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Hardening mechanisms of an alkaline-activated class F fly ash

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Abstract

The hardening mechanism of a paste composed of a low calcium fly ash and alkali was investigated. It was found that a fraction of fly ash reacted with water-glass and formed amorphous or low-ordered crystalline compounds of the type of $Na_2O-Al_2O_3-SiO_2$, after the paste was cured at 60°C for 24 h. For the water-glass with a modulus of 1.64, the strength of the paste is mainly attributed to the gel-like reaction products that bind the particles of fly ash together. When the modulus is decreased to 1.0, crystalline sodium silicate is formed in the matrix, which helps to achieve high strengths.

Keywords: Alkali-activated cement; Fly ash

1. Introduction

There have been extensive efforts to convert fly ash into useful binding materials by means of alkaline activation. Two different processes have been developed so far [1–4]. One is a direct method, in which fly ash is mixed with certain activators and then the mixture is cured under a certain temperature to make solid materials. The other is an indirect method, in which the mixture of fly ash and activators is converted into cement clinker first, and then the cement can be used to make concrete. Comparatively, the first approach is much easier to apply mainly due to its simple processing technique and low treatment temperatures. In practice, no matter which method is used, the selection of proper activators is the most important part of the technology.

The alkaline activators that have been used for activating fly ash include Portland cement, lime, NaOH, $NaCO_3$, and water-glass (sodium silicate solution). The effect of activation strongly depends on the physical–chemical nature of the fly ash and the type of activator. In general, fly ash is an acidic material containing acidic oxides such as Al_2O_3, SiO_2, and Fe_2O_3, thus it possesses a potential to react with alkalis. It is believed that in the hardened mixture of fly ash and alkaline activators, there are gel-like compounds formed as well as hydrated phases with different degrees of crystallinity, e.g., thomosonite, hydronepheline, natrolite, zeolite and even hydrated silicates like C-S-H (II) gel [5,6]. Partly because of a wide variety of compositions of fly ash and the types of activators used, and partly because of the difficulty in direct observation of reaction products, the mineralogical composition of the reaction products in alkali-activated fly ash has not been studied in detail, and therefore, the hardening mechanisms of the pastes made of fly ash and activators have not been understood very well.

In the previous work [3], it was found that using class F fly ash and water-glass, a high strength paste can be made with compressive strengths up to 8000 psi after curing at 60°C for 24 h. The control parameters that are particularly important for the paste have been identified, namely, the ratio of total activation chemicals to fly ash, the molar ratio of silica dioxide to sodium oxide (SiO_2/Na_2O, also known as the modulus of water-glass).

In addition to the paste made of the fly ash and the activator, fine and coarse aggregates have also been added to the mixture to make concrete. In this case, it was found that the water to binder ratio (binder is the sum of water-glass and fly ash) is very important. Other control parameters are similar to those for Portland cement concrete, such as binder to aggregate ratio and coarse to fine aggregate ratio.

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Table 1
Chemical composition of fly ash (%)

CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	Na_2O
2.6	49.1	30.3	13.7	0.5	1.2	0.4

The ratio of total activation chemical to fly ash has a significant effect on both ultimate strength and strength development. The basic trend is that the higher the ratio, the higher the resulting strength of the paste. For economical reasons, the ratio should be kept below 20%. The molar ratio SiO_2/Na_2O of water-glass has critical effect on both ultimate strength and strength development. Our extensive test results showed that the molar ratio corresponding to the maximum strength varies upon specific chemical composition of the ash used, particularly on Al_2O_3 and SiO_2 contents of the ash. In general, the basic trend is that the strength increases with decrease of the molar ratio. The water to binder ratio has similar effect as water to cement ratio in regular concrete.

The processing temperature of 55°C is a dividing line. Strength of the paste and concrete cured at temperatures below 55°C is very low, and the further gain of strength above 55°C is not significant. Therefore, the optimum processing temperature is 55°C, and the optimum curing time is 12 h.

This paper is a continuation of the previous work [3,4]. Our main objective is to understand the hardening mechanisms of this material under a relatively low curing temperature and within a short period of curing time. An experimental study on the class F fly ash activated by water-glass and sodium hydroxide was conducted by means of XRD and SEM–EDS techniques. The mineralogical compositions of the paste will be identified; and the microstructure of the hardened paste will be analyzed. These will provide valuable information to answer important questions such as why the strength increases with decrease of modulus of water-glass.

2. Materials

The chemical composition of the class F fly ash used in the present study is shown in Table 1 and the chemical composition of the water-glass is listed in Table 2. It should be pointed out that the fly ash used in this study has a high fraction of reactive oxides ($Al_2O_3+SiO_2+Fe_2O_3>93\%$), which means that it has high reactivity with water-glass and thus leads to high strength within a short time and under a relatively lower temperature.

Table 2
Specification of water-glass

Na_2O	SiO_2	Total solid	SiO_2/Na_2O	Consistence
16.12%	26.52%	42.65%	1.64	50.3B$^{\infty}$

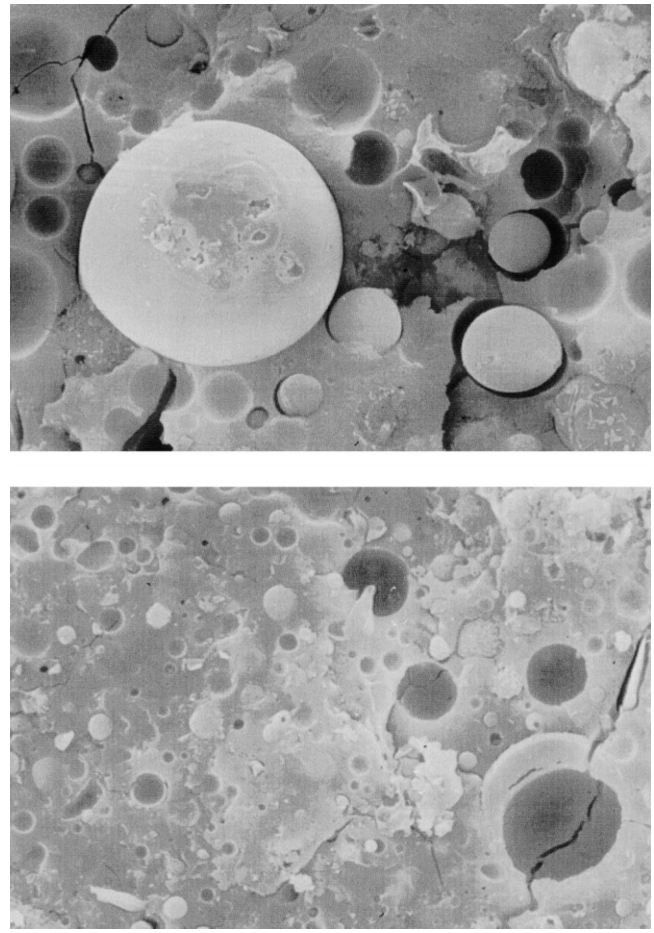

Fig. 1. SEM micrographs of the hardened paste of fly ash and water glass. (1) ×2000, (2) ×750.

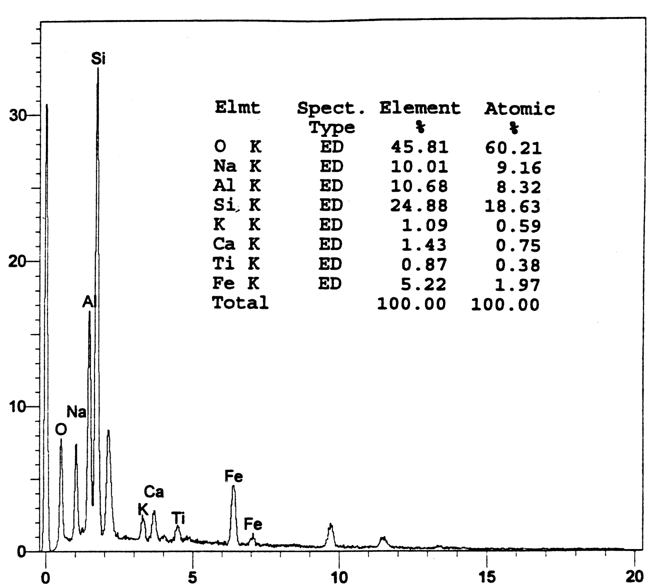

Fig. 2. Elements in the matrix of the hardened paste by EDS.

3. Experimental results

3.1. The paste made of the fly ash and water-glass

First, the water-glass with modulus of 1.64 was used to mix with the fly ash. The weight ratio of fly ash, water-glass and water was 26:15:1. The paste held in a closed mould was cured in an oven of 60°C for 24 h prior to XRD and SEM–EDS analyses.

SEM micrographs reveal that the hardened paste of fly ash and water-glass is composed of the spherical fly ash particles and gelatinous matrix (Fig. 1). One can see from the SEM images that a lot of fly ash particles reacted with water-glass on the surface, having needle-shaped mullite crystals visible which originally present in fly ash before the reaction [7]. This indicates that a fraction of glass phase in fly ash has dissolved into the matrix. The loose contact between the matrix and fly ash spheres (Fig. 1) suggests that the outer shell of ash spheres dissolve and the inner layer expose to the matrix. EDS analysis (Fig. 2) confirms that there is a reaction between water-glass and fly ash. It shows that the matrix contains many Al, Fe, and Ca elements derived from the fly ash, and apart from Si and Na.

In order to verify the information obtained from SEM and EDS, XRD analysis was conducted. Fig. 3 is a comparison of the XRD pattern of the original fly ash to that of the hardened paste. It can be seen that the hardened paste contains quartz, hematite, mullite, and magnetite, which originally exist in the fly ash and have not been changed in the hardened paste. Meanwhile, it is noticed that there are many small peaks scattering in the spectrum, as compared to the XRD pattern of the original fly ash. These are the reaction products of the dissolved fly ash and water-glass in a state of low-ordered crystalline structure.

3.2. The paste made of fly ash, water-glass, and sodium hydroxide

In the present study, another type of paste was made of fly ash, water-glass, and sodium hydroxide. The weight ratio of fly ash/water-glass/sodium hydroxide was 26:15:2. In this mixture, the modulus of water-glass was reduced to 1.0 with the addition of sodium hydroxide.

The hardened paste of this mixture exhibits quite different microstructure under SEM (see Fig. 4). It was evidenced that large quantity of tabular crystals appeared in the paste. EDS analysis shows that these crystals contain large fractions of Si, Na in a ratio of Si/Na of about 1.0 (Fig. 5). However, the XRD of the specimens shows the same pattern as the specimens made of fly ash and water-glass without sodium hydroxide. This simply means that no new crystals formed in this paste. It is believed that the crystals observed by SEM (Fig. 4) are sodium silicate hydrates, with small amounts of Al and Fe. As the silicates with formula

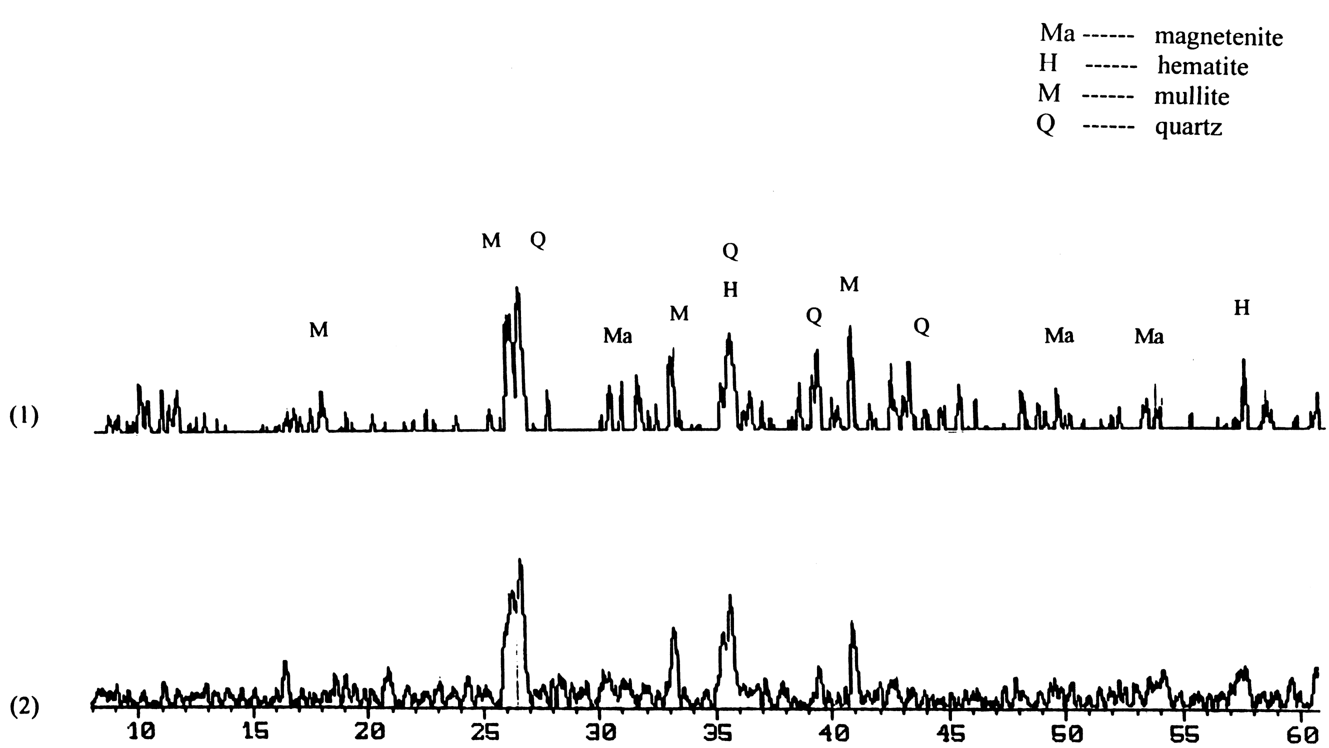

Fig. 3. XRD patterns of fly ash and the hardened paste. (1) XRD from original fly ash; (2) XRD from hardened paste.

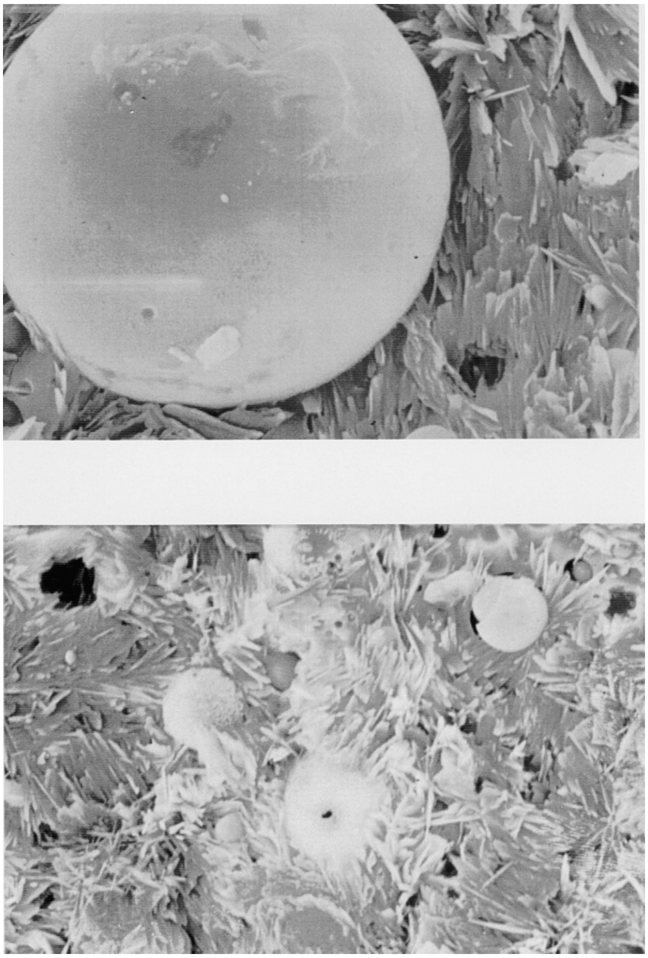

Fig. 4. SEM micrographs of a hardened paste with mix ratio. (1) × 10000, (2) × 750. Fly-ash/water-glass/sodium hydroxide = 26:15:2.

$Na_2O \cdot SiO_2 \cdot 5{-}9H_2O$ are highly soluble in water [8], the crystals dissolve due to absorption of the moisture in air during preparation of XRD samples, and thus cannot be detected by XRD.

4. Discussion

Based on the above experimental analyses, the dominant hardening mechanism of the mixture of the class F fly ash and water-glass can be described as in Eq. (1). First, sodium silicate hydrolyzes when mixed with water:

$$Na_2O \cdot nSiO_2 + (2n+1)H_2O \Longleftrightarrow 2NaOH + nSi(OH)_4 \qquad (1)$$

Secondly, the hydrolysis product, sodium hydroxide, would activate the acidic compositions such as Al_2O_3, Fe_2O_3, and SiO_2 in the fly ash under proper temperature. The products of the activation reactions may be in an amorphous state or in a low-ordered crystalline structure, which do not exhibit distinguishable peaks in the XRD pattern, but appears as low and scattered bands. The reaction products in the pastes made of fly ash and alkaline activator(s) may be the compounds of the type $Na_2O{-}Al_2O_3{-}SiO_2$ with a small amount of CaO, MgO, and Fe_2O_3 incorporated in them. Thirdly, the compound $Na_2O{-}Al_2O_3{-}SiO_2$ together with another hydrolysis product (i.e., silica gel) binds the particles of fly ash and results in the high strength of the pastes.

Previous experiments showed that the activation reactions do not proceed in a sufficient rate to produce high strength paste under ambient temperature [3]. Elevated temperatures are necessary to accelerate the reactions. When the modulus of water-glass was reduced from 1.64 to about 1.0 by the addition of sodium hydroxide, the excessive or unreacted sodium silicate would crystallize under the experimental condition. The tabular crystals attribute additional strength to the paste. Moreover, the unreacted spherical particles of fly ash in this structure had strong bond with the matrix, which also helps to gain high strength. This explains why the strength of the paste increases as modulus of water-glass decreases.

5. Conclusions

(1) In the mixture of the class F fly ash and water-glass, sodium hydroxide, as one of the hydrolysis products of sodium silicate, reacts with the acidic compositions in the fly ash and form compounds of the type of $Na_2O{-}Al_2O_3{-}SiO_2$ that is in an amorphous state or low-ordered crystalline structure.

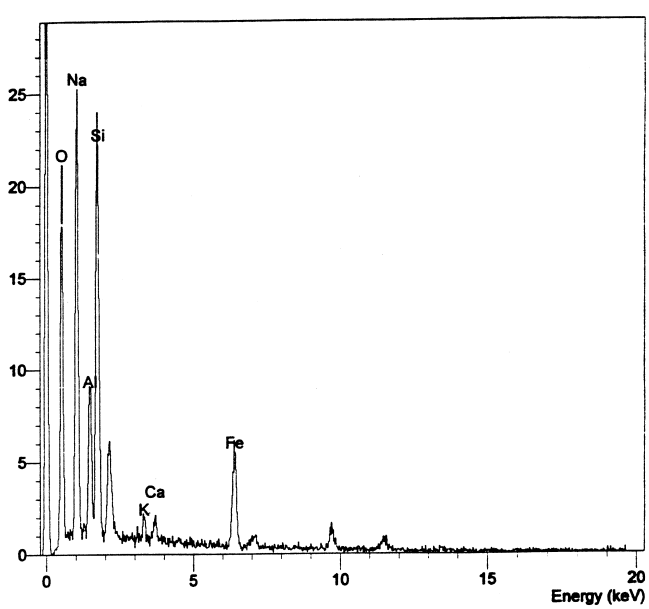

Fig. 5. EDS analysis of the crystal in the paste.

(2) When the water-glass has a modulus of 1.64, the gelatinous compound $Na_2O-Al_2O_3-SiO_2$ together with another hydrolysis product, i.e., silica gel, serve as the binder that hardens the fly ash mixture and results in the high strength.

(3) With the decrease of the modulus of water-glass from 1.64 to 1.0, the excessive sodium silicate crystallizes and the crystalline sodium silicate in the paste results in a compact structure, which contributes to the higher strength of the material.

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