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The contribution of class-F fly ash to the strength of cementitious mixtures

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Abstract

The contribution of fly ash to the physical properties of cementitious mixtures has received considerable attention since its inclusion as an essential ingredient of High Performance Concrete (HPC). However, the chemical contribution to the overall structure development has not been fully understood because of the masking of its hydration products by those of cement. In a mixture of class-F fly ash and lime (Ca/Si=2), portlandite diminishes and C_4AH_{13} forms due to addition of Al to solution. The latter converts to hydrogarnet and C_3ASH_4. CSH is detected at 3 days and continues to increase in intensity. The ^{29}Si magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) showed that the Al/Si ratio is 0.24 and the average chain length is 10 units. The presence of Al as approximately one-fifth of the Si in a chain length of 10 units suggests that Al tetrahedra may be present in bridging positions.

Keywords: C_4AH_{13}; C_3ASH_4; Hydrogarnet; Fly ash; Mass NMR; Zeta-potential

1. Introduction

With the introduction of High Performance Concrete (HPC), and inclusion in a variety of building products, fly ash has become an essential ingredient in concrete mixtures. It improves workability and reduces water and water reducing admixture demands. It reduces cracking due to autogenous and plastic shrinkage. It increases the packing density of the cementitious system, thus creating a less permeable structure. It significantly reduces concrete's permeability to chloride, water, and oxygen and increases concrete's resistance to alkali silica reaction, sulfate attack, and other chemical attack. In addition, as a pozzolana, it consumes calcium hydroxide and creates more calcium aluminate silicate hydrates. Fly ashes are also used in mixtures with industrial by products (such as kiln dust), in Aerated Autoclaved Concrete (AAC), and were claimed to be useful in producing zeolite like structures in blends containing them. Although the physical contribution of fly ash to concrete is very well documented, the chemical contribution to the overall structure development has not been fully understood. Part of the problem is the small extent of the hydration products produced from fly ash, which lets them be masked by the hydration products of cement.

The purpose of this paper is to report on mechanisms of hydration of fly ash/lime mixtures. The hydration reaction was monitored by zeta-potential and X-ray diffraction at various ages. Solid-state ^{29}Si magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) was used to characterize the detailed structure of hydration products after 28 days.

2. Materials and method

In this study, Micron 3 class-F fly ash (Boral Material Technologies, San Antonio, TX) was used. The chemical composition of the fly ash, as provided by the supplier, is as follows: 50.77% SiO_2, 26.65% Al_2O_3, 3.76% Fe_2O_3, 11.30% CaO, 2.15% MgO, 1.20% SO_3, 1.17% total alkalis

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(as Na_2O), strength activity index 105% (7 days) and 114% (28 days). The average particle size is 3 μm, and 90% is <7.0 μm (as determined by laser diffraction analysis), specific gravity=2.53 g/cc.

Calcium hydroxide was added to aqueous suspensions of the fly ash so that the Ca/Si ratio in the mixture was equal to 2. The suspension was stirred continuously, in sealed containers, for 28 days at 42 °C. At designated ages (1, 3, 7, 15, 21, 28 days), the containers are taken to a glove compartment flooded with nitrogen gas to avoid carbonation, and a drop of the suspension was withdrawn and diluted with the filtered solution at the same age so that the composition of the interface is not altered, and subjected to zeta-potential measurement. The zeta-potential was measured using Brookhaven Phase Analysis by Light Scattering (PALS) zeta-potential analyzer. The technique depends on determination of the phase change of laser scattered light as a result of the particle movement under the effect of an alternating current [1]. The technique is sensitive to very small movements of the particles. This is particularly useful for particles carrying small charge, such as particles of cementitious materials. Unlike the other techniques where very large voltage is needed to impose a readable movement of the particles resulting in highly scattered results as in case of cement [2], this technique requires only a small voltage and results in very accurate determination of zeta-potential.

At the end of 1, 3, 7, 15, 21, 28 days, the solid residues were collected, freeze dried, and characterized by X-ray diffraction to monitor the phase changes in hydration products as a function of time. A computerized search/match program was used to identify the nature and quantity of each hydration product. The solid-state ^{29}Si magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) was used to characterize the detailed structure of hydration products after 28 days. The NMR spectra were referenced to tetramethylsilane (TMS). The signals due to ^{1}H were decoupled so that the signals due to Si–O–Si and Si–O–Al connectivities are not affected by the proton signals.

3. Results and discussion

The Zeta-potential of fly ash particles (before mixing with lime) was found to be −27 mv. The zeta-potential of the fly ash/lime mixtures shows a sharp change to more positive potentials during the first few minutes of reaction due to adsorption of Ca^{++} ions on the surface particles. It does not, however, show any subsequent decrease toward less-positive potentials, and the zeta-potential reaches a plateau, which continues unchanged afterwards.

The variation in X-ray peak intensities of fly ash/lime mixture (Fig. 1) shows that portlandite continues to diminish with time. C_4AH_{13} forms within the first few days of hydration and continues to increase up to 7 days, then it converts to the more stable phases, hydrogarnet and C_3ASH_4.[1] C–S–H is detected at 3 days and continues to increase in intensity.

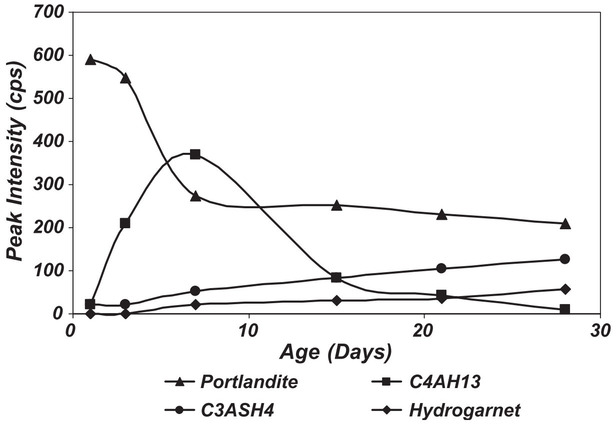

Fig. 1. Variation of X-ray peak intensity versus time of class-F fly ash/lime mixture.

The mechanism of hydration can be explained as follows. The first step is the adsorption of Ca^{++} ions from solution on the surface of the negatively charged fly ash particles. This is immediately followed by an attack on the Al_2O_3–SiO_2 framework in the glassy phase of the fly ash by the OH^- ions resulting in the breakdown of the Al–O and Si–O bonds. The breakdown of the aluminosilicate framework will release alkali ions (K^+ and Na^+) into solution. The immediate product is likely to be an amorphous material with K^+ and Na^+ as the dominant cations [3]. The abundant supply of Ca^{++} and the lower solubility of C–S–H are an indication that the C–S–H gel is the first intermediate product formed. Afterwards, due to the removal of Ca^{++} and depression of solubility of lime under the effect of increasing alkali concentration in solution, a low Ca/Si ratio C–S–H is expected to form. The addition of Al ions in solution will promote the formation of C_4AH_{13}, which later converts to hydrogarnet and C_3ASH_4. Sersale [4] argues that there exists a strong dependency of the breaking down of the glass phase on the alkalinity of solution, which becomes significant only after few days, which may explain the early incubation period in fly ash hydration. This incubation period is decreased with temperature due to increased solubility of the glass. In addition, the reactivity of fly ash/lime mixtures increases by optimization of the fine particle range, due to two factors: enlargement of the reaction surface area and the enrichment of chemically active constituents. The relative concentrations of CaO, SiO_2, and Al_2O_3 define the nature of hydration products formed. Therefore, low concentrations of CaO and high concentrations of SiO_2 and Al_2O_3 favours stratlingite formation, whereas high concentrations of CaO, SiO2 and low concentration of Al_2O_3 favours the formation of

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[1] $CASH_4$ has a garnet structure with Si in four coordination and Al in six coordination. Two (OH)$_4$ groups substitute for two SiO4 groups in the original garnet structure (C_3AS_3).

C_4AH_{13} [4]. The later compound converts with age to more stable phases, such as hydrogarnet and C_3ASH_4.

The solid-state ^{29}Si magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) spectra of the dried mixtures after 28 days of hydration were obtained. The signals due to ^1H have been decoupled so that the signals due to Si–O–Si and Si–O–Al connectivities are not affected by the proton signals. It should be noticed that Q^0, Q^1, Q^2, Q^3, Q^4 correspond to a SiO_4 tetrahedron connected to 0, 1, 2, 3, and 4 SiO_4 tetrahedra, respectively, whereas $Q^n(0\ \mathrm{Al})$, $Q^n(1\ \mathrm{Al})$, $Q^n(2\ \mathrm{Al})$, $Q^n(3\ \mathrm{Al})$, $Q^n(4\ \mathrm{Al})$ correspond to SiO_4 tetrahedron connected to 0, 1, 2, 3, and 4 AlO_4 tetrahedra, respectively.

The NMR pattern of fly ash/lime mixtures shows a small peak at -107 ppm, which is assigned to the unreacted fly ash. In addition, peaks at ~ -79 and ~ -85 ppm are attributed to Q^1 (0 Al) and Q^2 (0 Al) species, respectively. That is terminal and middle (unbranched) silicon tretrahedra, respectively. An additional peak at ~ -81 ppm is assigned to Q^2 (1 Al). The deconvoluted peak areas were calculated, and the average chain lengths were calculated from the formula [5].

$$\text{Av. Chain Length} = \frac{1/2Q^1(0\ \mathrm{Al})}{Q^1(0\ \mathrm{Al}) + Q^2(0\ \mathrm{Al}) + Q^2(1\ \mathrm{Al})} \tag{1}$$

The deconvoluted peak areas are used to calculate average Al/Si from the formula [6].

$$\mathrm{Al/Si} = \frac{1/2Q^2(1\ \mathrm{Al})}{Q^1(0\ \mathrm{Al}) + Q^2(0\ \mathrm{Al}) + Q^2\ (1\ \mathrm{Al})} \tag{2}$$

The Al/Si ratio was found to be 0.24. The average chain length is 10 units. The presence of Al as approximately one-fifth of the Si in a chain length of 10 units suggests that Al tetrahedra may be present in bridging positions.

4. Conclusions

The mechanism of hydration of class-F fly ash/lime mixtures was monitored by X-ray diffraction at various ages where the changes in phase composition were studied. Solid-state ^{29}Si magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) was used to characterize the detailed structure of hydration products after 28 days.

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