Construction and Building Materials 146 (2017) 493–501

Contents lists available at ScienceDirect

Construction and Building Materials

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

Chloride transport and microstructure of concrete with/without fly ash under atmospheric chloride condition

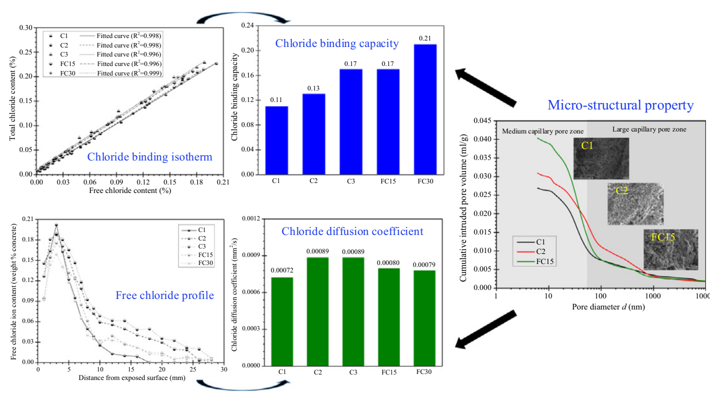
Jun Liu [a], Guangfeng Ou [b], Qiwen Qiu [c,*], Xiaochi Chen [a], Jing Hong [b], Feng Xing [a]

[a] Guangdong Provincial Key Laboratory of Durability for Marine Civil Engineering, Shenzhen University, Shenzhen 518060, Guangdong, China
[b] Department of Civil and Environmental Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China
[c] Department of Architecture and Civil Engineering, City University of Hong Kong, Hong Kong, China

HIGHLIGHTS

- Atmospheric chloride transport through concrete deviates the Fick's diffusion law.
- A linear chloride binding isotherm occurs in marine atmosphere environment.
- Increasing the w/c ratio enhances chloride binding but promotes chloride diffusion.
- Fly ash benefits the chloride binding and resists the chloride diffusion.
- Formation of pore structure influences the transport mechanism of chloride aerosol.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 October 2016
Received in revised form 9 March 2017
Accepted 5 April 2017

Keywords:
Concrete
Fly ash
Transport property
Microstructure
Atmospheric chloride
Durability

ABSTRACT

This paper presents a comprehensive investigation regarding the chloride transport and microstructure of plain concrete and fly ash blended concrete under atmospheric chloride environment. Experimental results demonstrate that all the free, bound, and total chlorides show a build-up of ion concentration in the chloride profile. A linear relationship between the total and free chloride content is observed. Both water-to-cement ratio and fly ash content have great impact on the chloride binding capacity and the chloride diffusion coefficient. Microscopic properties (e.g. morphology, pore size distribution, porosity) are evaluated for chloride-contaminated concrete, and their correlation with the chloride transport behavior is discussed.

1. Introduction

Reinforced concretes undergo deterioration when they are exposed to aggressive substances from severe environments. It is acknowledged that chloride ions usually corrode the steel bars embedded in concrete when the chloride concentration reaches a critical level [1–4]. The chloride-induced steel corrosion is serious when the concrete structures are located in the coastal zone [5,6]. Corrosion of steel reinforcing bars can initiate a great deal of problematic consequences such as the loss of cross-sectional area of the steel bar, growth of concrete cracks and even the spalling of concrete cover [7,8]. Due to the significance of this problem, investigations concerning the mechanism of chloride ion transport in

* Corresponding author.
E-mail address: qiuqiwen0422@gmail.com (Q. Qiu).

http://dx.doi.org/10.1016/j.conbuildmat.2017.04.018
0950-0618/

concrete have been extensively carried out [9–13]. Up to present, a multitude of studies concerning the chloride attack have been conducted by using salt immersion tests [14–18], and the traditional Fick's law has been basically adopted to describe the behavior of chloride transport. The Fick's second law or its modified form to express chloride transport is satisfactory to be adopted when the concrete materials are immersed into chloride solution. However, deviation from Fick's diffusion can be occurred when the reinforced concretes are subjected to atmospheric chlorides in aerated salt spray zones [19]. In general, the atmospheric chlorides (e.g. chloride aerosol) can accumulate on the surface of concrete, resulting in the penetration of chlorides though the concrete given that the exposure time is long enough. The mechanism of chloride transport in atmospheric chloride environment is more complicated because of the cyclic drying-wetting condition and the presence of outside air pressure. However, research work with respect to the mechanism of chloride aerosol ingress is still rare. It is of great importance to investigate the chloride ion transport in concrete under atmospheric salt condition with the goal for better understanding the durability performance of concrete materials used in marine environments.

In recent decades, pozzolan material (a by-product or combustion residue from the coal-burning electric power plant) has been commonly used as a mineral admixture in cement and concrete materials [20–25]. Fly ash is one of the most common pozzolan materials, which has numerous advantages that favor it as an additive of concrete material, for instance, low initial capital cost of raw material, the associated energy savings, and improvement of concrete workability [26,27]. In addition to these beneficial aspects, many researchers claim that blending fly ash into concrete contributes to enhance the material durability due to the micro-aggregate filling effect and the pozzolanic activity [28,29]. It has been reported that the use of fly ash as a replacement of cement component in concrete can result in resisting the penetration of chloride ion [30–32]. Recently, the durability performance for fly ash concrete used in atmospheric chloride environments has begun to attract attention, but until now no clear understanding has been reached with respect to the effect of fly ash incorporation on the chloride transport and the microstructure of concrete under chloride aerosol ingress. It is expected to include the factor of fly ash addition on the chloride transport in the modeling of service life for steel reinforced concrete structures; nevertheless, this requires the comprehensive understanding of chloride transport mechanism of fly ash concrete in atmospheric marine environments.

In the present study, the transport property and microstructure of concrete with/without fly ash under the atmospheric chloride environment is experimentally investigated. Chloride-contained salt spraying test is carried out to simulate the marine aerosol environment. Chloride profile, diffusion coefficient, and binding capacity of concretes are determined to elucidate the chloride transport mechanism. Pore properties (e.g. micro-morphology and pore size distribution) of the chloride-contaminated concrete are explored by the use of mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM). Effects of water-to-cement ratio and fly ash content on the chloride transport and microstructure are evaluated.

2. Experimental

2.1. Materials and specimen preparation

Portland cement supplied by Shenzhen Haixing Onoda Cement Co. Ltd., Shenzhen, China, was used as the cementitious material. Class F fly ash obtained by Mawan Power Plant, Shenzhen, China, was used as partial replacement of cement. The chemical compositions of the cement and fly ash are listed in Table 1. Loss on ignitions for cement and fly ash were 1.03 and 3.12, respectively. River sand with the fineness modulus of 2.61 and the apparent density of 2632 kg/m^3 was used as fine aggregate. Gravel with a size ranging from 5 to 20 mm and the apparent density of 2700 kg/m^3 was used as coarse aggregate.

The mix proportions of concretes with and without fly ash are listed in Table 2. Three water-to-cement (w/c) ratios (0.53, 0.47, and 0.38) were considered for the ordinary Portland cement (OPC) concrete. For fly ash blended concretes, two dosages of fly ash addition (15% and 30%) were considered. All the mixtures were cast into steel mold with the dimensions of $100 \times 100 \times 100$ mm^3, and cured for 56 days under the condition that the temperature was 20 ± 2 °C and the relative humidity was approximately 95%. After curing, five surfaces of the concrete specimens were sealed with epoxy resin, as depicted in Fig. 1(a). This was to implement the one-dimensional penetration of chloride ions.

2.2. Atmospheric chloride conditioning test

In this study, concrete specimens were subjected to salt spraying test that can simulate the marine atmospheric environment. The salt spraying test was carried out for a period of 28 days in a chamber which was provided by Sunan Experimental Equipment Co. Ltd., Wuxi, China. According to the local climate data of coastal region in Shenzhen city, the temperature and the relative humidity in the environmental chamber were set as at 35 ± 2 °C and 70 ± 2%, respectively. Generally, the rate of chloride diffusion through the concrete material rises with increase in the temperature, as reported by the following literatures [33,34]. It is believed that the setting of 35 ± 2 °C during the accelerated atmospheric chloride test can achieve more obvious results in the given short period of 28 days in this test. In addition, such temperature and relative humidity are considered to simulate the tropical environment or hot climate regions, which are also regarded to be conservative for durability assessment of concrete materials in construction field. During the test, 5% NaCl solution was atomized by means of spray nozzles using pressurized air. Based on the climate data towards the coastal region of Shenzhen city, the rainy-to-sunny days ratio is around 2:3. In order to simulate the exposure condition in a more realistic manner, the cyclic drying-wetting action was performed in a testing day (i.e. 10 h for chloride aerosol spraying and 14 h for drying condition).

2.3. Chemical titration and chloride ion content measurement

After salt spraying test, the concrete samples were powdered by gridding machine layer-by-layer from the exposed surface (with an interval of 1 mm for the first 10 mm, and with an interval of 2 mm in the range from 10 to 30 mm), as shown in Fig. 1(b). Then, the concrete powders were collected as shown in Fig. 1 (c), and dried in an oven at 105 °C for 24 h to constant weight. In this work, both the free and the total chloride contents were measured separately based on AASHTO T260-97 standard [35]. After chemical titration with silver nitrate ($AgNO_3$), the chloride ion concentration was determined with a Metrohm 809 Titrando automatic potentiometric titrator.

2.4. Pore structure characterization

The pore size distribution of concrete after subjecting to chloride aerosol spraying was obtained by MIP test. A well-known Washburn equation was applied for calculating the pore diameter [36], as expressed in Eq. (1).

$$d = \frac{-4\gamma\cos\theta}{P} \tag{1}$$

where d represents the pore diameter (m), γ represents the surface tension (N/m), θ represents the contact angle between mercury and pore wall (°), and P represents the applied pressure (MPa). As shown in Fig. 2(a), the MIP test was conducted by the use of Mocromeritics AutoPore IV 9500 (Micromeritics, GA, USA) which provided a maximum operating pressure of 210 Mpa corresponding to a minimum detectable pore diameter of 6 nm. The chosen value for the contact angle and the surface tension were 130° and 480 mN/m respectively, according to recommendations from the literatures [37,38]. The cumulative intruded pore volume with diameter was recorded, and the total porosity of concrete specimen could be obtained when the maximum applied pressure was reached. In addition, the pore size distribution (PSD) curve was obtained by logarithmic differentiation of the cumulative pore volume curve.

In order to optically analyze the morphological surface of concrete at 28 days of chloride aerosol exposure in the lab, SEM test was carried out as shown in Fig. 2(b). Prior to SEM test, the concrete specimens were fractured into small pieces and then vacuum dried at 50 °C until constant weight. A thin gold layer was coated on the concrete piece under the SEM test.

3. Results and discussion

3.1. Free, bound and total chloride profile

In this research, the chloride content is defined as the percentage of chloride ions by mass of concrete sample. Based on plotting