ELSEVIER

Zeolite-Based Additives for High Alumina Cement Products

Yan Fu,* Jian Ding,* and J.J. Beaudoin†
*Department of Civil Engineering, University of Ottawa, Ontario, Canada and
†Materials Laboratory, Institute for Research in Construction, National Research Council,
Ottawa, Ontario, Canada

Use of zeolites as conversion-preventing additives (CPA) for inhibition of hydrogarnet formation in high alumina cement (HAC) products is reported. Compressive strength development of HAC mortars containing the CPA additive was studied. The effect of curing conditions, from low initial temperatures to final high temperatures, on strength development was also investigated. X-ray diffraction (XRD) analysis was used to identify the hydration products in the HAC paste containing CPA. No strength reduction occurred for the HAC mortar (containing 12% CPA by mass of HAC) water-cured at 38°C. Strälingite preferentially formed in the HAC paste containing the CPA additive. Little or no hydrogarnet phase in the paste was detected by XRD analysis. Advanced Cement Based Materials 1996, 3, 37–42

KEY WORDS: Additive, Compressive strength, Conversion, Curing temperature, High alumina cement, Zeolite

High alumina cement (HAC) was invented in 1908 by J. Bied at the Pavin de Lafarge Company in France. Spackman was the first to obtain a U.S. patent for this material [1]. Commercial HAC was produced by the Lafarge company in 1913. This cement is based upon calcium monoaluminate (CA). Hydration eventually results in formation of hydrogarnet (C_3AH_6) crystalline phase, a thermodynamically stable calcium aluminate hydrate. High early strength, good chemical resistance, and high temperature resistance of HAC products encouraged the use of high alumina cement concrete in certain construction engineering applications. However, conversion of hexagonal calcium aluminate hydrates (CAH_{10} or C_2AH_8) to cubic hydrogarnet (C_3AH_6) in hydrated HAC concrete under certain environmental conditions, such as high temperature and relative humidity, has been a major problem limiting its use. The conversion process causes a decrease in the solid-phase volume, while the bulk dimensions of the hardened cement remain the same. This results in an increase in porosity and a loss of strength. Consequently, a significant reduction of strength during the service life of the concrete occurs. Many high alumina cement concrete structures built in the United Kingdom in the 1940s and 1950s collapsed due to later conversion. The British government as a direct result of those investigations issued a document that stated, "High alumina cement should not be used for structural work in buildings until further notice" [2]. The application of high alumina cement in structural members has been banned in virtually every country in the world.

The conversion process in the HAC system has been extensively studied for decades. An HAC-based blended cement containing about equal amounts of cement and ground granulated blast-furnace slag (ggbs) by mass was commercialized by the Building Research Establishment (BRE), U.K., with the trademark BRECEM. It was touted as a possible solution for prevention of the conversion reaction [3,6]. This was attributed to strätlingite formation in preference to the hydrogarnet. Other pozzolanic additives such as silica fume and fly ash have also been reported to favor the formation of strätlingite. The early strength of such material is significantly reduced as a large amount of HAC is replaced by ggbs. Strength slowly increases to a value approaching the 1-day strength of HAC concrete when water-cured at 20°C. Hydrogarnet was still formed at 38°C although the HAC/ggbs blended cement concrete had no strength reduction. Because hexagonal calcium aluminate hydrates are thermodynamically unstable at the temperature higher than 25°C, it was concluded that "the approach to aluminous cement concrete that seeks to avoid conversion is unrealistic" [7].

Reaction mechanisms involved in strätlingite formation in the HAC-microsilica-water system have been postulated by the authors [8,10]. This reaction involves the conversion of the unstable calcium aluminate hydrates to strätlingite contributing to strength development. Deleterious formation of hydrogarnet is avoided. It was determined that silicate plays a significant role in

---

Address correspondence to: J.J. Beaudoin, Materials Laboratory, National Research Council, Institute for Research in Construction, Ottawa, Ontario K1A OR6 Canada.
Received February 23, 1995; Accepted May 30, 1995

655 Avenue of the Americas, New York, NY 10010

ISSN 1065-7355/96/$15.00
SSDI 1065-7355(95)00043-Q

the process of strätlingite formation in the HAC-microsilica system. Silica reacts to form silicates in a high pH environment. This reaction is accelerated in the presence of alkali ions. The alkali ions probably act as a catalyst for reactions involving microsilica. Dissolved silicate anions then react with hydrated calcium aluminates (C_2AH_8 or CAH_{10}) to produce strätlingite. Taylor argued [11] that the pozzolanic reactivity of microsilica depends more on the nature of impurities, such as alkali content, than on the fineness or SiO_2 content. Natural zeolite is a porous silicoaluminate mineral. Its structure consists of a three-dimensional framework of SiO and AlO tetrahedra. Compositionally zeolites may be given the general formula:

$$(M^+{}_2, M^{2+}) \cdot O \cdot Al_2O_3 \cdot gSiO_2 \cdot zH_2O$$

M^+ is usually Na or K; M^{2+} is Mg, Ca, or Fe. Zeolite has high pozzolanic reactivity. It can react to form silicates in the HAC system.

A new zeolite-based conversion-preventing additive has been recently developed at the National Research Council, Canada [12]. The research included a study on conversion prevention mechanisms in high alumina cement systems. Investigations on the application of improved high alumina cement were also conducted. The results of an investigation to determine the strength characteristics of high alumina cement products containing zeolite-based conversion-preventing additives are reported.

Experimental

Materials

The materials used consisted of HAC (Ciment Fondu, containing SiO_2 4.5%, CaO 39.8%, Fe_2O_3 11.3%, Al_2O_3 41.2%, MgO 0.6%, $Na_2O + K_2O$ 0.1%, produced by Lafarge Calcium Aluminates, Virginia), natural zeolite A containing mainly clinoptilolite and gismondine (American Resource Corporation, Inc., California), natural zeolite B containing mainly clinoptilolite and gismondine (Polar Powder Technologies, Inc., Alberta, Canada), and natural zeolite C containing mainly clinoptilolite, levyne, and offretite (Zeotech Corporation, New Mexico). The X-ray diffraction patterns of the zeolites are shown in Figure 1 and the oxide compositions are listed in Table 1.

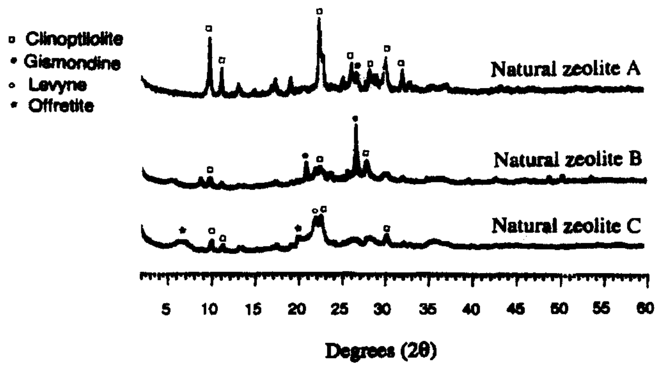

FIGURE 1. X-ray diffraction patterns of the zeolites.

TABLE 1. Oxide composition of selected natural zeolites

Oxides (% by mass)	Natural Zeolite A	Natural Zeolite B	Natural Zeolite C
SiO_2	69.1	65.8	65.7
Al_2O_3	11.9	14.3	12.5
CaO	0.7	3.4	2.0
Fe_2O_3	0.7	2.6	1.7
MgO	0.4	1.3	0.9
Na_2O	3.5	2.5	1.5
K_2O	3.8	2.7	1.7
MnO	4.9	0.04	0.9

Conversion-preventing additives (CPA) comprising a natural zeolite and sodium sulfate were also used. Heat treatment (calcination at about 800°C for 2 hours) was used during the preparation of selected zeolites. Different CPAs used in this study are listed in Table 2.

Sample Preparation

COMPRESSIVE STRENGTH TEST. Cement mortars were prepared for determination of compressive strength. The sand:cement ratio was 2.75 and the water:solid (HAC + additive) ratio was 0.40. Composition of the specimens is given in Table 3. The cement mortar was mixed for 3 minutes and then cast in 50.8 × 50.8 × 50.8-mm cubic molds. The specimens were demolded after 24 hours of moist-curing at 23°C. The 1-day compressive strength was determined after demolding. Companion specimens were placed in water at 38°C after demolding. Compressive strength was determined at designated ages.

MICROSTRUCTURE ANALYSIS. Mixes of the HAC pastes for microstructure analysis are listed in Table 4. The cement

TABLE 2. Different conversion-preventing additives

Additives	Composition (% by mass) Zeolite	Composition (% by mass) Sodium Sulfate	Natural Zeolites Type	Natural Zeolites Heat-Treatment
CPA-A	86	14	A	—
CPA-B	86	14	B	—
CPA-B(H)	95	5	B	800°C for 2 h
CPA-C	86	14	C	—
CPA-C(H)	93	7	C	800°C for 2 h

TABLE 3. Specimen composition (arbitrary mass units)

Specimens	HAC	Zeolite* (Type/Content)	CPA† (Type/Content)	Sand	Water
Plain HAC	1	—	—	2.75	0.4
Z-A	0.77	A/0.23	—	2.75	0.4
Z-B	0.77	B/0.23	—	2.75	0.4
CPA-1	0.89	—	CPA-A/0.11	2.75	0.4
CPA-2	0.89	—	CPA-B/0.11	2.75	0.4
CPA-3	0.89	—	CPA-C/0.11	2.75	0.4
CPA-4	0.83	—	CPA-B(H)/0.17	2.75	0.4
CPA-5	0.83	—	CPA-C(H)/0.17	2.75	0.4
CPA-6	0.67	—	CPA-C(H)/0.33	2.75	0.4

*Zeolite A and B contain no addition of sodium sulfate.
†All CPA materials contain addition of sodium sulfate.

paste samples were prepared with a high water: solid ratio (0.60) to allow rapid hydration of HAC. The paste samples were cast in 25-mm diameter bottles and rotated on a machine for 24 hours at 38°C. Samples were water-cured at 38°C after demolding. X-ray diffraction analysis was carried out on the wet sample after grinding in an agate mortar. Fractured surfaces were examined by scanning electron microscopy. A Rigaku X-ray diffractometer system Geigerflex D/Max-B was used for X-ray studies. A Cambridge Stereoscan S250 SEM was employed for scanning electron microscopy investigations.

Results and Discussion

The effect of zeolites on the strength of HAC mortars is shown in Figure 2. The compressive strength of plain HAC mortar was about 65 MPa after 24 hours of moist-curing at 23°C. Strength then decreased to about 35 MPa after 14 days water-curing at 38°C. A slight strength recovery occurred after 14 days. The compressive strength of HAC mortar containing 30% zeolites by mass of HAC was about 55 MPa after 24 hours of moist-curing at 23°C. The strength reduction of HAC mortar containing Zeolite-A appeared to be slightly reduced. Little or no effect of Zeolite-B on strength reduction of HAC mortar was found. Zeolite might accelerate the strength recovery. The 150-day strengths of HAC mortar containing Zeolite A or Zeolite B were approximately the same as plain HAC mortar. Evidence for invocation of the conversion reaction was also provided by the X-ray diffraction (XRD) analysis of each HAC paste after 60 days of water-curing at 38°C (Figure 3). Cubic hydrogarnet (C_3AH_6) crystals were found to be the major mineral phase present in all the samples. The hydrogarnet formation corresponds to the strength reduction.

The effect of conversion-preventing additives (CPAs) on strength development of HAC mortars is shown in Figure 4. It was found that the strength reduction of HAC mortar was prevented by using about 12% CPA by mass of HAC. The 1-day strength of HAC mortar containing CPA-A additive was 60 MPa. Little or no strength development occurred from 1 day to 28 days. Strength increased to 72 MPa at 150 days. The 1-day strength of HAC mortars containing CPA-B additive

TABLE 4. High alumina cement pastes used for microstructure analysis

Samples	HAC	Zeolite (Type/ Content)	Additive (Type/ Content)	Water
1	1	—	—	0.6
2	0.83	A/0.17	—	0.6
3	0.83	B/0.17	—	0.6
4	0.83	C/0.17	—	0.6
5	0.80	—	CPA/A/0.20	0.6
6	0.80	—	CPA-B/0.20	0.6
7	0.80	—	CPA-C/0.20	0.6

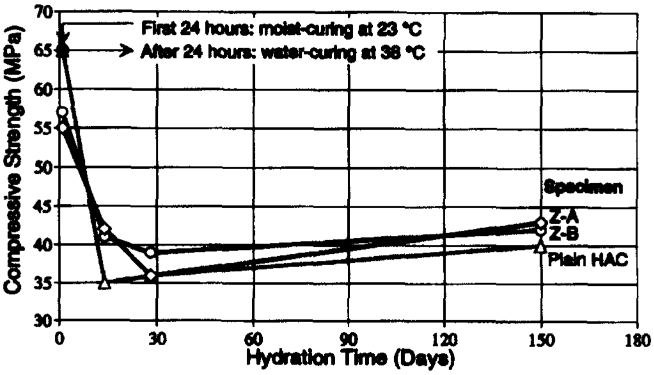

FIGURE 2. Effect of zeolite addition on compressive strength development of high alumina cement (HAC) mortars. Z-A contains natural zeolite A. Z-B contains natural zeolite B.

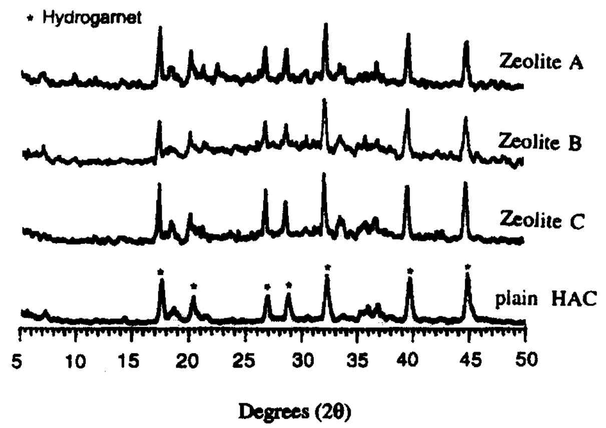

FIGURE 3. The X-ray diffraction spectra of the high alumina cement (HAC) pastes containing zeolites at 60 days.

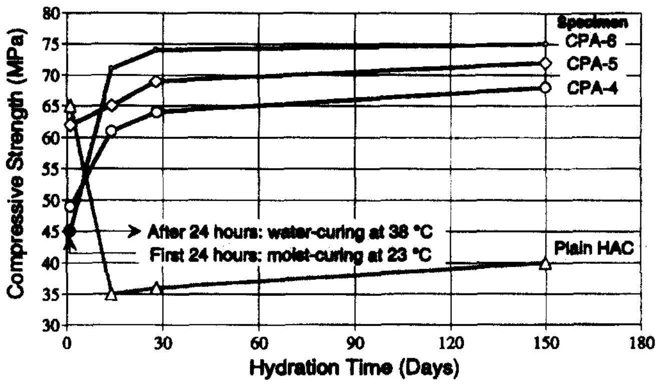

FIGURE 5. The effect of heat-treated conversion-prevention additives (CPAs) on compressive strength development of the high alumina cement (HAC) mortars. Specimen composition is given in Table 2.

was about 43 MPa. Its strength increased to 51 MPa in 28 days. No further strength change was found after 28 days. A large strength increase was recorded for the HAC mortar containing CPA-C additive. Its 28- and 150-day strength values were 57 and 65 MPa, respectively.

Heat treatment of the CPAs appeared to result in significant improvement in strength development of the HAC mortars (Figure 5). High strength developed in all the samples during 28 days of hydration. A significant strength increase was found in the HAC mortar (CPA-6) containing 50% CPA-C(H) additive. Its strength increased from 45 MPa at 1 day to 71 MPa at 14 days. The strength gain rate decreased after 14 days. The 28-day and 150-day strengths were 74 and 75 MPa, respectively. Decrease of CPA-C(H) additive addition (e.g., 20% by mass of HAC) greatly increased 1-day strength to about 62 MPa. It, however, resulted in less strength gain at later ages. Its strength values at 14, 28, and 150 days were 65, 69, and 72 MPa, respectively. The 1-day strength of the HAC mortar (CPA-4) containing 20% CPA-B(H) additive was much less than that containing CPA-C(H) additive (CPA-5). Its strength increased from 49 MPa at 1 day to 61 MPa at 14 days. The strength then slowly developed to 64 MPa at 28 days and to 68 MPa at 150 days.

The HAC concrete structure may not initially be cured at elevated temperature in practice. Strength reduction of the HAC concrete due to conversion occurs at later ages when the ambient temperature increases, for example, in the summer. The effect of a temperature shift from low to high on the strength change of the HAC mortars with age was studied (Figures 6 and 7). The specimens were moist-cured at 23°C for the first 28 days followed by water-curing at 38°C. The light and dark curves represent 23°C moist-curing and 38°C water-curing, respectively, in Figures 6 and 7. C_2AH_8 was the dominant phase of hydrated HAC at 28 days when

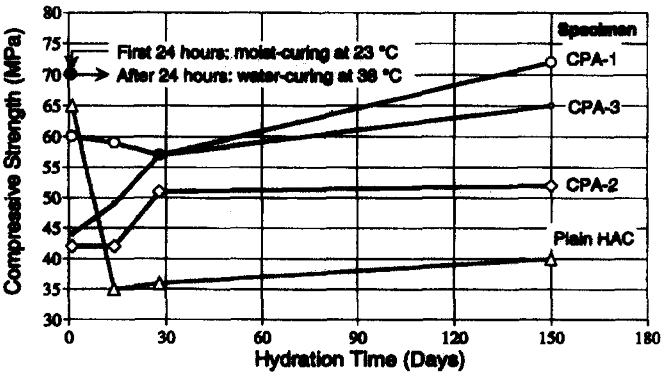

FIGURE 4. The effect of conversion-preventing additives (CPAs) on compressive strength development of high alumina cement (HAC) mortars. Specimen composition is given in Table 2.

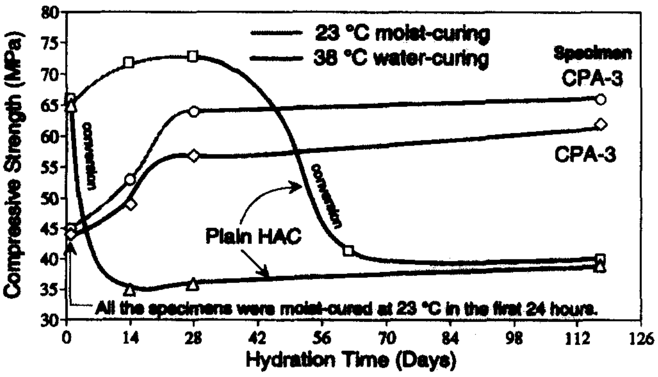

FIGURE 6. The effect of curing condition on compressive strength development of the high alumina cement (HAC) mortar containing a conversion-preventing additive (CPA-C; see Table 2).

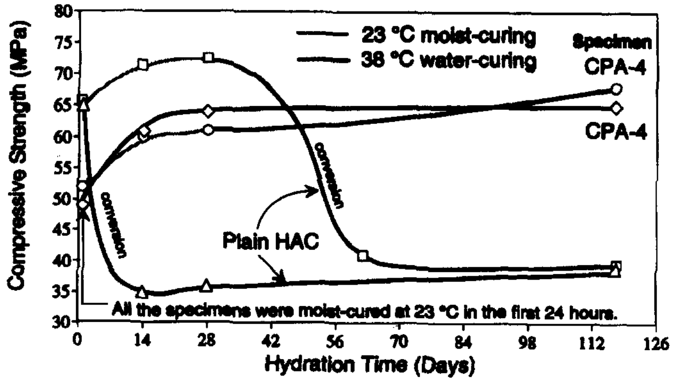

FIGURE 7. The effect of curing condition on compressive strength development of the high alumina cement (HAC) mortar containing a heat-treated conversion-preventing additive (CPA-B(H); see Table 2).

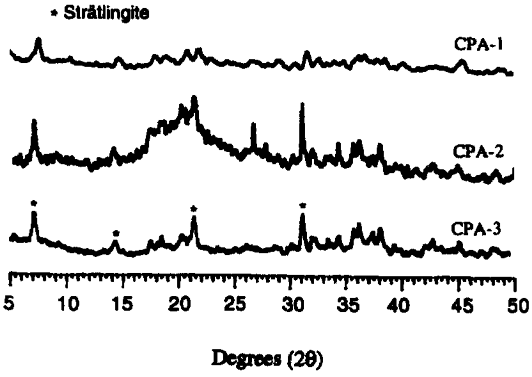

FIGURE 8. The X-ray diffraction spectra of the high alumina cement (HAC) pastes containing different conversion-preventing additives (CPAs) at 28 days.

moist-cured at 23°C. Significant strength reduction was found in the plain HAC mortar after the curing temperature shifted to 38°C. The compressive strength decreased from 72 MPa at 28 days (moist-curing at 23°C) to about 40 MPa at 60 days (following water-curing at 38°C after the first 28 days). Further strength reduction from 60 days to 150 days was minimal.

No strength reduction was found in the HAC mortar containing a CPA additive after the curing condition shifted from 23°C moist-curing to 38°C water-curing. The HAC mortar containing the CPA-C additive and moist-cured at 23°C had higher strength than the water-cured mortar at 38°C from 1 day to 28 days (Figure 6). There was a slight difference in the compressive strength of the HAC mortars containing the heat-treated CPA-B(H) additive at the two different initial curing conditions (Figure 7). The strength of all the specimens increased slowly from 28 days to 150 days when cured at 38°C.

The XRD spectra of the HAC pastes containing different conversion-preventing additives (comprising different types of zeolite) are shown in Figure 8. Little or no hydrogarnet was detected in the HAC pastes containing CPA. Strong peaks corresponding to the strätlingite phase were found in these samples. Strätlingite formation during HAC hydration has been reported to have a role in the prevention of strength reduction in HAC products [8,10]. The role of the sodium salt component of the CPAs has been studied. It appears that crystallization of hexagonal strätlingite plates in hydrated high alumina cement systems containing zeolites is significantly accelerated in the presence of sodium ions and its amount is greatly increased. Sodium ions appeared to play a significant role in strätlingite formation in HAC-zeolite systems. It is postulated that crystallization of strätlingite results from the reaction between CAH_{10} or C_2AH_8 and dissolved silica. Sodium ions promote increased dissolution of silica required for strätlingite formation. Hydration of zeolites in HAC paste without addition of sodium salt was relatively slow. Strätlingite nucleation and crystallization appears to be dependent on the dissolved silica concentration in the HAC-zeolite system. Strength reduction was prevented when strätlingite formed in preference to hydrogarnet. Well-developed plate-like strätlingite crystals were commonly found in the HAC paste containing CPA additives. A typical SEM micrograph (Figure 9) shows the presence of strätlingite in an HAC paste containing 20% CPA-C additive by mass of the HAC.

Conclusions

1. The use of newly developed CPAs in HAC mortars can effectively prevent strength reduction due

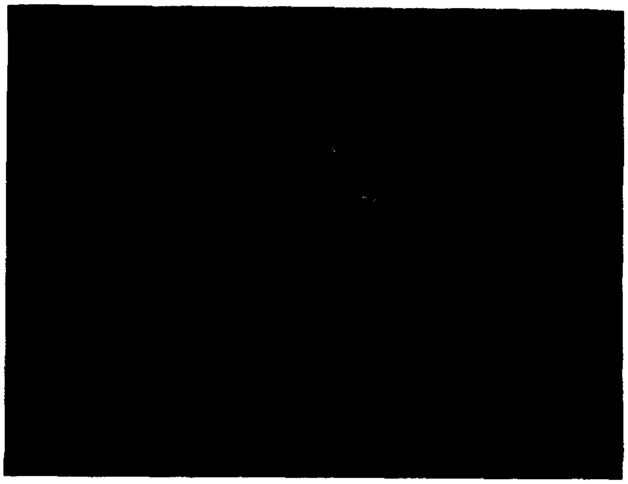

FIGURE 9. SEM micrographs of the high alumina cement (HAC) paste containing a conversion-preventing additive (CPA-C, see Table 2) at 60 days.

to conversion of hexagonal aluminate hydrates to hydrogarnet. The effective addition of CPA in HAC mortar ranges from 12 to 50% by mass of HAC.
2. Strätlingite rather than hydrogarnet is preferentially formed in HAC paste containing CPA.
3. The 1-day compressive strength of HAC mortar containing CPA and moist-cured at 23°C ranges from 40 to 60 MPa.
4. The compressive strength of HAC mortar water-cued at 38°C and containing CPA slowly increases with the hydration time.
5. Addition of heat-treated CPA to HAC mortar results in much higher 1-day compressive strength values than non-heat-treated CPA.
6. Increase of heat-treated CPA content in amounts greater than 50% in the HAC products decreases the 1-day compressive strength values but significantly increases strength after 14 days.
7. A shift in curing temperature from initially low to finally high values does not adversely affect strength development of HAC mortar containing CPA.

Acknowledgment

Financial support from Natural Sciences and Engineering Research Council of Canada and the Network of Centers of Excellence on High Performance Concrete is gratefully acknowledged.

References

1. Spackman, H.S. *Proc. Am. Soc. Test. Mater.* **1910,** *10,* 315.
2. *High Alumina Cement Concrete in Buildings;* Ref. BRA 1068/2; July 20, 1974.
3. Majumdar, A.J.; Singh, B.; Edmonds, R.N. *Cem. Concr. Res.* **1990,** *20,* 197.
4. Singh, B.; Majumdar, A.J. *Cem. Concr. Res.* **1992,** *22,* 1019.
5. Majumdar, A.J.; Singh, B. *Cem. Concr. Res.* **1992,** *22,* 1101.
6. Rayment, D.L.; Majumdar, A.J. *Cem. Concr. Res.* **1994,** *24,* 335.
7. George, C.M. In *Calcium Aluminate Cements;* Chapman & Hall: New York, 1990; p 126.
8. Ding, J.; Fu, Y.; Beaudoin, J.J. Submitted for publication.
9. Ding, J.; Fu, Y.; Beaudoin, J.J. *Cem. Concr. Res.* **1995,** *25,* 1311.
10. Ding, J.; Fu, Y.; Beaudoin, J.J. *Adv. Cem. Res.,* in press.
11. Taylor, H.F.W. *Cement Chemistry;* Academic Press: London, 1990; pp 305–306.
12. Fu, Y.; Ding, J.; Beaudoin, J.J. *U.S. Patent Application,* No. 081377,109, filed on Jan. 23, 1995.