholly Al_2O_3 based specimens were unable due to reason which has been given elsewhere (8,9)). These comparison specimens (based on non cementitious compounds) were prepared to examine the effects of high alumina cement on durability related performances. Some of the standard specimens were heat treated at 300°C for 24 hours and were used to evaluate the responsibility of polymer matrix on expansion and weight gain.

Measurements. The heat cured specimens were tested for flexural strength. Half of each specimen was subjected to a three point bend test in which the original strength and the modulus of elasticity of the specimen was measured. Deflection of the specimens was measured by a displacement transducer and the span/depth ratio of the three point bend test was 30 to 40 for strength and elastic modulus test. The remaining part of the specimens, in sets of more than six, were immersed in the water at 20, 40, 60 and 80°C. The residual strength and modulus of the specimens in each of the above storage conditions were again measured in the same manner at prescribed time intervals.

Changes in length and weight were also measured. Changes in length were measured in accordance with the comparator method of JIS A 1129 (Methods of Test for Length Change of Mortar and Concrete). 15 mm diameter milky glasses with fine straight lines perpendicular to each other were stuck to the surface of the specimens using epoxy resin before being placed in each storage condition. Distance between the marks before placing was about 100 mm. Linear expansion and change of weight were expressed as the ratio of changes in length and weight to the value before placement. Pore diameters in the range of 3 nm to 60 μm were measured by mercury intrusion porosimetry (MIP). The samples for MIP were 5 × 5 mm in size and immersed in water at 40°C. Samples were taken out at prescribed time intervals, were immersed in acetone, were dried at 100°C for 24 hours and then tested in porosimeter.

Results

Initial Strength. The initial flexural strength for the "standard" specimens was 123 ± 7 MPa and the initial flexural strength of the "comparison" specimens was 88 ± 5 MPa. The other

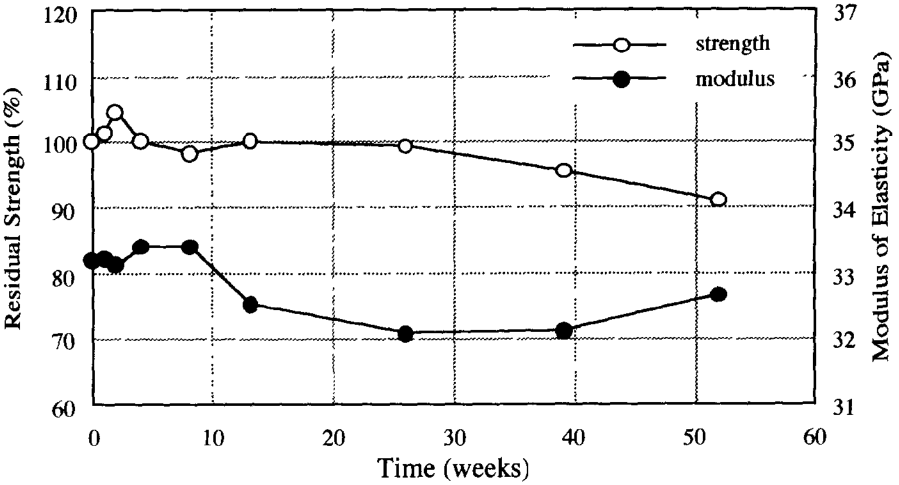

FIG. 1.
Durability characteristics of standard specimens for one year at 20°C water immersion.

study (9) showed that porosity and pore size of the comparison specimens made by the same mix proportion were lower than that of the "standard," still, strength was lower than the "standard."

Effect of Immersion in Water at 20°C. Durability data for the standard specimens for one year at 20°C water immersion are presented in Fig. 1. Strength loss for one year at 20°C water immersion was only 9%, and the elastic modulus remained relatively unchanged. This strength and modulus data ensured the considerable stability of the phenol resin cement system for structural uses.

Linear Expansion and Change of Weight. The standard specimens and heat treated specimens at 300°C for 24 hours were immersed in water at 20°C. Heating at 300°C significantly reduced the strength to 43 MPa, since the phenol resin was partially burnt off by heating. Linear expansion and weight change of standard and heat treated specimens over one year in 20°C water are shown in Fig. 2. Both expansion and weight gain of the standard specimens are lower than that of the heat treated specimen as can be seen in the Fig. 2. The standard specimens have reached 0.12% expansion level after one year in water. It has been shown experimentally (10) that sintered high alumina cement samples expand 0.03% after 28 days at 20°C water. None of the specimens made from the standard mix proportion reached this expansion level during the first 56 days.

Effect of Water at 40°C. The standard and comparison specimens were immersed in water at 40°C. Two sets of each type were taken out at prescribed time intervals; one set was tested for strength and modulus, the other set was dried at 80°C in an oven until constant weight had been achieved. Then the specimens were tested for strength and modulus. Fig. 3 shows that the strength of the standard specimens tends to increase or remains unchanged within the first 14 days of immersion and after further immersion tends to decrease gradually. An interesting aspect of these results is that both the wet and dry strengths of the standard specimens marked

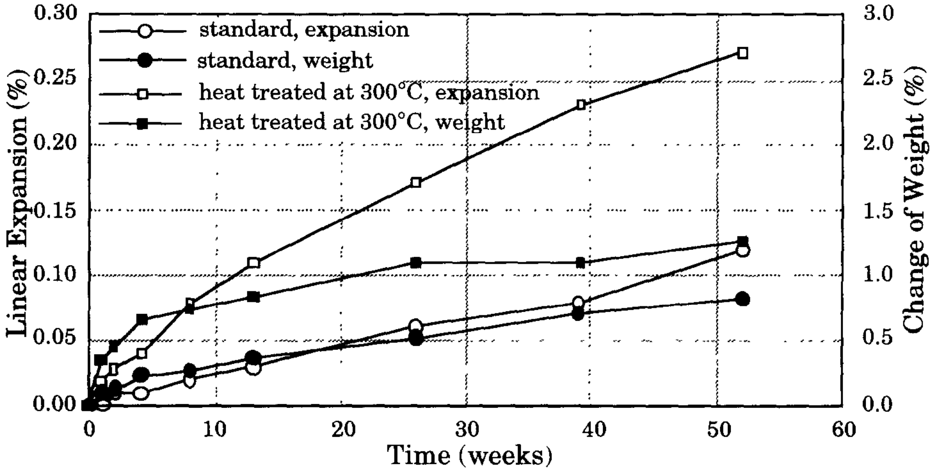

FIG. 2.

Linear expansion and weight change of standard and treated specimens over one year in 20°C water.

the highest residual strength on the 14th day over this time scale. The strength of the "comparison" specimens dropped immediately within the first 21 days and they maintained their flexural strength until test termination. The results (Table 2 and Fig. 3) show that, unlike standard, comparison specimens when dried, regain their flexural strength, up to more than 80% of the initial strength.

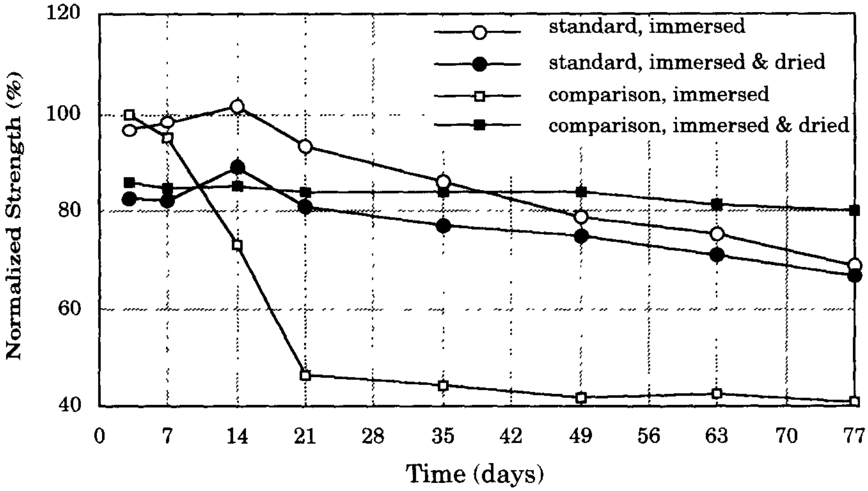

FIG. 3.

The normalized strengths of the standard and comparison specimens after storage in 40°C water and dried at 80°C.

TABLE 2
The Bending Modulus of Elasticity of the Standard and Comparison Specimens After Storage in Water in 40°C and Dried at 80°C

		Initial		14 days		77 days	
Type of Specimens	State	Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)
Standard	immersed	123	33.2	125	32.4	85	31.9
	immersed & dried			109	32.0	82	32.1
Comparison	immersed	88	28.1	64	23.5	36	21.7
	immersed & dried			75	26.4	71	25.6

Storage in Water at Temperatures Higher than 40°C. The standard specimens were immersed in water at 60 and 80°C for 7 days to understand the effect of the temperature on strength. As Fig. 4 illustrates, the strengths in water at 20 and 40°C remain relatively unchanged, but in water at 60 and 80°C the strength losses are 10 and 30%, respectively. In addition, the bending modulus at each temperature level was the same as the original.

Effect of "Immunization". Some of the standard specimens were immunized before storage at 20°C water. Immunization was done in following manner. The standard specimens were cured in water at 20°C for 14 days and then heat cured in an oven at 80°C for 24 hours. The purpose of immunization was to restrain the disadvantage of making unstable alumina cement hydrates when immersed in water at ambient temperature. Curing specimens in water at 20°C produces the metastable phases CAH_{10} and alumina gel; following heat curing, it causes the stable phases C_3AH_6 and AH_3 to be produced, but with a 15% loss in strength. As reflected in Fig. 5, on immersion in water at 20°C strength of immunized specimens seemed

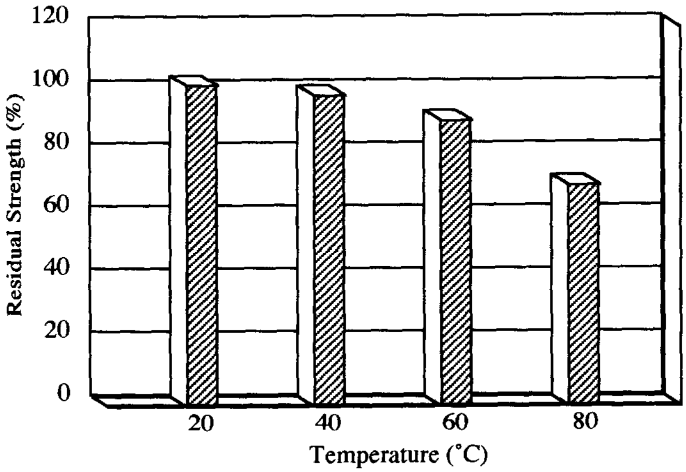

FIG. 4.
The residual strengths of the standard specimens after storage in water at 20, 40, 60 and 80°C for 7 days.

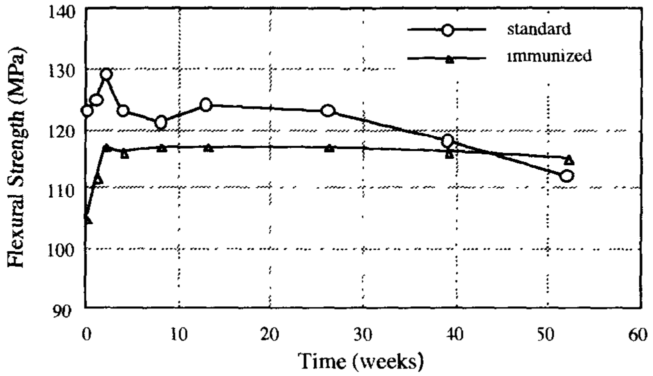

FIG. 5.
The effect of immunization on stability in water at 20°C.

to have reached a plateau over the measured time scale while the strength of standard specimens drops slightly, particularly after the first 26 weeks.

Effect of Specimen Thickness. Fig. 6 shows the effect of specimen thickness on durability in water at 40°C. Four categories of specimens with different thicknesses were compared. It should be noted that all the specimens investigated in this experiment were prepared according to "standard" mix proportion given in Table 1. The effect of hot water on the thicker specimens was less harmful.

Discussion

From the results of the present study and particularly in light of the studies on chemical characterization (8,9,11), it is obvious that the high strength of phenol resin-alumina cement composite is due to the existence of a strong organic/inorganic interphase and physical adhesion between particles and polymer. The lower strength and durability of non-cement

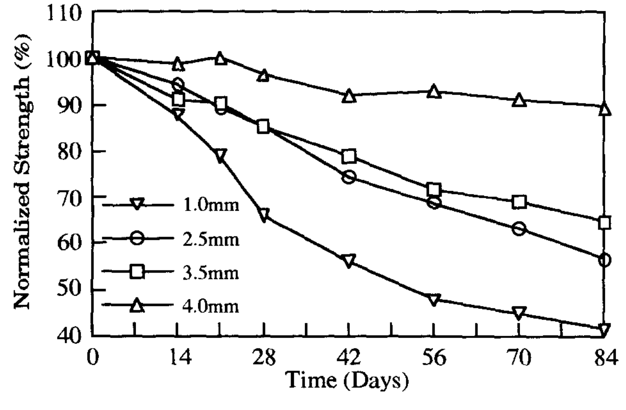

FIG. 6.
The effect of specimen thickness on durability in water at 40°C.

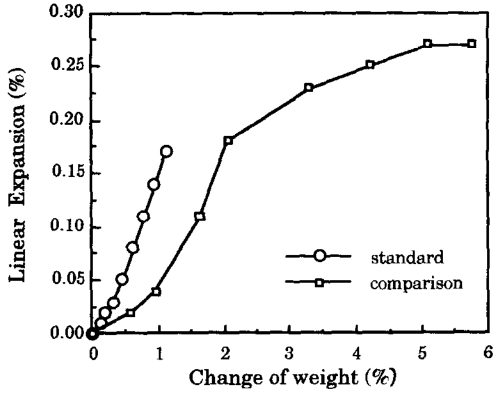

FIG. 7.

Relation between change in weight and linear expansion in water at 40°C for prescribed time intervals up to 77 days.

based material conforms to this idea. Moreover, organic/inorganic interphase considerably obstructs the water ingress into the structure; therefore, it restrains the negative influences of water on mechanical properties. In absence of a strong interphase, water ingress into the microstructure through the interfacial capillary paths becomes more rigorous (Fig. 7); thus, the mechanical breaking of weak van der Waals bonds occurs progressively. The effect of interfacial conditions on water uptake into the epoxy/soda lime glass microsphere matrix was studied by Lekatou and co-workers (12). Accordingly, composites filled with silane-coated glass microspheres exhibited lower water accumulation than those filled with uncoated microspheres. Their explanations of the lower water uptake is the silane bonding in the coated beads. Lower water accumulation of high alumina cement/phenol system also may be attributed to the chemical bonding between high alumina cement and phenol resin, it needs to function as a barrier, slowing down the water uptake.

Kataoka and Igarashi (2) have investigated the influence of the unhydrated cement on linear expansion in the PVA/HAC system of MDF. As they observed the specimens heat treated at 200, 400, 700, 900°C for 8 hours showed lower linear expansion than unheat-treated original specimens and they suggested that the post hydration of the unhydrated HAC in the system seems not to be a cause of the expansion in itself. By contrast, the linear expansion of the heat treated (at 300°C) phenol resin/HAC specimens is more than twice that of standard (Fig. 2). These results confirm HAC to be the main reason of the expansion of phenol resin/HAC system.

Moreover, an interesting observation is that the linear expansion of the standard specimens is higher than that of the comparison for an equal amount of water absorption, as seen in Fig. 7. This reveals that high alumina cement is more susceptible to water from the expansion point of view, in contrast with the non-cementitious compounds Al_2O_3 and $Al(OH)_3$. Thus, it is easily inferred that the linear expansion of the alumina cement based specimens is a function of the prolonged hydration.

As we have seen, the bulk polymer region rarely transports water into the structure and also does not alter with moisture, since the bending modulus remains unchanged after immersion in water at both 20 and 40°C. As Fig. 1 demonstrates, a longer time (one year) is required to show a slight reduction in strength; thus degradation is a much slower process. In addition,

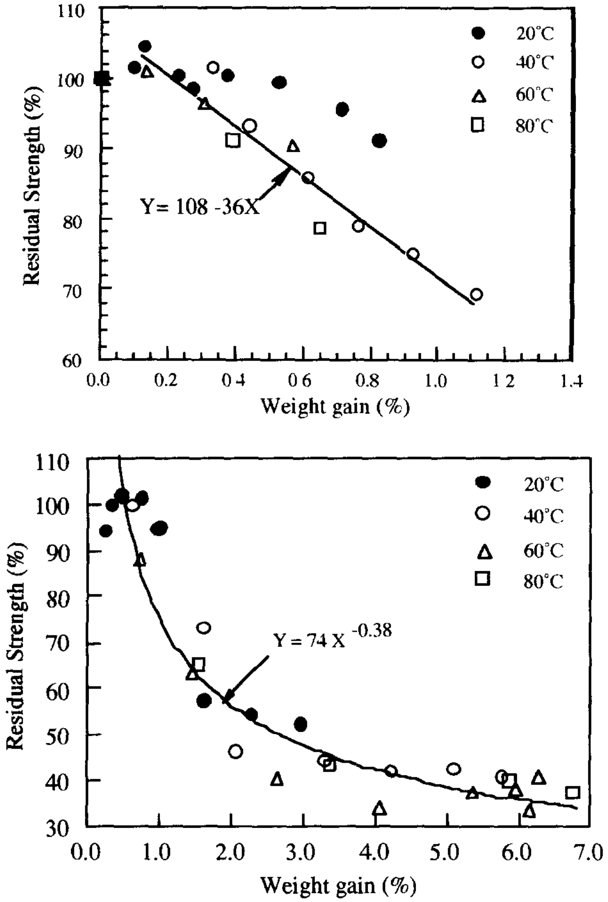

FIG. 8.

(a) Residual strengths of the standard specimens immersed in water at 20, 40, 60 and 80°C as a function of the weight gain. (b) Residual strengths of the comparison specimens immersed in water at 20, 40, 60 and 80°C as a function of the weight gain.

immersion of the standard specimens in water at 40°C resulted in a fall in flexural strength, which is irreversible on drying. Meanwhile, the comparison specimens when dried regained their flexural strength, up to more than 80% of their initial strength [Fig. 3]. This result shows that certain irreversible changes have been induced on the cement during water immersion. It appears that over longer periods of immersion, the strength of immersed and immersed/dried specimens approach the same final value, substantiating that standard specimens reached equilibrium within 77 days by complete hydration and conversion of hydrates products to a stable state.

Fig. 8(a) shows residual strengths of the standard specimens immersed in water at 20, 40, 60 and 80°C as a function of weight gain. As Fig. 8(a) reveals there is clear discrepancy between residual strengths in water at 20°C and at the higher temperatures. Residual strength of the standard specimens immersed in water at 20°C showed lower strength loss than those of the higher temperatures for an equal amount of water absorption. In spite of this, strength

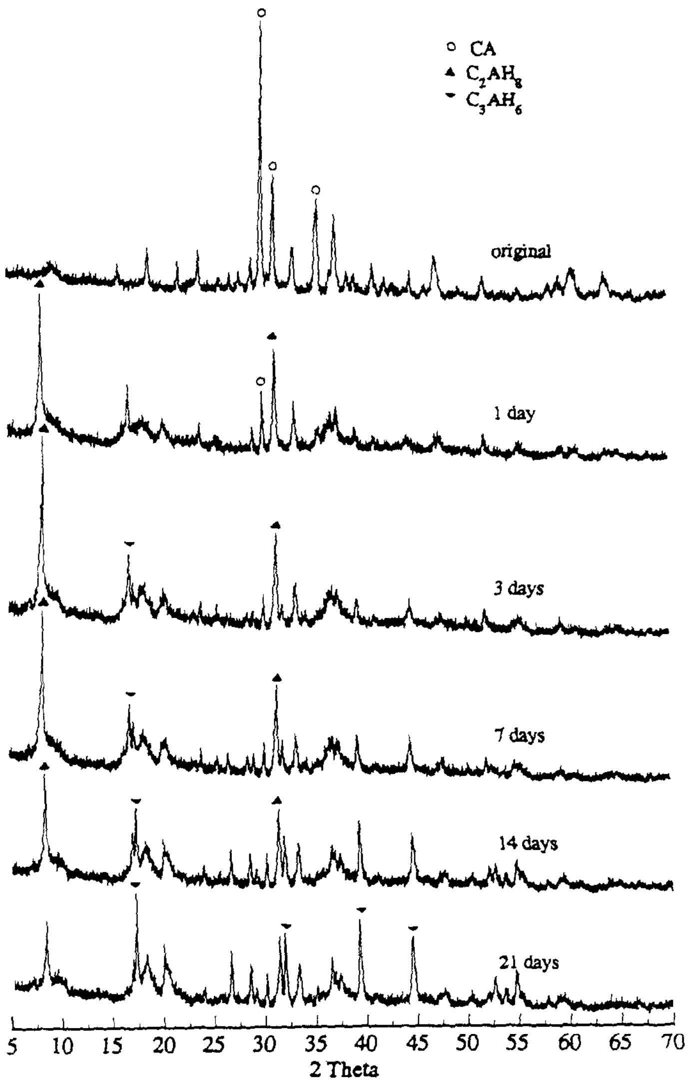

FIG. 9.

The X-ray profiles of fine powder made by grinding the standard original specimens after having been cured in water at 40°C for prescribed time intervals.

loss of comparison specimens is independent from the temperature of the water (see Fig. 8(b)). Thus, we can logically infer that loss of strength is not only a simple function of water absorption, but interplay between temperature, water absorption and the accompanied hydration products.

However, using X-ray diffraction no peaks of calcium aluminate hydrates were detected in the fine powder made by grinding the standard specimens which were immersed in water at 40°C. This is probably because hydration products are formed only on the surface of the specimen. The hydration in the material might have occurred on progressing from the surface

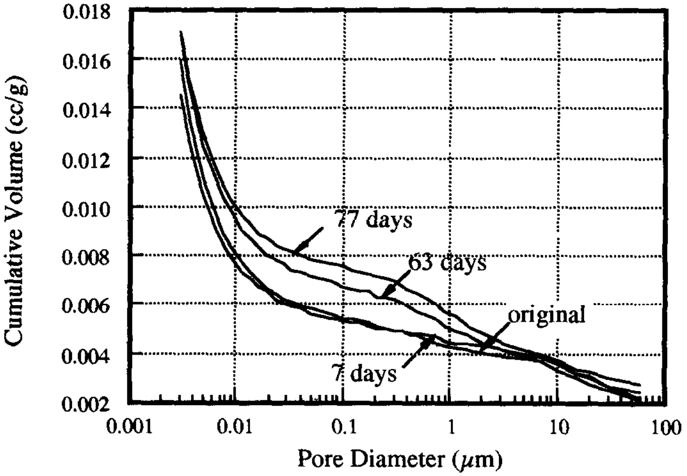

FIG. 10.

The mercury intrusion porosimetry results for "standard" samples immersed at 40°C water for 7, 63, 77 days and original.

to the bulk since lower porosity restrains water penetration into its interior. This assumption is in good agreement with the higher resistivity demonstrated by thicker specimens (see Fig. 6). The effect of the surface deterioration on the strength of the material decreases with longer the distance between the neutral axis and the surface of the specimens.

To understand the prolonged hydration and accompanied mineralogical changes that may have occurred on the outermost surface of the specimens, fine powder made by grinding the standard original specimens was examined in an X-ray diffractometer after having been cured in water at 40°C (original standard specimens were ground and sieved, then the fine powder was packed into filter bags and stored in water at 40°C). Fig. 9 shows the results. The symbols indicate that the three strongest peaks have been detected in each condition. As shown in Fig. 9, in the early stages up to 14 days, the main phase produced on hydration was C_2AH_8, followed by C_3AH_6; in other words, samples were in an intermediate stage called "half conversion" (13). Prolonged hydration changed this intermediate phase to stable C_3AH_6. This evidence revealed by X-ray diffraction analysis is in good agreement with the flexural strength results given in Fig. 3 that indicate a distinct plateau or small peak in flexural strength up to 14 days and an abrupt drop beyond 14 days. In addition, it is found to be C_3AH_6 which is the main mineralogical phase in the same fine powder after having been cured in water at 60 and 80°C for 7 days. The specimens immersed in water under the same condition showed an abrupt drop in strength (Fig. 4). This result also supports the above strength reduction mechanism.

Physical changes of the specimen surface in hot water immersion was investigated by porosimetry. Fig. 10 shows the mercury intrusion porosimetry results for "standard" samples immersed at 40°C water for 7, 63, 77 days and original. Seven days immersed samples showed the same features as the original. Samples immersed in hot water for 63 and 77 days showed greater cumulative intrusion of mercury in between the range of 4 μm and 5 nm. These porosity results are in good agreement with the strength reduction of the specimens immersed in water at 40°C for 63 and 77 days. In addition, examination by SEM (Fig. 11)

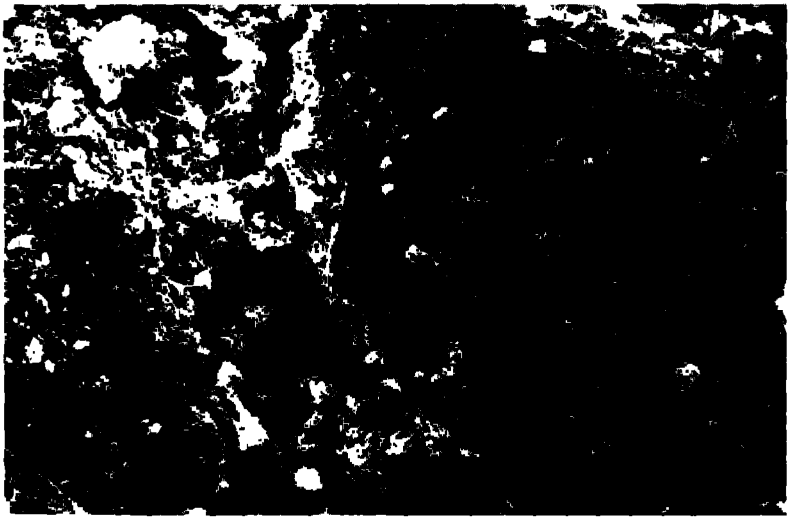

FIG. 11.
Surface of the standard specimen after 77 days, 40°C water immersion showing a split between cement particles (SEM).

of the surface after 40°C water immersion for 77 days showed that the split went through the cement/polymer interface. This observation supports the porosity results that showed greater cumulative intrusion of mercury in the 77 days hot water immersed samples. Midgley (13) has concluded that the reason of strength reduction is the increase in porosity of the set high alumina cement due to the change in density of the minerals. The observations of this study also support above hypothesis as the strength reduction mechanism of the phenol resin-alumina cement composite.

Further, another important achievement of the present study is that the flexural strength of the "immunized" samples is apparently unaffected by immersion in water at 20°C. It must therefore be deduced that there is a small but significant enhancement of long term durability due to stabilization on the surface of specimens, which we have already concluded as the most susceptible to hydration. In addition, we have recently found a more effective immunization system which is based on hydrating for 14 days in water at 40°C, followed by drying in an oven at 80°C; this effectively utilized knowledge gained by results demonstrated in Fig. 3 and X-ray diffraction analysis.

Conclusions

The strength loss of the phenol resin-alumina cement composite after immersion in water at 20°C for one year is only 9%, and the elastic modulus remains almost unchanged. Phenol resin-alumina cement composite specimens have reached 0.12% expansion level and accumulated 0.82% of water after immersion in water at 20°C for one year. These are very small values in comparison with many composite materials. However, standard specimens soaked in water at 40°C, 60°C, and 80°C showed a higher strength loss which increases with the increasing temperature of the water. The slight deterioration in water at 20°C and the large deterioration in hot water were attributed to further hydration of unreacted high alumina cement through absorption of water, allowing split growth in the polymer cement interface.

Stabilization of high alumina cement in the surface layer by hydrating at high temperatures for a specified time interval (the immunization) improves long term durability in ambient temperature.

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