Preparation and characterization of absorbent polymer-cement composites

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Abstract

Absorbent polymer-cement composites were fabricated by casting and pressing. Homogeneity was ascertained by semidry mixing of cements with absorbent polymer-absorbed theoretical water content. Because the cement-absorbent polymer composites were fabricated using homogeneous semidry mixing at low water-to-cement ratios, their total accumulation porosity was less than 5 vol% in terms of volumetric porosity. In particular, the composites showed a very small volume of pores larger than 1 μm pore; hence, the flexural strength of composites apparently were increased over that of neat cement pastes. The average flexural strength was up to 280 kgf/cm^2 for hydrated composites with 1 wt% absorbent polymer added and cured for 28 days. When adding absorbent polymer from 0.5 to 2.0 wt% was added to Portland cement, the hydration of cement was not retarded. Because the absorbent polymer filled interparticle capillary pores and hydrates in the form of thin plate dominated, the microstructure of the absorbent polymer-cement composite was denser and the capillary pore structure changed intermittently. Accordingly, the mechanical properties of absorbent polymer-cement composite improved.   © 1999 Elsevier Science Ltd. All rights reserved.

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Cement-based materials traditionally have been formed by casting. The amount of water used determines the porosity of the hardened materials. The excess water requirements needed to raise the workability of cement paste and the tendency for cement grains to agglomerate result in hardened cement paste having high porosity and a wide range of pore sizes [1–3]. Consequently, these materials are not very strong, and they contain critical flaws and an open microstructure. Because most absorbent polymers have a general absorption mechanism driven by the ion concentration gradient, they show very stable water absorbency under physical conditions such as temperature and applied load, but various absorbency and absorption forms under chemical conditions such as high-valence metal ions and pH of the solvent [4]. Absorbent polymers used in this study have higher cross-linking density than that of water-soluble polymer, which has been used to fabricate the MDF-cement composite [1], and released the water with a change in only a chemical condition such as pH or ion concentration. Because the cations leached from the surface of cement grains to water, the pH of the cement solution rose to 12.5 to 13.5

in a few minutes. If both are mixed, the cements dissolve gradually and the absorbent polymer releases the water with the passing of time. The leaching of some multivalent ions from cement grains accelerates the rate of water release, and the rate of hydration depends on the quantity of water released by absorbent polymer. Therefore, we considered the addition of absorbent polymer to cement in this study from the following standpoints.

1. Optimization of fabricating absorbent polymer-cement composite,
2. Effect of absorbent polymer on the physical properties of the absorbent polymer-cement composite, and
3. Variation of the cement hydration process for adding absorbent polymer.

1. Experimental

1.1. Materials

Ordinary Portland cement (OPC) of industrial origin (ASTM type I) with fineness of 3483 cm^2/g was used. Table 1 lists its chemical composition. Absorbent polymers used in this study were all acryl groups. Absorbent polymer A is a degenerated acrylic polymer, polymer B is a condensed

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Table 1
Chemical composition of ordinary Portland cement

Composition	Wt%
SiO_2	21.48
Al_2O_3	5.29
Fe_2O_3	3.03
CaO	63.31
MgO	2.80
SO_3	2.45
Na_2O	0.072
K_2O	0.873
Alkali	0.80
Ignition loss	1.16

acrylic polymer, and polymer C is an acrylic sodium salt [4,5]. The three absorbent polymers used have spherical morphologies. Table 2 lists their physical properties. Absorbent power 0.7%, 0.85%, and 1.0% by weight was mixed with cement powder. Cement and absorbent polymer were mixed in powder form in a rotating ball mill and water sprayed from inside [6]. Cement grains surrounded the wet polymer gel and formed agglomerates of 100 to 200 μm. Macroscopic homogeneity was ascertained by this process, named the semidry mixing process. After mixing, the mixture was compacted at a pressure of 30 kgf/cm^2. Initial water-to-cement ratios were 0.20, 0.25, 0.30, and 0.35 before compaction and final ratios were 0.10, 0.15, 0.20, and 0.20. The samples were fabricated by casting and cured for 28 days in a cylindrical box at room temperature.

1.2. X-ray diffractometry

The samples were examined by X-ray diffractometry (XRD) after curing for 3, 7, and 28 days using powdered samples, ground in porcelain and agate mortars. XRD patterns were obtained with a D-MAX/3CX diffractometer (Rigaku Co., Japan) using Cu Kα radiation. The operating conditions were 30-KeV accelerating voltage, 15-mA current, 5° to 60° 2θ, and scanning range 1000 counts/s.

1.3. Scanning electron microscopy

To investigate the effect of absorbent polymer on the microstructure of hydrated paste, we observed the fracture surfaces of samples using scanning electron microscopy (JSM-5400, JEOL Co., Japan).

1.4. Porosimetry

Mercury intrusion porosimetry (evacuation pressure 40 mmHg, evacuation time 5 min, mercury filling pressure 1.0186 psi, equlibrium time 10 s, range 0.0030 to 300 μm) was used to measure the porosity and pore size distribution of the samples.

2. Results and discussion

2.1. Characteristics and effects of absorbent polymer on the hardened pastes

We examined the absorption power of the three different absorbent polymers in three kinds of solvents for application to cement. Figs. 1–3 show the absorbency of absorbent polymers under the different conditions. The acrylic acid-system condensed polymer B and the acrylic sodium-salt polymer C showed about 550× absorbency of their own weight, but the degenerated acrylic system-condensed polymer A showed about 250× absorbency of its own weight. In order of absorption rate was fine particle polymer A, spherical polymer C, and crushed polymer B. The absorbency of the degenerated polymer A was stable in NaCl and CaCl$_2$ solution, but polymers B and C showed a large reduction of absorbency. Because the polymer A was degenerated, the ionic electrolyte did not incorporate very well into the network of polymer main chains. The absorbency of polymers B and C decreased only slowly with increasing NaCl concentration, but abruptly in CaCl$_2$ solutions. It is thought that the absorbency of polymer depends on the valence of ionic electrolytes in accordance with the Flory's three-dimensional network theory [4]. The absorbency of the polymers in solution leached from cement pastes is shown in Fig. 3.
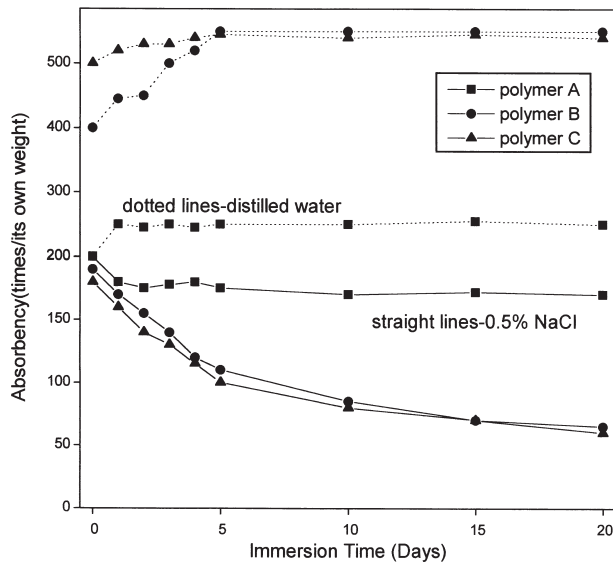
Table 2
Physical properties of the absorbent polymers

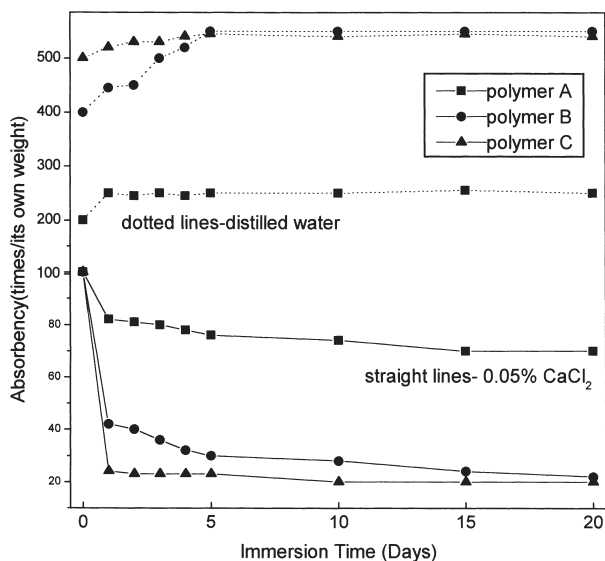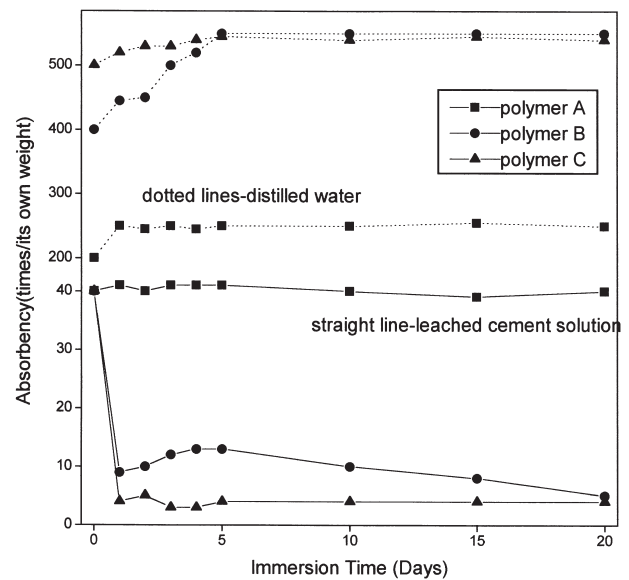|	Polymer		
Property	A	B	C
Appearance	White spherical fine powder	White crushed fine powder	White spherical powder
Average particle size			
Before absorbing	0.1–l μm	80–120 μm	20–30 μm
After absorbing	Emulsion + gel	150–300 μm	40–90 μm
Density			
Apparent density	—	0.95–1	0.95–1
True density	1.354 g/cm^3	1.2746 g/cm^3	1.5547 g/cm^3
Water content	~5%	~5%	~5%
pH (0.1% dispersion)	Neutral	Neutral	Neutral
Leaching rate (0.1% dispersion)	—	1%	1%
Absorbency (times/own weight)	200–250	500–550	500–550

Fig. 1. Absorbency of polymers with time (0.5% NaCl solution).

Fig. 3. Absorbency of polymers with time (leached cement solution).

For polymer C, its absorbency behaved similar aspects as that in $CaCl_2$ solution and much reduced to $4\times$ absorbency of its own weight. It was considered from these results that the contribution of polymer C to initial hydration in cement matrix would be the largest because the $4\times$ remnant water should affect the long hydration time and improve the long-term flexural strength. To choose a polymer suitable for this study, experiments of flexural strength were carried out. Fig. 4 shows the flexural strength of cement composites containing three kinds of the absorbent polymers. It was observed that adding polymer C resulted in the highest flexural strength at all hydration times, because polymer C had excellent mixing properties with cements. Therefore, we re-

garded the absorbent polymer C as the suitable polymer for cement composite. From this point on, polymer means the absorbent polymer C. Fig. 5 shows the flexural strength of cement composites as a function of water-to-cement ratio. Flexural strength increased as the W/C ratio increased up to W/C = 0.30. It also increased as the polymer content increased up to 1.0 wt%, as shown in Fig. 6. It is considered that less agglomerated cement particles did not hydrate well, whereas excess polymer particles formed mostly polymer-polymer contacts when content was above 1.0 wt%. Because the isolated particle size of the polymers surrounded by cement grains increased, the flexural strength did not increase as the absorbent polymer added rose to

Fig. 2. Absorbency of polymers with time (0.05% $CaCl_2$ solution).
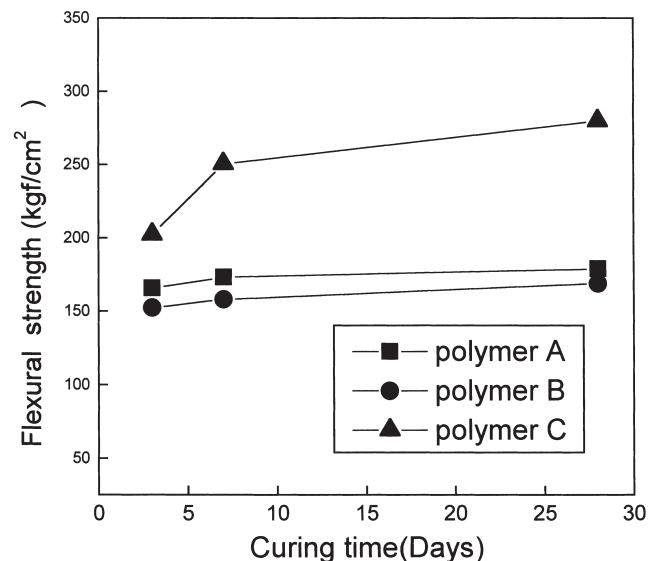

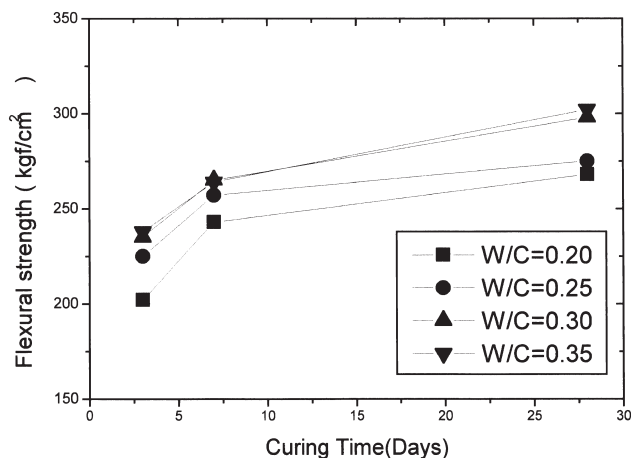Fig. 4. Flexural strength of hydrated cement-various polymer composites.

Fig. 5. Flexural strength of cement-absorbent polymer C composite as a function of initial water-to-cement (W/C) ratios.

above 1.0 wt%. The results of pore size distribution for the absorbent polymer-cement composite are shown in Fig. 7. Compared to the controls that did not contain absorbent polymer, specimens containing 0.85 and 1.0 wt% of absorbent polymer decreased in pore volume approximately 4.2% and 3.7%, respectively. It is considered that because homogeneity was ascertained by semidry mixing with absorbent polymer, the pore volume containing macropores (pores larger than 1 μm) of the absorbent polymer-cement composite was significantly lower than that of the controls [5].

2.2. Effects of absorbent polymer on cement hydration

To determine the effects of absorbent polymer on cement hydration, calorimetric and XRD analyses were performed. The results are shown in Figs. 8–12. As polymer content increased from 0.5 to 2.0 wt%, the initial heat evolution curves of cement hydration showed two stages. The initial heat evolved increased as the polymer content increased at stage 1, but the heat evolution curves showed a similar tendency to that of controls after 0.3 h. In the initial hydration
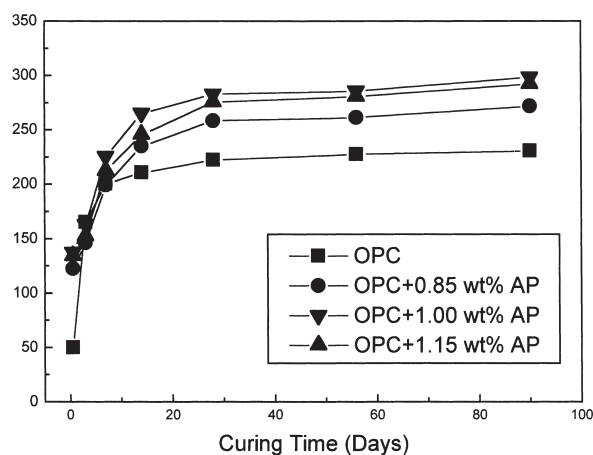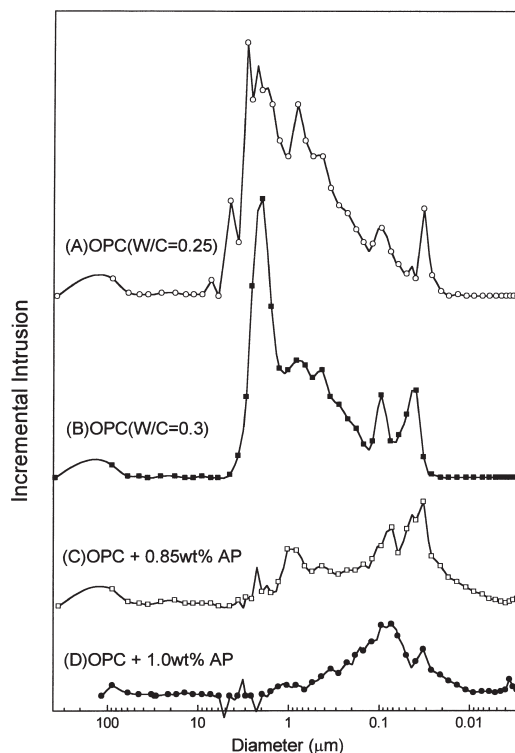

Fig. 7. Pore size distribution of cement-absorbent polymer by mercury intrusion porosimetry.

period, additional heat is considered to have evolved when the polymer was converted to polyacrylic acid under high pH and some of the polyacrylic acid cross-linked with metal ions leached from cement grains to form metal polyacrylate. After 0.3 h, the heat evolution curves showed the plateau at stage 2 because the equilibrium of dissolution and precipitation of polymer functions was reached. In Fig. 9, the heat evolution curves up to 72 h did not show a difference between the absorbent polymer-cement composite and controls. It is considered that because extraction of water from polymer chains was very fast, absorbent polymer did not disturb hydration of cement. Retardation of cement hydration by the absorbent polymer was not observed below 2
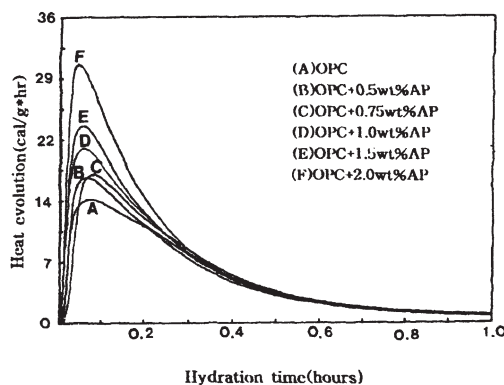

Fig. 6. Flexural strength of cement-absorbent polymer composites.

Fig. 8. Heat evolution curves of cement polymer mixture during 1 h.
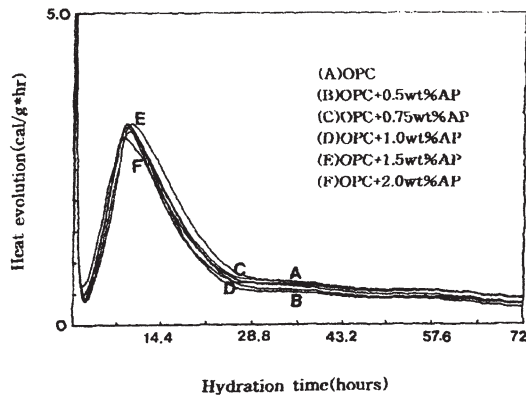
Fig. 9. Heat evolution curves of cement polymer mixture during 72 h.

Fig. 11. XRD patterns of specimens hydrated for 7 days.

wt% absorbent polymer. The X-ray diffractograms of neat cement and absorbent polymer-cement for 3, 7 and 28 days of hydration are shown in Figs. 10–12.

In both cases the hydration process increased with time. As expected, the peak of $Ca(OH)_2$ ($2\theta = 18.1$) grows in intensity, whereas those of C_3S ($2\theta = 4 1.6$) decrease in intensity.

One of the most striking features of the absorbent polymer-cement composite viewed by SEM, shown in Fig. 13, was the lack of defects such as air bubbles and cracks that normally occur in cement pastes cast at higher water-to-solid ratios. Because the absorbent polymer filled interparticle capillary pores, the microstructure of absorbent polymer-cement composite was denser than that of controls and capillary pore structure of absorbent polymer-cement composite changed intermittently. The crystalline plate, thought to be calcium hydroxide in terms of crystallone feature, reinforced the microstructure of the cement-absorbent polymer composite like the precipitators in general composites. The microstructure of the absorbent polymer-cement composite was denser and flatter than that of neat cement paste.
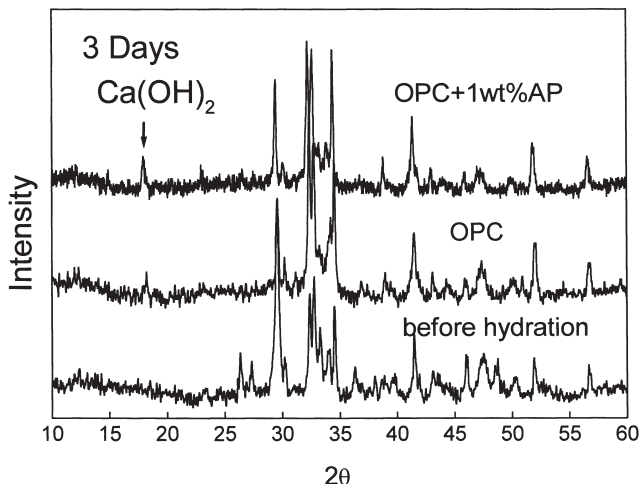
3. Conclusions

1. Homogeneity was ascertained by semipowder mixing of cements with absorbent polymer-absorbed theoretical water requirements and the formability of absorbent polymer-cement composite was approved.
2. Compared to controls that did not contain absorbent polymer, the absorbent polymer-cement composites containing 0.85 and 1.0 wt% absorbent polymer decreased in pore volume approximately 4.2 and 3.7 vol%, respectively. The principal mean pore size of the absorbent polymer-cement composites was about 0.1 μm of pore radius.
3. The average flexural strength was up to 280 kgf/cm^2 in the case of hydrated composites with 1 wt% of the absorbent polymer cured for 28 days.
4. When absorbent polymer from 0.5 to 2.0 wt% was added, retardation of cement hydration was not observed.

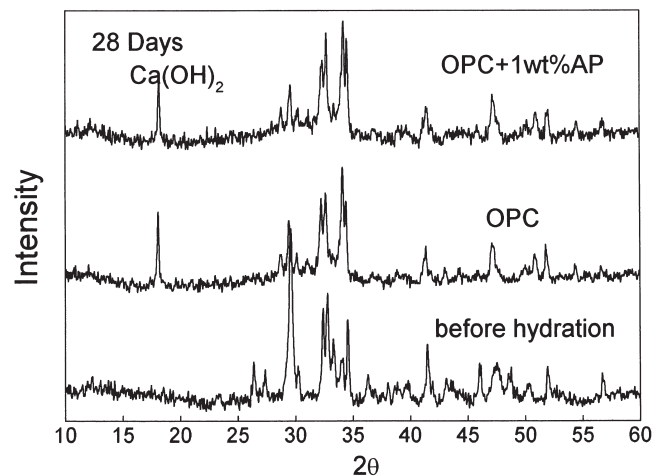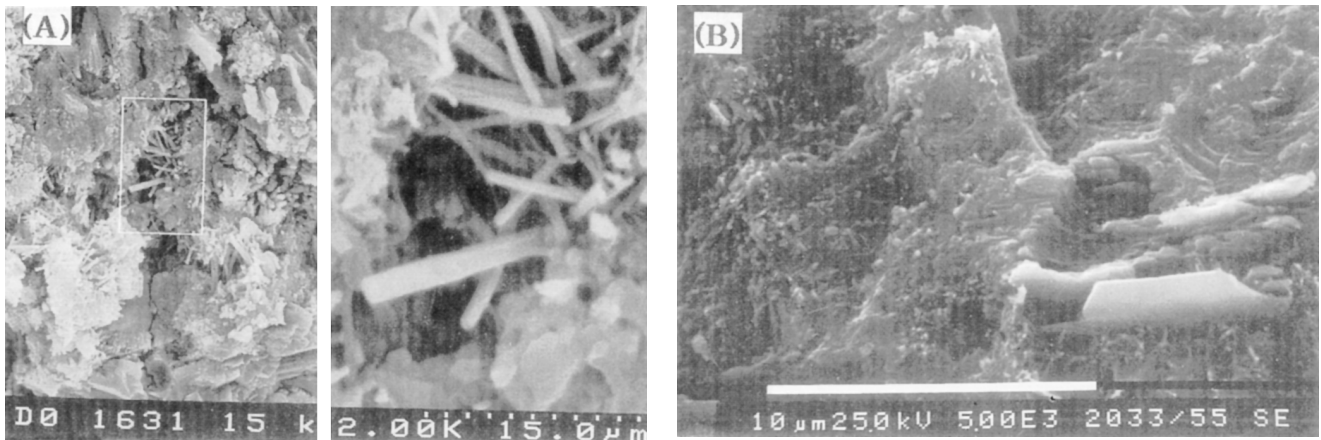Fig. 10. XRD patterns of specimens hydrated for 3 days.

Fig. 12. XRD patterns of specimens hydrated for 28 days.

Fig. 13. Scanning electron microscopic photographs of OPC and absorbent polymer-cement composite hydrated for 28 days. (*A*) OPC; (*B*) OPC + 1 wt% AP (absorbent polymer).

5. Hydrates in the form of a plate predominated, and the inner microstructure of the composite was denser than that of neat cement paste.

Acknowledgments

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