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Electrochemical feature for chloride ion transportation in fly ash blended cementitious materials

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HIGHLIGHTS

- EIS is used to study Cl^- transportation in fly ash blended cementitious materials.
- Fly ash affected on Cl^- penetration performance is interpreted by EC model.
- Relationship among penetration time(t)-depth (D)-model parameter(R_{ct1}) is deduced.

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ABSTRACT

The chloride transport behavior of fly ash blended cement material was investigated in this study by using electrochemical impedance spectroscopy (EIS). The chloride penetration was studied by means of EIS. A new equivalent circuit model was applied to describe the electrochemical system of fly ash blended cementitious materials. Experimental results demonstrate that the increase in the fly ash replacement ratio of sample can increase the penetration depth of chloride ion. In addition, the increase in the fly ash replacement ratio of sample can enlarge the Nyquist curve semi-circle, and improve ion transfer resistance at the solid-liquid phase interface. We determined the quantitative relationship between electrochemical properties and chloride penetration depth in order to successfully predict the chloride ion penetration depth of blended cements with varying fly ash content. It is expected to complement the existing test standards regarding the durability evaluation of construction materials.

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1. Introduction

Ordinary Portland cement is an essential component of concrete and one of the most widely used building materials in the world. However, the over-production of cement has a dangerous environmental impact. Fly ash is a coal combustion by-product in power plants and is widely used in concrete as a cement replacement [1–8]. As a by-product of industrial process, the utilization of fly ash has contributed to the progress made in addressing sustainable construction challenges. Fly ash as a mineral admixture not only improves concrete performance by reducing hydration heat, but also reduces carbon dioxide production [9]. Moreover, Fly ash is beneficial to the strength and durability of concrete structures, and can be used to reduce waste [10].

Concrete is often subject to aggressive penetrating substances such as chloride salt in coastal environments. If chloride ion concentration near steel bars exceeds a certain threshold value, the protective film around the steel will become unstable. When the protective film is broken down, steel corrosion is occurring [11]. The influence of fly ash on cement properties has been studied extensively in Greece and Turkey [12,13]. Antiohos et al. [14] showed that increasing active silica content had a greater influence on cement hydration and fly ash. Bentur et al. showed the effectiveness of mineral additives in respect to chloride ion penetration in concrete [15], that the use of fly ash in cement matrices had a positive influence on concrete impermeability [16]. However, the role of fly ash on the electrochemical behavior of cement under chloride ion transportation has not yet been studied.

Conventional testing methods (e.g., the titrimetric Volhard method) which based on chemical composition change have been applied for a chloride corrosion assessment that exploited solubilized chloride precipitation with silver nitrate [17]. However, these methods often destroy the samples. The measurement accuracy depend on test duration and inspector experience. In recent years, electrochemical impedance spectroscopy has been recently proposed to test different material system with non-destructive measurement [18–23]. Penetration of chloride ion is a complicated

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physical and chemical process. The evolution of impedance spectra can be used to characterize the reaction mechanism and dynamic properties. It is of great importance for durability characterization in the construction industry to understand the influence of fly ash on the electrochemical properties of chloride ion transportation. The chloride ion penetration rate in concrete is very slow under natural conditions. The long-term chloride immersion methods are laborious, time-consuming, and costly. In this paper, the rapid chloride migration test (RCM) was used to overcome these disadvantages [24,25].

This study aims to elucidate the electrochemical behavior of chloride ion transportation systems of fly ash blended cement materials. The effects of fly ash on chloride ion permeability is analysed by impedance spectroscopy. Fly ash also influences chloride ion penetration depth and electrochemical systems. In this work, an equivalent circuit model has been applied to quantitatively describe the EIS data. In addition, the relationship between chloride penetration depth and electrochemical parameters were studied and the penetration depth was predicted accordingly.

2. Experiments

2.1. Materials, mixture proportions, and specimen details

The cement used in this study was Type I ordinary Portland cement (OPC) made by Onoda Cement Limited Company of Shenzhen, China. The chemical composition and physical properties of the cement are presented in Table 1. The fly ash used was Class I fly ash with the composition also shown in Table 1. Normal tap water was used, and a mixture design of fly ash blended cement pastes were made to study chloride ion penetration of cement pastes with different mixing proportions (Table 2).

Cement and water were first mixed in a blender, and then the mixture was cast in a cylindrical mold with dimensions of φ100 mm × 50 mm, and demolded after 24 h in a curing chamber (95 ± 5% relative humidity, 20 ± 2 °C) for 28 days. The samples were subjected to wax treatment on lateral surfaces before ion penetration to ensure one-dimensional chloride ion penetration (Fig. 1).

2.2. Rapid chloride migration test (RCM) test

We used a detailed RCM test procedure and chloride migration coefficient calculation method [26,27]. The seal test sample was arranged in the rubber barrel. The bottom of sample arranged in the rubber tube. Test block high rubber outer tubular mounting was composed of two high 25 mm hoops and tightened, and 300 mL potassium hydroxide solution was poured into the rubber barrel. At the end of the test block, the rubber tube was immersed in a chloride solution for rapid infiltration (Fig. 2).

Table 1
Chemical composition and physical properties of cement.

Chemical composition and physical property	Cement	Fly ash
Calcium oxide (CaO)	64.67	3.06
Silica (SiO_2)	18.59	54.3
Alumina (Al_2O_3)	4.62	31.62
Iron oxide (Fe_2O_3)	4.17	6.27
Magnesium oxide (MgO)	2.35	0.99
Sulfer trioxide (SO_3)	3.32	1.07
Potassium oxide (K_2O)	0.92	0.56
Loss on ignition (LOI)	1.03	2.13
Specific surface area (m^2/kg)	345	391
80 μm sieving fineness (%)	4.15	8.30

Table 2
Cement paste mix for testing.

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

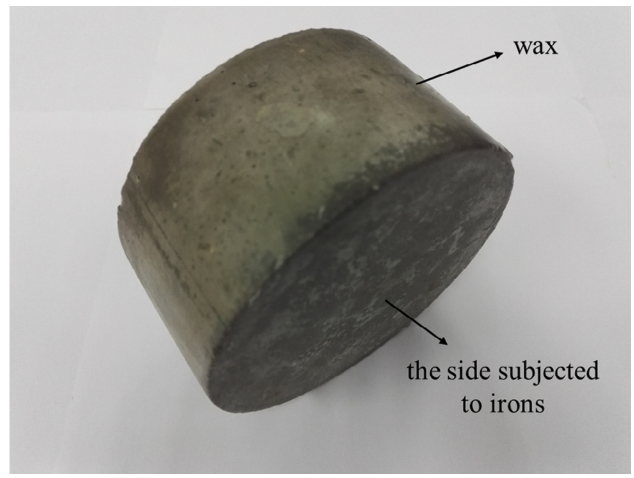

Fig. 1. The surface treatment before chloride penetration test.

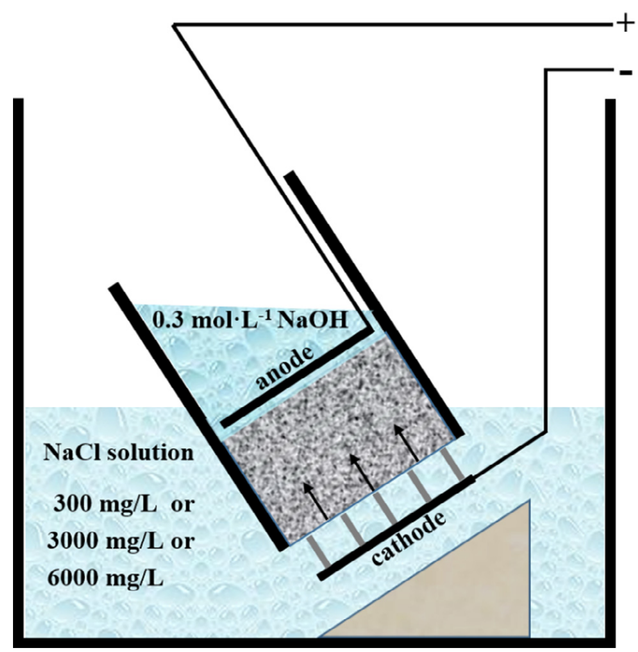

Fig. 2. Rapid chloride migration test.

2.3. Penetration time and penetration depth test

The test samples were conducted at 30.0 V constant voltage for rapid penetration. Test samples were subjected to electrochemical impedance spectroscopy at 0, 8, 16, 24, 32 and 40 h. In accordance with study norms, we attempted to cut the average block in half in order to clean up powder remnants in the section. The test samples were sprayed with 0.1 mol/L $AgNO_3$ solution. Then the section were measured at every 2 cm after 30 s and measured the two sides of each point of penetration depth by vernier caliper (Fig. 3).

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