Materials Letters 174 (2016) 234–237

Contents lists available at ScienceDirect

Materials Letters

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

Characterization of sulfate diffusion into cement paste by low frequency impedance spectroscopy

Chuansheng Xiong [a], Linhua Jiang [a,b,*], Yan Zhang [a], Hongqiang Chu [a], Peng Jiang [a]

[a] College of Mechanics and Materials, Hohai University, Nanjing 210098, PR China
[b] National Engineering Research Center of Water Resources Efficient Utilization and Engineering Safety, Nanjing 210098, PR China

ARTICLE INFO

Article history:
Received 2 July 2015
Received in revised form
24 February 2016
Accepted 23 March 2016
Available online 25 March 2016

Keywords:
Cement paste
Corrosion
Diffusion
Crystal growth
Impedance spectroscopy

ABSTRACT

In this study, EIS was used to investigate sulfate diffusion process into cement paste. Cement paste samples with w/c ratio of 0.35 and 0.45 were immersed in 10 wt% sodium sulfate solutions for different durations. An equivalent circuit model of cement paste exposed to sulfate attack was proposed, and some relevant parameters of the equivalent circuit were obtained by EIS analysis. The validations of the effectiveness of EIS on investigating the sulfate diffusion have been provided by SEM and XRD analysis. As the results shown, it is sensitive to use EIS to characterize the diffusion process of sulfate ions into cement paste. The relationship between ingress depth of sulfate obtained from EIS analysis and the square root of exposing time is approximately linear.

1. Introduction

In the field of concrete research, electrochemical impedance spectroscopy (EIS) has been widely used to study the corrosion and protection of reinforcement [1–3], hydration process of cement [4], pore structure and interface of concrete [5,6]. The frequency range of AC impedance used in concrete is generally from 10^{-6} to 10^{6} Hz. The impedance spectra in high frequency region (10^{4}–10^{6} Hz) mainly reflect capacitance of concrete, which is associated with the permittivity of concrete matrix (cement gel, aggregate and unhydrated cement etc.). In low frequency region (10^{-6}–10^{3} Hz), it ascribes to the properties of conductive path (pore structure and ionic concentration of the pore solution) [7].

Sulfate attack is a diffusion-reaction process of concrete when exposed to environment with sulfate [8]. This process often happens along with the variation of pore structures in concrete, which can be well measured by AC impedance spectra [5,6], especially in the low frequency section [9]. However, to the authors' knowledge, few investigations have been done on the characterization of sulfate attack on concrete by EIS. In this paper, a set of testing apparatus that can be used to determine the sulfate diffusion process into concrete by electrochemical impedance spectroscopy was designed. An equivalent circuit model of cement paste with sulfate attack was proposed, and some relevant parameters of the equivalent circuit were obtained and analyzed.

2. Materials and experiments

The cement used was P. II 42.5 (GB 175-2007) Portland cement. $40 \times 40 \times 50$ mm^3 prismatic specimens were prepared with pure cement paste. The water to cement (w/c) ratio of the cement pastes were 0.35 and 0.45. After curing for 91 days in saturated limewater, specimens were coated on the side surfaces with epoxy resin. The end surfaces were burnished with sandpapers. Two pieces of sheet titanium mesh electrode were stick onto the two end surfaces by conductive adhesive with two wires weld on them. Then, the whole sample was immersed in a 10 wt% sodium sulfate solution, and the solution was refreshed once a month. Subsequently, at each period of exposure duration, specimens were extracted to measure the electrochemical characteristics. The EIS was carried out with a Princeton Applied Research (PAR) START 2273 Potentiostat by applying a sinusoidal potential perturbation of 10 mV at the open circuit potentials with frequency sweep from 1 kHz to 10 mHz. In order to prove the effectiveness of characterization of sulfate diffusion process by using EIS, the mineral composition profiles from the exposed surface to interior of the investigated pastes were examined by X-ray diffraction (XRD) analysis. In addition, the microstructures of the sulfate migrated parts of the pastes were provided with SEM graphs.

* Corresponding author at: College of Mechanics and Materials, Hohai University, Nanjing 210098, PR China.
E-mail address: lhjiang@hhu.edu.cn (L. Jiang).

http://dx.doi.org/10.1016/j.matlet.2016.03.131
0167-577X/

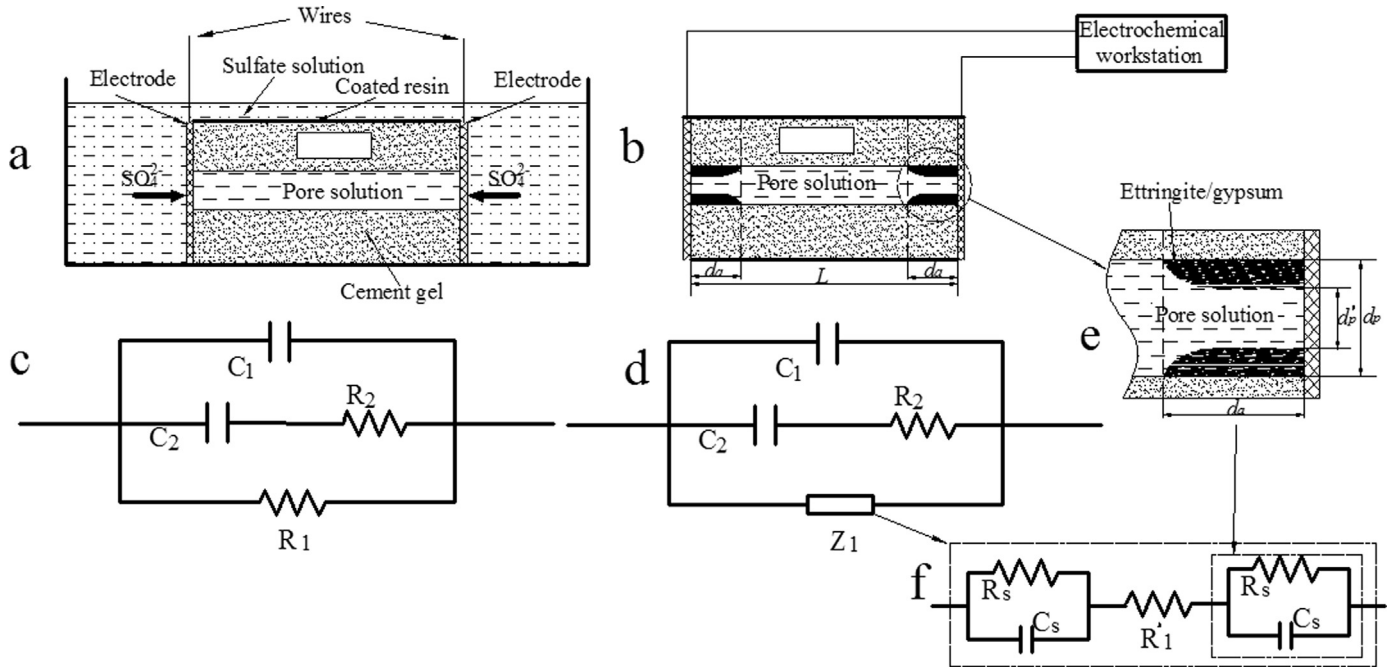

Fig. 1. Schematic diagram of testing apparatus and the relevant equivalent circuits: a. sulfate attack tests, b. cement paste samples with sulfate attack, c. equivalent circuit of cement paste before sulfate attack, d. equivalent circuit of cement paste with partially attacked, e. sedimentation of expansive products in interconnected pores, f. equivalent circuit of interconnected pores with expansive products deposited on the walls.

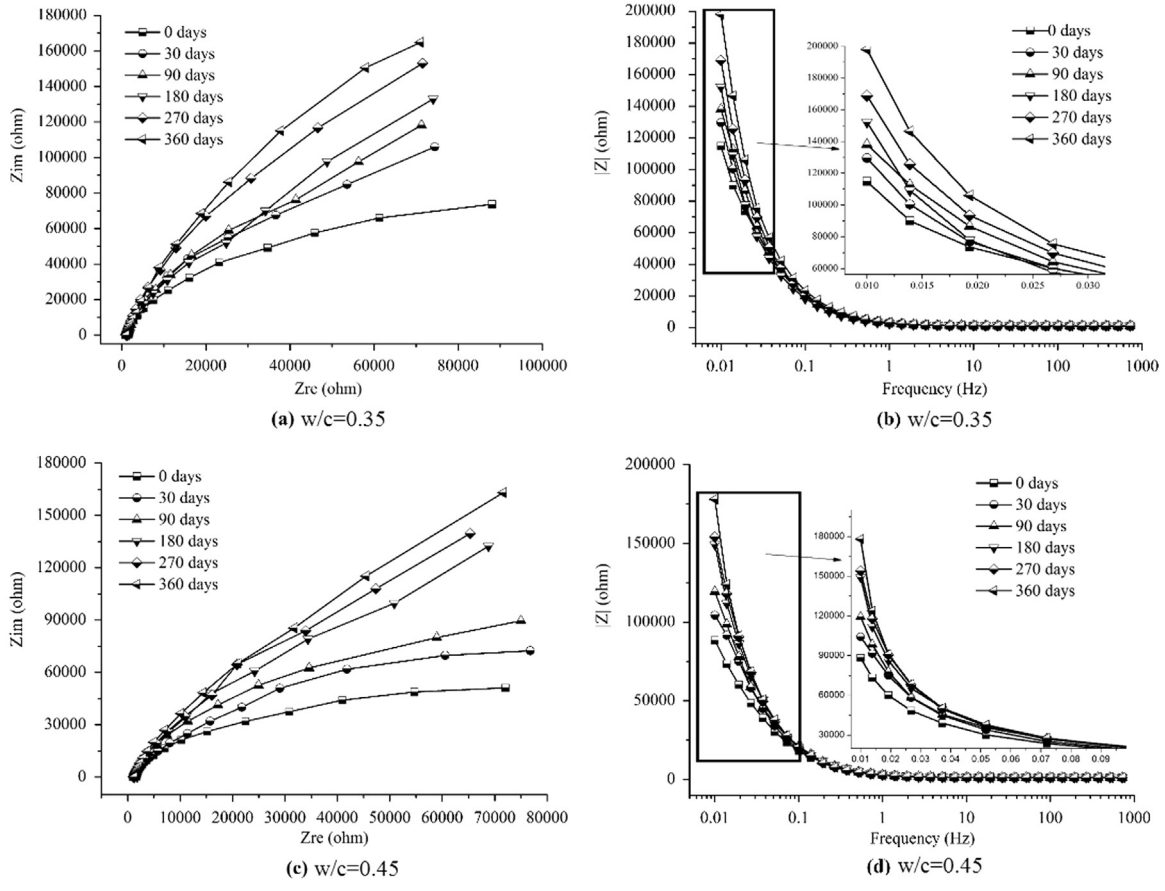

Fig. 2. The Nyquist and Bode diagrams of cement pastes with different w/c ratios exposed for different time in a 10% Na_2SO_4 solution.

3. Equivalent circuits of sulfate diffusion process

The microstructure of a hardened cement paste can be simplified into Fig. 1(a), where the shaded areas represent cement mix, the dashed areas stands for interconnected pores with pore solution and the white areas are closed pores filled with gas or pore solution. According to Song [10], current conduction occurs mainly through the interconnected pores and closed pores with