Cement and Concrete Composites 65 (2016) 118–127

Contents lists available at ScienceDirect

Cement and Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Characterization of carbonation behavior of fly ash blended cement materials by the electrochemical impedance spectroscopy method

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ARTICLE INFO

Article history:
Received 23 June 2014
Received in revised form
3 August 2015
Accepted 7 October 2015
Available online 22 October 2015

Keywords:
Fly ash blended cement materials
Pozzolanic reaction
Carbonation
Electrochemical impedance spectroscopy
Equivalent circuit model
Prediction

ABSTRACT

The carbonation behavior of fly ash blended cement materials is studied by the electrochemical impedance spectroscopy (EIS) method, and a novel equivalent circuit model $R_s(Q_1(R_{ct1}W_1))(Q_2(R_{ct2}W_2))$ is proposed to investigate the influence of fly ash on the carbonation process in the cementitious materials. The experimental results demonstrate that the diameter of the impedance arc in high frequency region increases as carbonation progresses. Increasing the amount of fly ash incorporated in the cement paste is also found to enlarge the high frequency arc. The carbonation process can be quantified by the parameter R_{ct2} extracted from the equivalent circuit model $R_s(Q_1(R_{ct1}W_1))(Q_2(R_{ct2}W_2))$. It is found that the R_{ct2} value increases with increase in fly ash content. A linear relationship between the R_{ct2} value and the carbonation time is also observed. As a consequence, prediction of the carbonation depth of fly ash bended cement materials can be achieved through knowledge of the R_{ct2} value.

1. Introduction

Cement, as a component of concrete, is one of the most widely used building materials in construction. However, the over-production of cement has been observed to have negative impacts on the environment (*e.g.*the production of a ton of cement emits almost one ton of carbon dioxide into the air) [1]. To mitigate the emission of carbon dioxide, the incorporation of fly ash (a by-product of coal combustion in power plants) is widely used as partial cement replacement in concrete [2–13]. The use of fly ash in concrete also brings other benefits, including the improvements of mechanical properties and workability [14–16].

Cement and concrete materials incorporating fly ash are heterogeneous and porous. During the service life of concrete structures, the aggressive substances like carbon dioxide, chlorides and sulfate salt can penetrate through the capillary pores into the concrete matrix and lead to physical/chemical damage of the concrete structures. In the case of carbonation, the chemical reaction between the carbon dioxide and the calcium hydroxide contained in cement leads to a reduction in the alkalinity of concrete [17]. However, the incorporation of fly ash into concrete makes the case more complicated. Some researchers have reported that fly ash can accelerate the carbonation process of concrete [18–20]. This may be attributed to the reduction of cement products (*e.g.* $Ca(OH)_2$) that can be carbonated. However, it has also been reported by other literature that the resistance to carbonation can be enhanced by fly ash incorporation due to the micro-filler effect of fly ash particle [21]. In addition, the fly ash has pozzolanic activity during the cement hydration in which the SiO_2 and Al_2O_3 contained in fly ash reacts with the hydration product $Ca(OH)_2$ [22]. The reaction forms the additional calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH), resulting in a denser concrete matrix with better durability. Based on the above discussion, a consistent conclusion has not yet been reached for the effect of fly ash on carbonation of cement and concrete materials [23].

Currently, there are a variety of methods that have been investigated to quantify the carbonation process, such as the phenolphthalein solution test [24], thermo-gravimetric analysis [25], rainbow indicator test (with a pH range of 5–13 and a reading derivation of 10%–15%) [26], pH meter test [27], and chemical analysis [28,29]. However, the aforementioned methods require samples to be removed from a concrete structure, which can cause

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http://dx.doi.org/10.1016/j.cemconcomp.2015.10.006
0958-9465/

damage in the structure. Among the testing methods for evaluating the carbonation of concrete, EIS is a non-destructive testing (NDT) method that has been extensively used to study the electrochemical properties of materials [30–40]. This methodology is based on detecting the electrochemical impedance response of a material under an applied alternative electrical field. The electrochemical properties of a cement-based material exposed to environmental actions (*e.g.* carbonation, chlorides ingress and sulfate attack) can be varied, which can be characterized by periodically measuring the electrochemical impedance. Therefore, it enables to monitor and even estimate the carbonation process of cement and concrete materials as long as the EIS measurement is conducted on a regular basis.

Previous studies have used the EIS method to investigate the carbonation behavior of Ordinary Portland Cement (OPC) and OPC mortar. The results demonstrate that the method is effective to evaluate the carbonation process of OPC and OPC mortar. However, there is still a deficiency of information about the EIS method for analyzing the carbonation of fly ash blended cement materials. The incorporation of fly ash in concrete can make the carbonation behavior more complicated. An effective method is underscored to accurately evaluate the carbonation behavior of fly ash blended cements. The aim of this research work is to investigate the carbonation behavior of fly ash blended cement materials on the basis of EIS measurements. A novel equivalent circuit model is proposed in this paper to interpret the carbonation features of the blended cements. The influence of fly ash content in cement on the carbonation and the time dependence of the carbonation are investigated. Obtaining the functional relationship between the fitted parameters of the model and the carbonation time, the carbonation depth can be predicted.

2. Experiments

Cement: P.O 52.5 Portland cement was used. The chemical composition and the physical property of the cement are given in Table 1.

Fly ash: type I fly ash was used in accordance with the GB/T 1596-2005 standard [41]. The chemical composition and the physical property of the fly ash is also provided in Table 1.

Water: normal tap water.

The mixing proportions of the fly ash and cement in the samples are shown in Table 2. Five fly ash contents were considered in this work: 0% (F-C0), 10% (F-C1), 20% (F-C2), 30% (F-C3), and 40% (F-C4). For each fly ash content, 24 samples were prepared to be tested. To prepare the specimens, cement powder and fly ash were at first uniformly mixed with water. Then, a steel mould with a dimension of 40 mm × 40 mm × 160 mm was used to cast the mixture. The specimens were cured at room temperature (20 °C) and 95% relative humidity for 28 days. After the curing, the specimens were put into an oven with the temperature of 40 °C for 1 day to dry out the surface moisture. The wax sealing (see Fig. 1(a)) was then performed on the dried side faces of the samples so that the

Table 1
Chemical composition (mass % as oxide) and physical property of cement and fly ash.

Chemical composition and physical property	Cement	Fly ash
Calcium oxide (CaO)	64.67	4.74
Silica (SiO_2)	18.59	62.32
Alumina (Al_2O_3)	4.62	23.95
Iron oxide (Fe_2O_3)	4.17	1.33
Magnesium oxide (MgO)	2.35	2.04
Sulfer trioxide (SO_3)	3.32	1.25
Potassium oxide (K_2O)	0.92	0.76
Loss on ignition (LOI)	1.03	3.12

Table 2
Mix design of fly ash blended cement pastes.

Sample	Fly ash content	W/B (water to binder ratio)
F-C0	0%	0.4
F-C1	10%	0.4
F-C2	20%	0.4
F-C3	30%	0.4
F-C4	40%	0.4

carbonation could only be preceded in one dimension from the end faces towards the cement matrix. The carbonation test was carried out in a carbonation accelerating chamber where the CO_2 concentration was 20%, the temperature was29 ~ 31 °C and the humidity was 65 ~ 70%.

The carbonation process was measured by means of an EIS machine (version: PAR Potentiostat/Galvanostat 283). As previously mentioned in the section of introduction, the principle of the EIS method is based on detecting the electrochemical impedance response of a material under an applied alternative electrical field. Under the action of carbonation, the electrochemical properties (*e.g.*resistance of charge transfer and diffusion) of fly ash blended materials can be modified and they can be characterized by the measured electrochemical impedance. In this test, the specimen was placed between two parallel electrodes mounted in a tested mould (Chinese Patent No. ZL 201120473976.2), as shown in Fig. 1(b). A thin and wet sponge was inserted between the specimen and the electrode so that a good contact can be ensured. The electrochemical impedance measurements were run over the frequency range from 0.01 Hz to 1000000 Hz. The tests were conducted at carbonation ages of 0, 7, 14, 21, 28, 36, 60, 90 and 120 days. On the other hand, the carbonation depth was measured according to the GBJ820-85 Standard Testing Method for the Long Term Performance and Durability of Ordinary Concrete [42]. The tested samples were split into two blocks with transverse exposed fresh surfaces. The surfaces were immediately cleaned and then sprayed with phenolphthalein pH indicator (1% ethanol solution with 1 g phenolphthalein and 90 ml 95.0 V/V% ethanol diluted in water to 100 ml solution). Each sample was tested with a digital caliper (measuring to the nearest 0.1 mm) at seven different points on a split face, perpendicularly from the carbonation front to the end edge. The carbonation depth was calculated by average of the seven tested points and recorded, as illustrated in Fig. 2.

3. Results and analysis

From an electrochemical point of view, an empirical electrochemical system usually includes electrodes and electrolyte. The electrolyte normally exists as a form of solution. The whole electrochemical system can be simplified into an equivalent circuit (in Fig. 3(a)), which is known as Randles circuit model [43]. The electrical circuit model can be described as $R_s(Q_1(R_{ct1}W_1))$ by using a circuit description code (CDC). The detailed physical significance of the circuit elements (*i.e.* R_s, Q_1, $R_{ct1,}$ W_1) are captioned in Fig. 3(a). Even though fitting an impedance spectrum with the Randles circuit is a convenient way of obtaining the quantitative electrochemical information carried by the circuit elements [44], the electrolyte in this electrochemical system is considered as a single component and the electrochemical reaction only occurs at the surface of the electrodes. However, in the case of fly ash blended cement materials, the electrochemical system is much more complicated. First of all, there is a non-negligible charge transfer process at the interface between the solid phases (*e.g.* CSH) and liquid phases (*e.g.* pore electrolyte). Therefore, in the study of fly ash blended cement materials by EIS method, not only the charge