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A study on pozzolanic reaction of fly ash cement paste activated by an injection of alkali solution

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HIGHLIGHTS

- We investigate the pozzolanic reaction of fly ash activated by alkali injection.
- Alkali injection increases the CH consumption by pozzolanic reaction.
- Alkali activation for 1 month decreases the volume fraction of 20–330 nm pores.
- Alkali activation for 1 month increases the volume fraction of 3–20 nm pores.
- Alkali injection accelerates the pozzolanic reaction of the fly ash cement paste.

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ABSTRACT

The purpose of this study is to investigate the pozzolanic reaction of the fly ash cement paste by an injection of an alkali solution after hardening. Cement pastes with 0%, 20%, and 40% of fly ash replacement ratios were used. An NaOH or saturated $Ca(OH)_2$ solution was injected into the paste through a syringe 1 month after casting at normal temperature. In addition to the reduction of the $Ca(OH)_2$ content, the consumptions of $Ca(OH)_2$ in the paste with 40% replacement of fly ash activated by NaOH and $Ca(OH)_2$ solution were observed to be 2.6 and 4.5 times as large as that with 20% replacement of fly ash. It indicates the alkali solution accelerates the pozzolanic reaction, together with the promotion of cement hydration. The results of pore structure analysis also confirmed this activation. As a result, it can be concluded that the 1-month alkali solution injection was effective in accelerating the pozzolanic reaction of the cement paste with 40% replacement of fly ash.

1. Introduction

Fly ash concrete has been applied extensively in the building construction because of taking the advantage of the enhanced durability, cost saving, and environmental protection [1,2]. However, it was reported that the early age strength of the fly ash concrete is one of its disadvantages due to the high replacement of cement with fly ash [3]. In addition, the slow pozzolanic reaction of fly ash is considered as one of factors which result in the low early age strength of the fly ash concrete [3–6].

Many researchers have focused on investigating the mechanism of the pozzolanic reaction and exploring the reasons of this slow reaction [7–11]. It is known that the pozzolanic reaction of the fly ash cement paste is the chemical reaction between reactive silica or alumina in the fly ash particles and calcium hydroxide ($Ca(OH)_2$–CH) formed from cement hydration in the presence of water at normal temperature [7]. Therefore, the cross-linked silica-tetrahedra (or cross-linked alumina-tetrahedra) in fly ash have to be broken so that the silica or alumina become reactive [9,10]. It was found that the disruption of these links occurs at a pH of 12.5 of pore solution in the paste at the room temperature [9] and more than 13 at 20 °C in NaOH solution [10]. This results in considering the addition of an alkali solution in order to increase the alkalinity of pore solution in the fly ash cement paste which owns the less alkalinity [10].

Hence, many methods of alkali activation have been investigated for accelerating the pozzolanic reaction of the fly ash cement paste [11–15]. However, this alkali activation in almost of these researches has been mainly carried out by adding an alkali solution or mixture of many alkali solutions in the water mixing of the fly ash cement paste which is cured at high temperature.

The aim of this paper is to investigate an influence of activation on the pozzolanic reaction of the fly ash cement paste at normal

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temperature by an injection of an alkali solution 1 month after casting through a syringe. In order to evaluate this influence, a quantitative analysis of the $Ca(OH)_2$ content and porosity of the fly ash cement paste was carried out by thermal gravimetric analysis and mercury intrusion porosimetry.

2. Experiments

2.1. Materials

The cementitious materials selected in this study were high-early-strength Portland cement, and low calcium fly ash which met the standard values of type II per JIS A 6201 (fly ash for concrete). The chemical composition and physical properties of these materials are shown in Table 1.

2.2. Preparation of paste specimens

Fly ash was used to replace high-early-strength Portland cement at ratios of 0%, 20% and 40% by mass (hereafter, abbreviated as FA0, FA20, and FA40, respectively). A water to binder ratio of 0.30 was kept constant. The pastes were mixed in a mechanical mixer and cast in 40 mm cube molds, and then sealed by aluminum tape to prevent water loss as well as carbonation. After that, a syringe with a capacity of 1 ml, of which the plunger was disconnected, was inserted in the specimen center (as shown in Fig. 1). All specimens were demolded 24 h after casting and cured in sealed condition at 20 °C.

2.3. Activation method

An activation was conducted by supplying an alkali solution 1 month after casting through a syringe, which was prepared in the Section 2.2. Two alkali activators, which were an NaOH solution (pH = 13.0) and a saturated $Ca(OH)_2$ solution (pH = 12.6), were injected naturally through the permeability of the pastes by themselves. Additionally, water was also injected instead of an alkali solution for the comparison.

2.4. Measurement of CH content

The CH content of the pastes at the age of 2 months was determined by thermal gravimetry analysis (TGA), using the half samples as shown in Fig. 1. The CH content of the sample was tested by each 4 mm-section from the surface to the point of the needle (as shown in Fig. 1). These samples were obtained in the form of a powder by a driller. Then, they were soaked in ethanol for 24 h to stop the further hydration, and dried in a vacuum desiccator for 24 h before measuring the CH content. The rate of the temperature increase of TGA equipment was installed at 20 °C/min up to 100 °C and kept at 100 °C for 30 min to remove evaporable water completely, and then at 20 °C/min up to 1000 °C. The CH content was calculated based on the ignited mass of the sample and the mass loss due to the dehydration of calcium hydroxide. This mass loss was picked up from differential thermal gravimetric (DTG) curves between the initial and final temperatures of the corresponding DTG peaks [16].

Table 1
Chemical composition and physical properties of cementitious materials.

Chemical composition and physical properties	Cement	Low calcium fly ash
SiO_2 (%)	20.30	57.7
Fe_2O_3 (%)	2.71	5.43
Al_2O_3 (%)	4.96	27.54
CaO (%)	65.49	1.26
MgO (%)	1.21	1.06
SO_3 (%)	2.98	0.36
Na_2O (%)	0.22	0.44
K_2O (%)	0.35	0.76
Loss on ignition (%)	1.19	2.8
Density (g/cm^3)	3.14	2.21
Blaine specific surface area (cm^2/g)	4590	3290

2.5. Measurement of porosity

The porosity of the pastes at the age of 2 months was measured by mercury intrusion porosimeter (MIP). The samples for test ranging 2.5–5 mm in size were obtained by crushing and choosing the area, which was around the position of the needle for the injection (as shown in Fig. 1). After that, these samples were soaked in ethanol for 24 h to stop the further hydration and dried in a vacuum desiccator for 24 h before MIP measurement. The MIP is built on the mercury intruded into the cylindrical pores under the strictly controlled pressure. The diameter of the cylindrical pore into which the mercury has been intruded is calculated according to the following Washburn equation [17].

$$D = -4\gamma \cos\theta / P \qquad (1)$$

where D: the diameter of pores (μm), γ: the surface tension of mercury (assuming a value of 480 mN/m), θ: the contact angle of mercury on the paste (taken as 140°), P: the pressure at which mercury is intruded into the pore (mN/m^2).

The MIP equipment used in this study has the maximum pressure of $414 \times 10^6\ N/m^2$. The porosity of the pastes at the age of 2 months was measured at a diameter range of 3 nm–300 μm.

3. Results and discussions

3.1. Effect of fly ash

3.1.1. CH content

The CH content of the control samples, which were the samples without the injection of water or alkali solution, at each 4 mm-section of the samples is shown in Fig. 2. It can be seen that the higher the replacement ratio of cement with fly ash, the less the CH content. This can be attributed to the high cement replacement with fly ash [3] and the consumption of CH by the pozzolanic reaction [6].

The consumption of CH by the pozzolanic reaction was calculated according to the following equation [18]:

$$CH_{cons.} = CH_{PC}\,(c/(c+f)) - CH_{FC}, \qquad (2)$$

where $CH_{cons.}$ is the consumption of CH by the pozzolanic reaction (%), CH_{PC} is the CH content in the plain cement paste – FA0 (%), CH_{FC} is the CH content in the fly ash cement paste – FA20 or FA40 (%), $(c/(c+f))$ is the mass ratio of cement in the mixture of cement and fly ash.

The consumption of CH by the pozzolanic reaction at each 4 mm-section of the samples is shown in Fig. 3 left. It shows the consumption of CH was increased significantly with the increase in the fly ash content (40% replacement of fly ash). This phenomenon was considered to be the result of the large quantity of fly ash used to replace the cement, resulting in the consumption of CH by the pozzolanic reaction. Comparing the consumption of CH between FA20 and FA40, the normalization is also shown in Fig. 3 right. It can be seen that the consumption of CH for FA40, which had 2 times as high the fly ash content as FA20, was less than 2 times of that for FA20. This may be due to the fact that the smaller $Ca(OH)_2$ content in FA40 than that in FA20 (as shown