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Effect of Different Inorganic Salts/Alkali on Conversion-Prevention in High Alumina Cement Products

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The hydration characteristics and strength development of a high alumina cement (HAC)/zeolite blended cement in combination with an inorganic salt or alkali, selected from a suite of compounds including sodium sulfate, sodium carbonate, sodium nitrate, sodium chloride, sodium bromide, sodium metaphosphate, sodium metasilicate, sodium hydroxide, potassium hydroxide, potassium carbonate, lithium chloride, copper sulfate, and aluminum sulfate, were studied. HAC/zeolite mortars containing a sodium salt experienced no strength reduction after being water-cured at 38°C for 150 days. Strätlingite formation is apparently promoted and hydrogarnet formation is significantly inhibited by the addition of sodium salts.

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High alumina cement (HAC), by virtue of its rapid hardening and good resistance to sulfate attack, has many specialized industrial applications including structural repair [1]. The use of HAC in structural applications is limited due to potential "conversion" of metastable calcium aluminate hydrates (hexagonal CAH_{10} or C_2AH_8) to stable hydrogarnet (cubic C_3AH_6). The conversion markedly increases the porosity of HAC products, because the density of C_3AH_6 is higher than that of CAH_{10} or C_2AH_8 [2]. The strength and durability of HAC decrease as a consequence. Three HAC concrete structures built in the United Kingdom in the 1950s and 1960s collapsed in the early 1970s. Strength reduction due to conversion was believed to be one of the contributions to the structural damage. HAC is no longer recommended for use in structural applications in the United Kingdom [3].

A number of studies have investigated alternative reaction paths for the metastable aluminates CAH_{10} or C_2AH_8 [e.g., forming strätlingite (C_2ASH_8) instead of converting to hydrogarnet] to avoid the strength reduction due to the conversion process. Midgley and Rao attempted to use hydrated portland cement as an additive for HAC to produce strätlingite; it was not successful [4]. A comparative study of the hydration of CA in the presence of C-S-H gel or βC_2S with varying degrees of fineness was reported by Rao and Viswanathan [5]. They observed that the metastable calcium aluminate hydrates could react with C-S-H gel to form strätlingite. The amount of strätlingite formed was dependent on the availability of C-S-H gel for reaction. Extensive research on the blended HAC/ground granulated blast-furnace slag (ggbs) system was carried out at the Building Research Establishment, United Kingdom. It was shown that the addition of a sufficient amount of ggbs to HAC cement could limit the conversion process [6,7]. Strength reduction due to conversion was eliminated in the HAC/ggbs concrete at later age; the 1-day strength was, however, significantly lower than that for plain HAC concrete [8–10]. The use of silica fume in combination with sodium tripolyphosphate in HAC mortars was reported by Marcdargent et al. [11]. It was shown that the sodium tripolyphosphate improved workability and minimized strength reduction of the HAC/silica fume mortar (w/c = 0.3) water-cured at 38°C. The action of sodium tripolyphosphate in minimizing strength reduction in the HAC/silica fume mortar was not understood. The significance of the role of alkali ions on strätlingite formation in the HAC-microsilica system was recently reported [12,13]. Microsilica reacts to form silicates in a high pH environment. This reaction is accelerated in the presence of an increased

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amount of alkali ions that may act as a catalyst activating microsilica surfaces. Silicate anions then react with hydrated calcium aluminates to produce strätlingite.

The work described in this paper is intended to demonstrate the effect of different inorganic salts and alkali on the strength development and formation of strätlingite and hydrogarnet in the HAC/zeolite blended cement systems.

Experimental

Materials

The materials for this study included the following: HAC, Ciment Fondu, was produced by Lafarge Calcium Aluminates, Virginia. Natural zeolite-A, containing mainly clinoptilolite, gismondine, and clay, was supplied by Polar Powder Technologies, Inc., Alberta, Canada. This material is gray in color with relatively low purity and low cost. It is extremely suitable for use in blended cement and was selected for compressive strength study. Natural zeolite-B, containing mainly clinoptilolite (+90%), levyne, and offretite, was supplied by Zeotech Corporation, New Mexico. This material is white in color and contains high purity zeolite minerals. It was selected for the study of strätlingite formation. Reagent grade salts that were used included sodium sulfate, sodium carbonate, sodium nitrate, sodium chloride, sodium bromide, sodium metaphosphate, sodium metasilicate, sodium hydroxide, potassium hydroxide, lithium chloride, potassium carbonate, copper sulfate, and aluminum sulfate. The oxide compositions of HAC, zeolite-A, and zeolite-B are listed in Table 1. Natural construction sand was used to make mortar specimens for the strength test. The sand is inert in the studied system. The sand grading is given in Table 2.

Test Methods and Analysis

COMPRESSIVE STRENGTH. Mortars were prepared for determination of compressive strength. Natural zeolite-A was used in this test. The sand/HAC ratio was 2.75 and the water/binder (HAC + zeolite) ratio was 0.40. Mix proportions of the specimens are given in Table 3. The mortar was mixed for 3 minutes and then cast in 50.8 × 50.8 × 50.8-mm cube molds. The specimens were demolded after 24 hours moist-curing at 23°C. The 1-day compressive strength was determined immediately after demolding. Companion specimens were placed in water at 38°C to continue hydration. Compressive strength was measured on the mortar specimens at 14, 28, and 150 days after mixing. An average of three specimens was used as reported strength. The relative error was less than 3%.

TABLE 1. Oxide composition (% by mass) of HAC and selected natural zeolites

Oxides (% by mass)	HAC	Natural Zeolite A	Natural Zeolite B
SiO_2	4.5	65.8	65.7
Al_2O_3	41.2	14.3	12.5
CaO	39.8	3.4	2.0
Fe_2O_3	11.3	2.6	1.7
MgO	0.6	1.3	0.9
Na_2O	0.1	2.5	1.5
K_2O	—	2.7	1.7
MnO	—	0.04	0.9

HAC = high alumina cement.

TABLE 2. Sand grading

Sieve	Percentage Passing
4.75 mm (No. 4)	100
3.33 mm (No. 6)	93
1.18 mm (No. 16)	81
850 μm (No. 20)	73
600 μm (No. 30)	60

X-RAY DIFFRACTION ANALYSIS. The composition of HAC pastes prepared for X-ray diffraction analysis (XRD) is provided in Table 4. Natural zeolite-B was used in this test. Samples 1 to 5 and 8 to 11 had the same alkali oxide (M_2O) content, that is, 3.4×10^{-4} mol M_2O per gram of HAC (arbitrarily selected). Samples 1 to 5 were intended to demonstrate the effect of sodium ions in the presence of different anions. Samples 1, 12, and 13 had the same sulfate content, that is, 3.4×10^{-4} mol SO_4 per gram of HAC (arbitrarily selected). These samples were used to demonstrate the effect of sulfate ions in the presence of different cations. Sodium metaphosphate and sodium metasilicate additions were found to retard the hardening of HAC paste. A relatively low content (i.e., amounts less than 3.4×10^{-4} mol M_2O per gram of HAC) was used with a minimal retardation according to trial tests. The dosage of aluminum sulfate was based on the formula $Al_2(SO_4)_3 \cdot 16H_2O$. Larger quantities of salts were used in the paste samples than in mortars to increase the effect of the salts on the hydration of HAC.

TABLE 3. Composition of HAC/zeolite mortars

Samples	Zeolite-A (mass % of HAC)	Sodium Salts: Anions	Sodium Salts: Content (mass % of HAC)
M-1	—	—	—
M-2	20.0	—	—
M-3	20.0	Sulfate	1.0
M-4	20.0	Silicate	1.0
M-5	20.0	Posphate	1.5
M-6	14.5	Carbonate	1.5
M-7	20.0	Nitrate	2.0

HAC = high alumina cement.

TABLE 4. Composition of HAC/zeolite pastes used in X-ray diffraction analysis (arbitrary mass units)

			Inorganic Chemicals Additive	
Samples	**HAC**	**Zeolite-B**	**Type**	**Content**
P-1	1	0.2	Na_2SO_4	0.048
P-2	1	0.2	Na_2CO_3	0.036
P-3	1	0.2	$NaNO_3$	0.057
P-4	1	0.2	NaCl	0.040
P-5	1	0.2	NaBr	0.069
P-6	1	0.2	Sodium metaphosphate	0.010
P-7	1	0.2	Sodium metasilicate	0.050
P-8	1	0.2	K_2CO_3	0.047
P-9	1	0.2	LiCl	0.028
P-10	1	0.2	NaOH	0.028
P-11	1	0.2	KOH	0.038
P-12	1	0.2	$CuSO_4 \cdot 5H_2O$	0.085
P-13	1	0.2	$Al_2(SO_4)_3 \cdot 14\text{-}18H_2O$	0.071

HAC = high alumina cement.

This was intended to facilitate investigation of the hydration mechanism of the studied system. The cement paste samples were prepared with a water/binder (HAC + zeolite) ratio = 0.60. The paste samples were cast in 25-mm diameter bottles and rotated for 24 hours at 38°C. Samples were water-cured at 38°C after demolding. XRD analysis was carried out on wet samples to study the effect of different salts on strätlingite and hydrogarnet formation in HAC/zeolite pastes. Samples were prepared by grinding in an agate mortar after 3, 7, 21, and 330 days. No carbonate phase was detected in the samples. The test was designed for the comparison of parallel samples prepared by an identical process. The comparison is based on significant differences between parallel samples. Some samples were repeated three times. The relative error of the peak height (e.g., C_2ASH_8 at d = 1.26 nm, calculated by Rigaku Standard Data Processing software) was about 10%. A Rigaku X-ray Diffractometer System Geigerflex D/Max -B was used for the X-ray studies.

Results

Compressive Strength

The effect of different sodium salts on the strength development of HAC/zeolite mortars is shown in Table 5. The plain HAC mortar had the highest compressive strength at 1 day. Its strength decreased dramatically at 14 days due to the conversion reaction. The strength then remained relatively constant up to 150 days. The HAC mortar containing zeolite alone had a lower 1-day strength value than the plain HAC mortar. Strength reduction still occurred in this sample. Slight strength recovery occurred with the strength increasing from 14 to 150 days. Addition of sodium sulfate to the blended cement mortar resulted in a high 1-day strength (62 MPa). The strength increased with hydration time. Sodium metasilicate and sodium phosphate significantly retarded the HAC hydration. They resulted in a low 1-day strength in the HAC/zeolite mortar. The strength then increased with age. The specimens had an increase in strength of about 40% from 1 to 28 days and a further 40% increase at 150 days. Sodium carbonate and sodium nitrate addition also resulted in a relatively low 1-day strength. These samples, however, exhibited a high rate of strength gain in the first 14 days. The 14-day compressive strength values of the HAC/zeolite mortars containing both these two salts were all above 50 MPa. Strength continuously increased until 150 days. It is apparent that no strength reduction due to curing at elevated temperature occurred in the HAC/zeolite mortars containing one of the sodium salts.

X-Ray Diffraction

The XRD spectra of plain HAC paste, HAC/zeolite paste, and HAC/zeolite paste containing sodium sulfate cured for 330 days at 38°C are shown in Figure 1. Similar large peaks of hydrogarnet (C_3AH_6) were found in both plain HAC and HAC/zeolite pastes. Only weak

TABLE 5. Compressive strength of HAC/zeolite mortars

	Compressive Strength (MPa)			
Samples	**1 Day***	**14 Days†**	**28 Days†**	**150 Days†**
M-1	65	34	36	34
M-2	57	38	40	45
M-3	62	65	69	72
M-4	29	35	41	57
M-5	30	38	45	59
M-6	40	53	57	57
M-7	34	50	52	63

*Moist-cured at 23°C.
†Water-cuared at 38°C after the first 24 hours moist-curing at 23°C.
HAC = high alumina cement.

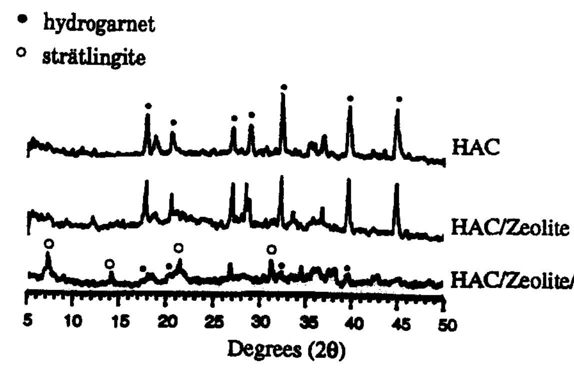

FIGURE 1. X-ray diffraction spectra of plain high alumina cement (HAC) paste, the HAC/zeolite paste, and the HAC/zeolite paste containing sodium sulfate at 330 days.

peaks of hydrogarnet were detected in the HAC/zeolite paste containing sodium sulfate. Strätlingite was clearly detected in the HAC/zeolite paste containing sodium sulfate.

The qualitative description of the height of major peaks attributed to strätlingite and hydrogarnet in the XRD analysis of the HAC/zeolite pastes containing the different inorganic salts is given in Table 6.

Large strätlingite peaks were clearly detected in the HAC/zeolite pastes containing Na_2SO_4, Na_2CO_3, Na_2NO_3, and NaCl. Strätlingite formed at 3 days. Only very small peaks of hydrogarnet were traced in these samples suggesting hydrogarnet formation was inhibited. Lesser amounts of strätlingite were also found in the samples containing sodium bromide at all ages together with a very small amount of hydrogarnet.

Strätlingite was not detected in the sample containing sodium metaphosphate at 3 days. However distinct peaks were observed at 330 days. Sodium metasilicate apparently promoted strätlingite formation in the HAC/zeolite system. Large peaks of strätlingite were recorded at 330 days. A very small amount of hydrogarnet was detected in the samples containing sodium metaphosphate or sodium metasilicate.

The strätlingite peaks were observed in the sample containing potassium carbonate. Potassium carbonate had less effect in promoting strätlingite formation than sodium carbonate. Weak peaks of hydrogarnet were found in potassium carbonate samples at all ages.

Strätlingite was not detected at 3 and 21 days in the sample containing lithium chloride. A small amount was observed at 330 days. Lithium ions did not appear to promote strätlingite formation. Large peaks of hydrogarnet were found in samples containing lithium chloride after 21 days.

Addition of either NaOH or KOH to HAC paste results in rapid setting. Large amounts of strätlingite formed in both samples. Significant quantities of hydrogarnet also formed in the samples containing alkali hydroxides, indicating that the very high pH environment promoted the hydrogarnet formation.

Very small strätlingite peaks and large hydrogarnet peaks were found in the samples containing $CuSO_4 \cdot 5H_2O$ and $Al_2(SO_4)_3 \cdot 14\text{-}18H_2O$.

Conclusions

1. The 1-day compressive strength of the HAC/zeolite mortars containing a sodium salt (sodium sulfate, sodium carbonate, sodium nitrate, sodium

TABLE 6. X-ray diffraction analysis on HAC pastes

		Test Age (days)					
		Strätlingite (C_2ASH_8)			Hydrogarnet (C_3AH_6)		
Sample	Inorganic Salts/Alkali	3	21	330	3	21	330
HAC	HAC alone	N	N	N	VS	VS	VS
HAC/nz	HAC + zeolite-B without Na-salt	W	W	W	VS	VS	VS
P-1	Na_2SO_4	VS	VS	VS	N	W	W
P-2	Na_2CO_3	VS	VS	VS	W	W	W
P-3	$NaNO_3$	VS	VS	VS	W	W	W
P-4	NaCl	VS	VS	VS	N	W	W
P-5	NaBr	S	S	S	N	W	W
P-6	Sodium metaphosphate	N	X	VS	N	X	W
P-7	Sodium metasilicate	S	X	VS	N	X	W
P-8	K_2CO_3	S	S	S	W	W	W
P-9	LiCl	N	N	W	W	VS	VS
P-10	NaOH	S	S	S	W	S	VS
P-11	KOH	W	S	S	VS	VS	VS
P-12	$CuSO_4 \cdot 5H_2O$	N	W	W	W	VS	VS
P-13	$Al_2(SO_4)_3 \cdot 14\text{-}18H_2O$	W	W	W	VS	VS	VS

HAC = high alumina cement; VS = very strong peaks were detected; S = strong peaks were detected; W = weak peaks were traced; N = no peak was found; X = not tested.

metaphosphate, and sodium metasilicate) is in the range of 30 to 60 MPa. No strength reduction occurs in these mortars water-cured at 38°C for 150 days.

2. Strätlingite formation is apparently promoted and hydrogarnet formation is significantly inhibited, by the addition of sodium salts, for example, sodium carbonate, sodium nitrate, sodium chloride, sodium sulfate, sodium metaphosphate, or sodium metasilicate, to the HAC/zeolite system.
3. The beneficial effects of the additives utilized in this study are generally independent of anion type.

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