Pergamon

Cement and Concrete Research, Vol. 28, No. 6, pp. 829–839, 1998

0008-8846/98 $19.00 + .00

PII S0008-8846(98)00058-1

HYDRATION AND STRENGTH DEVELOPMENT OF BINDER BASED ON HIGH-CALCIUM OIL SHALE FLY ASH

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(Received July 14, 1997; in final form April 14, 1998)

ABSTRACT

The properties of high-calcium oil shale fly ash and low-calcium coal fly ash, which are produced in Israeli power stations, were investigated. High-calcium oil shale fly ash was found to contain a great amount of CaO_{free} and SO_3 in the form of lime and anhydrite. Mixtures of high-calcium oil shale fly ash and low-calcium coal fly ash, termed fly ash binder, were shown to cure and have improved strength. The influence of the composition and curing conditions on the compressive strength of fly ash binders was examined. The microstructure and the composition of fly ash binder after curing and long-term exposure in moist air, water and open air conditions were studied. It was determined that ettringite is the main variable in the strength and durability of cured systems. The positive effect of calcium silicate hydrates, CSH, which are formed by interaction of high-calcium oil shale fly ash and low-calcium coal fly ash components, on the carbonation and dehydration resistance of fly ash binder in open air is pronounced. It was concluded that high-calcium oil shale fly ash with high CaO_{free} and SO_3 content can be used as a binder for building products.

Introduction

High-calcium oil shale fly ashes (HCOSFA) from Spain, Greece, Turkey, France, Estonia, Israel, and other countries contain up to 43–60% CaO (1–3). Some of them contain free CaO and SO_3 in the form of lime and anhydrite. In addition to pozzolanic properties, they can have hydraulic activity with just the ash itself. These ashes can form, with water, relatively strong materials without the need for an activator.

Extensive studies of HCOSFA have previously been conducted in Israel (3–5). It has been found that fly ash of oil shales from Tzefa Efee (Israel) consisted mainly of clinker minerals (β-C_2S, C_3A, C_4AF), anhydrite ($CaSO_4$), calcite ($CaCO_3$), lime (CaO_{free}) and quartz (SiO_2). Investigations indicated that the hydration of HCOSFA includes mainly two reactions: interaction of aluminate phases with CaO_{free} and $CaSO_4$, and reaction of β-C_2S with water to form C-S-H having surface area similar to that of Portland cement gel (4,5). The first reaction proceeds quickly at ordinary temperatures, and HCOSFA forms ettringite as a stable product of hydration. Ettringite is stable in an aqueous solution at temperatures up to 90°C and higher (6–8). However, it behaves differently in air. Ettringite dehydration and carbon-

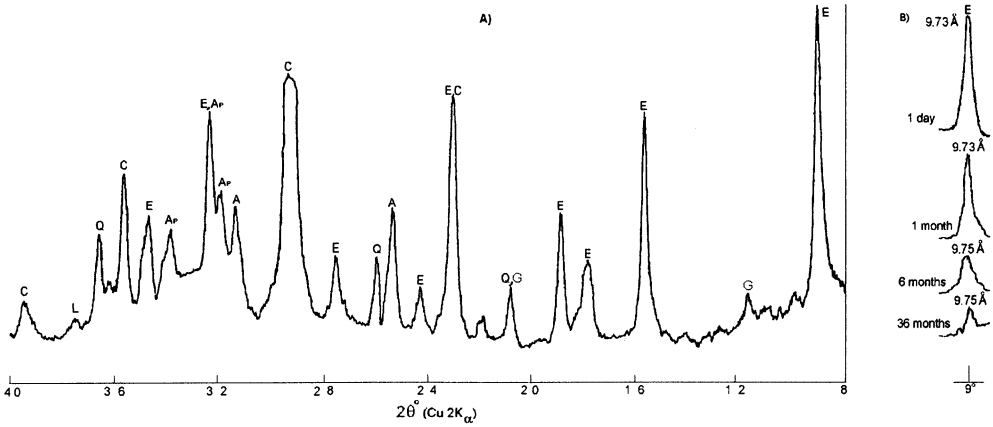

FIG. 1.

XRD patterns of high-calcium oil shale fly ash binder pastes. A, Anhydrite; Ap, Apatite; C, Calcite; G, Gypsum; Lm, Lime; Q, Quartz. *A*) Full XRD of 28-day moist curing specimen. *B*) Evaluation of the 9.74–9.75 Å peak of ettringite with time of exposure to air.

ation processes that take place in air diminish its amount, and gypsum, calcium carbonate, and alumina gel form in its place (9,10). In such a situation the cured ettringite-containing system can decompose and lose its strength (11).

Our preliminary examinations, which were performed on Israeli HCOSFA pastes that contained 30% water (from weight of fly ash) and on a mortar (called Mortar 2) consisting of 60% HCOSFA + 40% sand and 30% water (from weight of solid components), have confirmed these known facts. (The chemical and mineralogical composition of HCOSFA and methods of experimental procedure are described below in the section "Experimental.")

Figure 1 shows by XRD what happens to ettringite after a long-time exposure of cured HCOSFA paste specimens to the open air.

The small portion of the XRD patterns on the right in Figure 1 is concerned with ettringite only. A marked reduction can be seen in the intensity of the ettringite peaks in region of 9.73–9.75 Å. This suggests that the amount of ettringite in open air is decreased. These phenomena are evidently conditioned by the processes of dehydration and carbonation of ettringite, which were noted in (9,10). As a result, hardened HCOSFA binder can lose its strength.

This can be seen from the curves in Figure 2. The compressive strength of mortar specimens began to decrease significantly starting at 1–3 months of exposure in open air. Reduction in strength continued during the whole period of the experiment. The sharpest drop in strength occurred after 3 to 6–12 months of exposure. A leveling of strength did not occur even after 36 months in spite of the fact that the shrinkage of specimens stopped after 6–12 months.

In our opinion, the negative consequences of ettringite collapse can be moderated or prevented by the forming of an additional quantity of more stable binder phases in the initial stage of HCOSFA curing. This effect can be obtained by a combined hydration of HCOSFA and low-calcium coal fly ash (LCCFA). The CaO_{free} of HCOSFA and active SiO_2 of LCCFA would give secondary high-strength and more stable calcium silicate hydrates (CSH), which should improve the durability of the hardened system in open air.

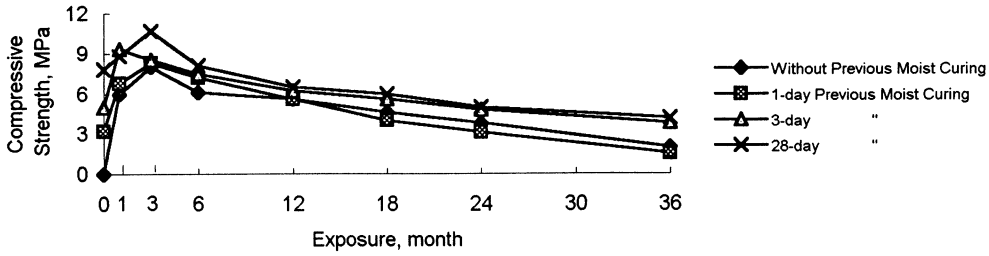

FIG. 2.
Development of compressive strength of mortar 2 in open air conditions. Mortar 2 Composition: 60% high-calcium oil shale fly ash + 40% sand plus 30% mixing water (from weight of solid).

In the present paper the development of strength and hydration of fly ash binder (FAB) based on HCOSFA and LCCFA is demonstrated.

Experimental

Materials

The HCOSFA was obtained from the Pama plant, located in the Negev (Developing Energy Resources LTD, Israel), which burns local oil shales. Israeli oil shales are a fossil fuel containing 12–15% of organic matter in a matrix of calcite, quartz, apatite [$Ca_{10}(PO_4)_6F_2$] and minor amounts of other crystalline and amorphous matters (12). Before being burned, the oil shale is ground by special equipment. Sieve analysis, which is carried out by the plant laboratory on a regular basis, shows that ground oil shale consists of particles equal to and smaller than 4–6 mm in diameter. Moist particles (55–60%) measure less than 0.8 mm, and 20–25% measure less than160 μk in diameter. Ground oil shale is combusted in a fluidized bed combustor at temperatures in the range from 850 to 900°C. Fuel particles remain in fluidized bed combustion process for an average of a few minutes. Anhydrite, calcite, lime, quartz, apatite, and clinker minerals β-C_2S, C_3A and C_4AF) are the main crystalline phases found in HCOSFA by XRD (Fig. 3). These minerals were also discovered in HCOSFA by other researchers (5,12,13). It is necessary to point to the existence (and especially the co-existence) of three high-temperature clinker phases mentioned with calcite in HCOSFA. The formation of clinker minerals can be explained as follows: Although the nominal combustion temperature is around 850–900°C, much hotter zones ("hot spots") with temperature well in excess of 1200°C exist. This should also have produced melt and left glass in the combustion ash. In its liquid phase, clinker mineral compound reactions are possible. The presence of calcite in fly ash is conditioned by the parameters of oil shale combustion-fluidized bed combustion. Low combustion temperature (850–900°C) and excess pressure don't allow the calcite to calcine completely to lime. As a result, both calcite and lime are present in HCOSFA.

In Figure 3, the XRD of HCOSFA and LCCFA used in the research are presented.

The LCCFA was obtained from a coal-burning power station in Hadera (Israel). It consists of glassy spherical particles which incorporate mullite and quartz crystals recognized by

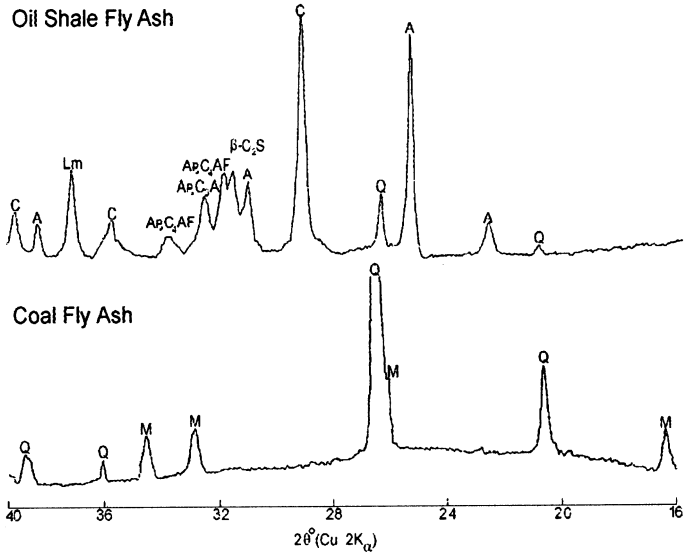

FIG. 3.
XRD of high-calcium oil shale fly ash (HCOSFA) and low-calcium coal fly ash (LCCFA): A, Anhydrite; Ap, Apatite; C, Calcite; Lm, Lime; M, Mullite; Q, Quartz; β-C_2S, $2CaO{\cdot}SiO_2$; C_3A, $3CaO{\cdot}Al_2O_3$; C_4AF, $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$.

XRD (Fig. 3). Results of chemical and physical tests on HCOSFA and LCCFA as defined in ASTM C 618 are given in Tables 1 and 2.

Natural quartz sand was used for the preparation of mortar test specimens. The sand had the fineness modulus of 2.83, a specific gravity of 2.61 g/cm^3, and the bulk specific gravity of 1470 kg/m^3.

TABLE 1
Chemical analysis of fly ashes
% (by weight) [ASTM 618].

Oxides	HCOSFA	LCCFA
SiO_2	16.3	45.6
Al_2O_3	5.6	33.5
Fe_2O_3	3.6	3.5
CaO_{total}	52.3	5.4
CaO_{free}	10.1	—
MgO	0.8	1.6
SO_3	10.7	0.4
P_2O_5	2.5	1.6
Na_2O	0.3	0.5
K_2O	0.4	0.3
Loss on $Ignition_{950°C}$	5.1	5.9

TABLE 2
Physical properties of fly ashes [ASTM 618].

	HCOSFA	LCCFA
Fineness: passing 45 μk, %	18.7	12.1
Specific Gravity, g/cm^3	2.3	2.5
Bulk Specific Gravity, kg/m^3	690	810
Soundness: Autoclave Expansion, %	0.1	0.03

Experimental Procedure

The pressed test specimens were prepared in two different batches. The first batch was used for determining the effect of HCOSFA content and amount of mixing water (W) on compressive strength, and for the development of FAB compressive strength in moist-air conditions, water conditions, and open-air conditions. Cylindrical specimens of 5.70 cm in height and diameter were in this batch. They were made from fly ash-sand mortars, containing 60% mix of HCOSFA + LCCFA and 40% sand.

To study the effect of HCOSFA content on FAB strength, the ratios of HCOSFA and LCCFA in fly ash mix were varied from 20:80% to 60:40%, resulting in HCOSFA contents from 12 to 36% in mortars. W amount was in the range of 15–25%. The examination of the influence of amount of mixing water (W) on fly ash binder strength was performed on the mortar containing 36% HCOSFA, 24% LCCFA, and 40% sand (Mortar 1). W amount was varied from 10 to 30% of mortar solid component weight. The lower limit of W was set by the necessity of obtaining homogeneous mortars from the constituent raw materials. The upper limit of W was defined by the possibility producing mortar test specimens that would not lose free water during pressing using as the method of their molding.

The development of compressive strength of fly ash binder in air and water was investigated using the mortar specimens prepared from 36% HCOSFA, 24% LCCFA, 40% sand, and 25% W (Mortar 1). This composition was considered to be representative of the other mortar compositions.

For comparison, the same experiments were done on mortar with 60% HCOSFA + 40% sand and 30% W (Mortar 2) without LCCFA.

The second batch of specimens was designed for examinations of hydration of FAB and products of its curing. Specimen-discs of 15 mm in height and 57 mm in diameter were molded from the mix of 60% HCOSFA and 40% LCCFA (by weight), plus 30% water of solid weight.

The first batch mortar specimens were produced by preparing HCOSFA and LCCFA mixtures by hand. Sand and water were then added to the ash mixture and the mixing continued until the paste was homogeneous. Test specimens were molded by pressing on a Carver laboratory hand press at the compaction pressure of 4 MPa. The second batch paste specimens were made in the same way.

Exposure and Curing Conditions of Test Specimens

After molding, test specimens of both batches were cured: (1) in a moisture chamber with a temperature of 23 ± 1°C and RH > 96% (moist curing and moist air conditions); (2) in water

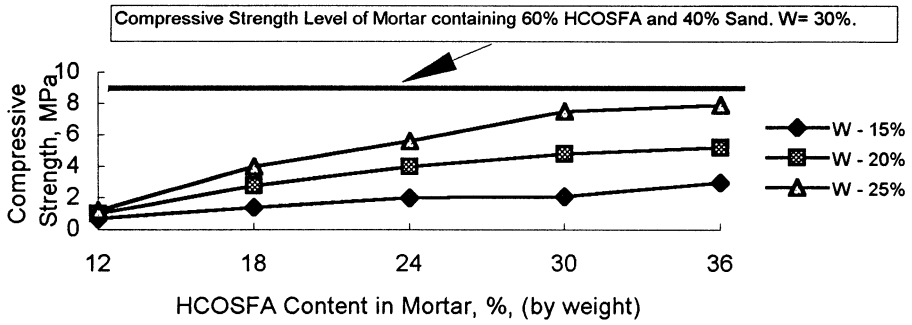

FIG. 4.
28-day compressive strength of moist curing mortar specimens with various contents of HCOSFA. Mortar composition: 60% HCOSFA and LCCFA Mix + 40% sand.

at a temperature between 20–23°C (water curing and water saturated conditions); and (3) in open air at a temperature between 18–23°C and RH 35–60% (air curing and open air conditions). A part of the mortar specimens that were designed for testing in water conditions as well as in open air conditions were cured previously in the moisture curing chamber for 1, 3, and 28 days (previous moist curing). After these periods of previous moist curing they were submerged in water (water conditions) or put in open air (open air conditions).

Testing of Specimens

After a certain period of curing and exposure in one of the above- mentioned trial environments, the mortar specimens of the first batch were tested for compressive strength. At the same time the paste specimens of the second batch were analyzed by X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM), and a composition and structure for new formations of the cementing matter of FAB was determined. XRD analysis and SEM were also used for identification of the mineralogical composition of the raw materials, HCOSFA and LCCFA.

Results and Discussion

Compressive Strength

Effect of HCOSFA Content and Amount of Mixing Water. The dependence of the compressive strength of 28-day moist cured specimens with HCOSFA content is presented in Figure 4.

From Figure 4 it can be seen that an increase of HCOSFA content raises the compressive strength independently of W amount. In the interval of HCOSFA content of 12–30%, the relationship has a straight line character. The compressive strength of mortar with 36% HCOSFA and 24% LCCFA and W of 25% was equal to 7.9 MPa and approaches that with 60% HCOSFA without LCCFA (8.8 MPa). This shows that LCFA participates actively in curing process of FAB.

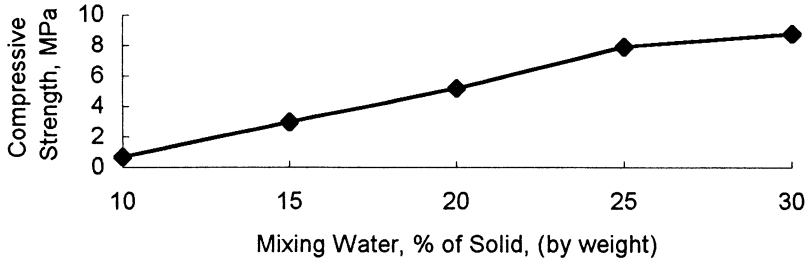

FIG. 5.
28-day compressive strength of moist curing mortar specimens with various amounts of mixing water (Mortar 1: 36% HCOSFA, 24% LCCFA and 40% sand).

Positive W influence on compressive strength is shown on Figure 5. In the range of 10–25% W there is a linear relation between increasing strength and water amount. At 30% W the compressive strength of mortar with 36% HCOSFA and 24% LCCFA and mortar with 60% HCOSFA without LCCFA are both equal to 8.8 MPa. Thus it is apparent that for the best use of cementitious potential of HCOSFA, and to obtain the maximal strength of fly ash binders, a maximal amount of mixing water will be needed. This amount will be defined by workability in fabricating building materials.

Effect of Curing and Exposure Conditions: Moist Air and Water Conditions. Typical curves showing the change of compressive strength of mortars cured in moist air and water for 36 months are presented in Figure 6.

Results obtained from testing moist cured specimens (Fig. 6a) allow us to make several conclusions. The curing of mortars is accompanied by increasing compressive strength. Hardening progressed rapidly in the initial period up to 1–3 months and the strength of specimens reached 60–65% of the 36-month value. Thereafter, growth of the strength is slowed. Stabilization of the strength is noted after 18 months. To 18 months the compressive strength of mortar composition 1 prepared from 36% HCOSFA+ 24% LCCFA is close to that of mortar prepared with 60% HCOSFA without LCCFA: 12.4 and 12.8 MPa, respectively.

Tests results for water and moist-cured mortars are alike (Fig. 6a and 6b). A continuous growth of the compressive strength of the mortars was observed during the whole exposure period in water. But strength growth occurs in water more than in moist air. As a result, compressive strength in water is greater than that in moist air. It should be noted that compressive strength of specimens that had been given 28 days previous curing reached a stable strength after 3 months of water curing.

Effect of Curing and Exposure Conditions: Open Air Conditions. The typical behavior of FAB compressive strength in open air conditions can be seen in the example of mortar 1 (Fig. 7).

The compressive strength curves have three clear-cut portions. The first part correlates with an increase of the compressive strength over 1 month. The second part corresponds to a decrease in compressive strength over the period from 1 to 6 months. The third part characterizes a stabilization of compressive strength starting at 6 months.

During the first stage, specimens dried, lost water and grew in strength. The second stage

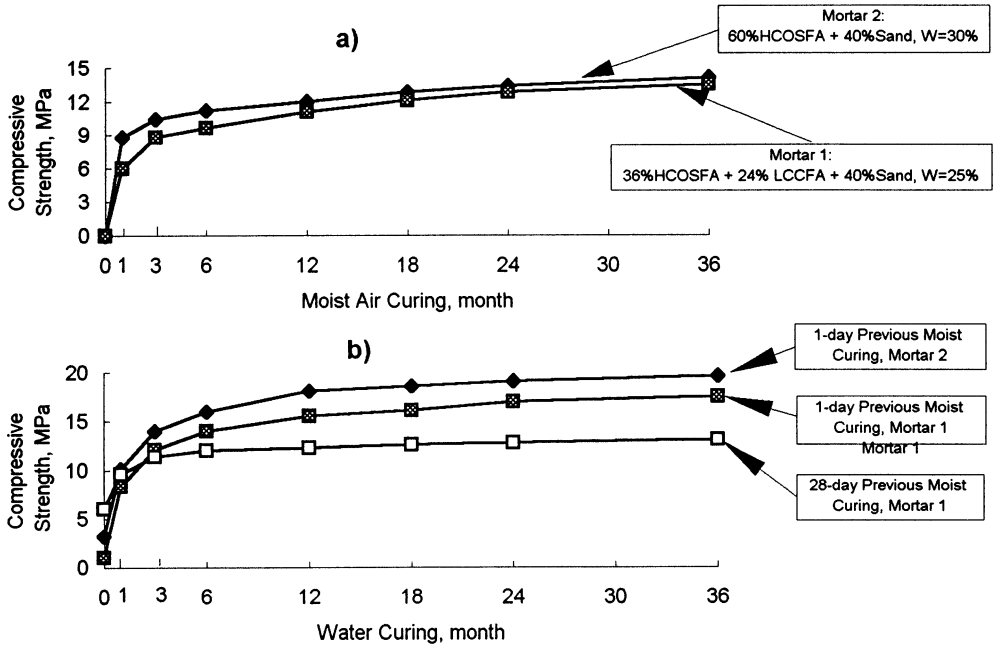

FIG. 6.
Development of compressive strength: *A*) moist air conditions; *B*) water conditions.

is accompanied by additional drying and a drop of compressive strength. The magnitude of this decrease depends on the duration of previous moist curing and the initial compressive strength. The third stage of behavior indicates that the destructive processes in hardening FAB are essentially finished in 12 months, after which the compressive strength remains almost constant. A comparison of Figure 7 and Figure 2 shows the positive effect of the LCCFA additions on the compressive strength of FAB based on HCOSFA in open air.

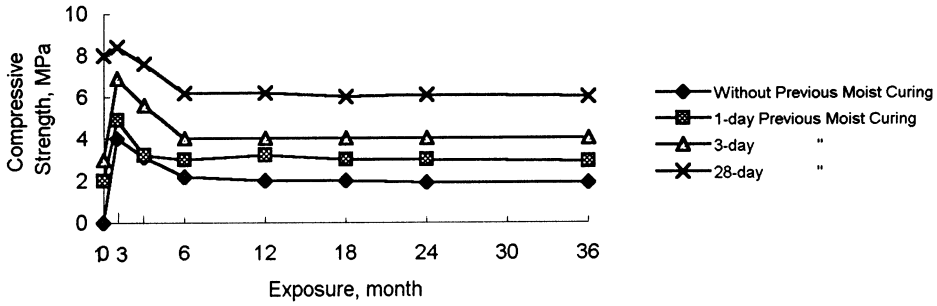

FIG. 7.
Development of compressive strength of mortar 1 in open air conditions.

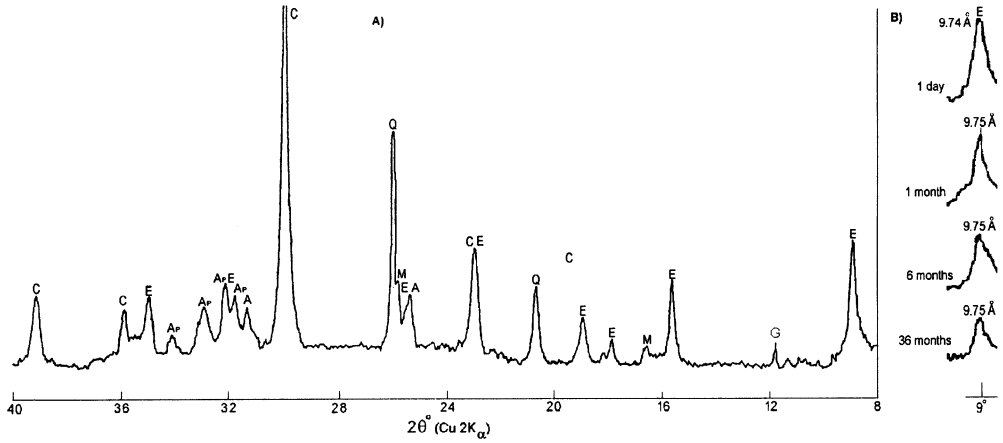

FIG. 8.

XRD Patterns of high-calcium oil shale fly ash + low-calcium coal fly ash binder pastes (A, Anhydrite; Ap, Apatite; C, Calcite; G, Gypsum; Lm, Lime; M, Mullite; Q, Quartz). *A*) Full XRD of 28-day moist curing specimen. *B*) Evaluation of the 9.74–9.75 Å peak of ettringite with time of exposure to air.

Composition and Structure of Cured Fly Ash Binder

In Figures 8 and 9, typical XRD patterns and SEM micrographs of the second batch paste specimens after curing in moist air and open air conditions are presented.

The comparison of XRD patterns of moist curing HCOSFA + LCCFA paste specimens (Fig. 8) and the same HCOSFA paste specimens (Fig. 1) shows that the crystalline phases are identical. The differences are in reduced intensity of XRD peaks of HCOSFA + LCCFA specimens and in the presence of mullite, attributable to LCCFA. Evidently, the differences are a result of special initial compositions of specimens. The direct evidence for calcium silicate hydrates (CSH) was not noted. It is likely that this may be linked to X-ray amorphousness of CSH. But there is circumstantial evidence of CSH obtained in the examination of the effect of mortar composition on the strength. For example, the compressive strength of mortar specimens, in which HCOSFA content was decreased from 60% to 36% by

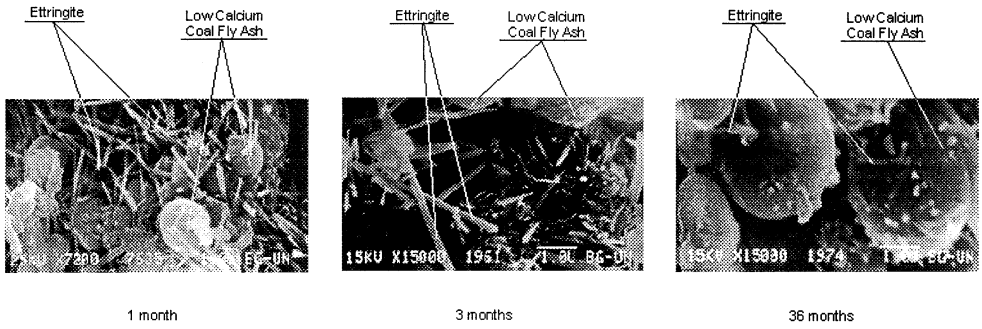

FIG. 9.

SEM observations of ettringite in open air exposure of HCOSFA + LCCFA binder paste.

substitution with LCCFA, was 90–100% of that for mortars containing 60% HCOSFA (Figs. 4 and 5). This can be explained only by a reaction of CaO_{free} of HCOSFA and active SiO_2 of LCCFA to form additional cementing matter in the manner of CSH. The CSH strength-hardened system should improve degradation of the mortar in air. Other methods should be employed to detect CSH.

XRD pattern segments of open-air-exposed HCOSFA + LCCFA specimens, which focus on ettringite only, indicate a marked lessening in the intensity of the 9.74–9.75 ettringite peaks (Fig. 8). This is a result of a decomposition of ettringite. The same observations were made in the case of HCOSFA pastes (Fig. 1).

In the micrographs of paste specimens kept 1, 3, and 36 months in open air, essential alterations can be seen in their microstructure (Fig. 9).

Many needle crystals of ettringite are observed in specimen that was exposed in open air for 1 month. After 3 months their quantity is significantly decreased. In the micrograph of the paste specimen exposed 36 months in open air, a small amount of the individual ettringite crystals is found.

Conclusions

The following conclusions can be drawn from present study:

1. In open air ettringite is not stable. Its amount is diminished, and gypsum, calcium carbonate, and alumina gel are formed. Starting from a certain period this process can decrease the strength of cured HCOSFA binder. The sharpest drop in strength occurred after 3 to 6–12 months of air exposure. A leveling of strength did not occur even after 36 months.
2. The negative effect of ettringite degradation can be reduced by introduction of LCCFA to HCOSFA binder. Combined hydration of HCOSFA and LCCFA, which gives an additional amount of high-strength and more stable CSH, improves the durability of the hardened system in open air. But after a certain period of the exposure (from 1 to 6 months) a decrease in strength is still observed.
3. The compressive strength of FAB is determined by the ratio of HCOSFA and LCCFA, as well as by the amount of mixing water.
4. Moist air and water conditions are the most favorable conditions for the curing and development of compressive strength of fly ash binders.

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