ARTICLE IN PRESS

Cement and Concrete Research xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Cement and Concrete Research

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

Water and chloride ions migration in porous cementitious materials: An experimental and molecular dynamics investigation

Peng Zhang[a,b], Dongshuai Hou[a,*], Qing Liu[a], Zhaolin Liu[a], Jiao Yu[a]

[a] Centre for Durability & Sustainability Studies, Qingdao University of Technology, 266033 Qingdao, China
[b] Institute of Concrete Structures and Building Materials, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany

ARTICLE INFO

Keywords:
Water penetration
Chloride ions migration
Neutron radiography
Molecular dynamics
Time correlation function
Radial distribution function

ABSTRACT

The interactions of water and chloride ions penetration into porous mortar have been investigated experimentally and modelled by molecular dynamics. The water distribution visualized by neutron radiography and chloride penetration by Electron Probe Micro-Analysis indicate that separation of chloride ions from water during the penetration process took place and water ran much deeper into the material than chloride ions. The relationship between the penetration depth of water and chloride ions can be described by a linear function despite different water-cement ratio. Furthermore, molecular dynamics attributes the different transport mechanisms of water and ions in porous cementitious materials to three reasons: the nanostructure of hydration product play filtering role to screen chloride ions with larger hydration shell; as compared with water, ions reside in the calcium silicate surface for longer time due to the strong interfacial bonding; chloride ions accumulate and form CaCl ionic cluster, slowing down the migrating rate.

1. Introduction

Nowadays, service life and sustainability of reinforced concrete structures have become a crucial issue due to the economic and ecologic implications [1,2]. The durability of concrete is shortened by all kinds of damage, and most of these deterioration mechanisms are tightly related to the existence and movement of water. Water serves as a carrier to transport the aggressive substances such as chloride ions into the pore structure of concrete. This causes the steel reinforcement corrosion which finally reduces the durability of reinforced concrete structures.

If placed in a dry environment, cement-based materials such as mortar and concrete are extremely durable. Under these conditions concrete from the Roman Empire has survived > 2000 years. If cement-based materials are exposed permanently or temporarily to water, however, they may be seriously damaged in a short period. For instance, water saturated concrete is frost sensitive. Binding compounds such as $Ca(OH)_2$, $CaCO_3$, and CSH gel may be leached out by hydrolysis. Aggressive chemical compounds may be transported deep into the pore space of concrete by capillary suction and deteriorate the porous material by accelerated leaching or by internal pressure after ion exchange. Moisture content variations in cement-based materials cause dimensional changes, swelling and shrinkage. The rate of corrosion of steel in reinforced concrete also depends on the moisture content. These are just a few arbitrarily chosen examples of direct or indirect damaging mechanisms of water in concrete. There are more examples which all show that there is a need to understand processes of water transport and the development of moisture distribution in porous cement-based materials in order to improve durability and serviceability of building structures. Therefore, it becomes important to measure the moisture conditions in building materials in an accurate way.

For the determination of the moisture content in cement-based materials such as mortar or concrete there are several destructive and non-destructive testing methods, which may be subdivided into five groups. (1) Gravimetric method [3]: This method is simple and widely used. With care, it is possible to collect data about the quantity of moisture inside the specimen, but its distribution cannot be established by this technique and it is destructive. (2) Electrical techniques [4,5]: They utilize the relationship between the electrical properties, such as resistance, permittivity or capacitance of cement-based materials and their water content. It can offer a quick, non-destructive measurement of surface moisture. (3) Nuclear magnetic resonance (NMR) spectroscopy [6]: It has been used in a variety of disciplines to examine moisture content in materials since 30 years ago. (4) Humidity sensors [7]: Most frequently the change of electric properties of implemented sensors made of ceramics, polymers or other materials can be measured to determine moisture content of the surrounding material. (5) Radiation attenuation techniques: These include X-ray [8], gamma ray [9,10]

* Corresponding author.
E-mail address: dshou@outlook.com (D. Hou).

http://dx.doi.org/10.1016/j.cemconres.2017.09.010
Received 16 February 2017; Received in revised form 9 May 2017; Accepted 18 September 2017

and neutron imaging method [11–14]. Their attenuations can be related to water content within the materials. With calibration, absolute moisture content can be measured. Excellent accuracy and resolution can be achieved with this method of measurement, however, the equipment required to achieve this can be highly sophisticated. There are also some other methods which can be used to measure the moisture condition in cement-based materials, such as pressure method, time domain reflectometry method which originally used in soil sciences, and microwave reflection method [15]. Recently, a RILEM Technical Committee 248-MMB was initiated, summarizing the state-of-the-art report on methods of measuring moisture in building materials and structures.

Among these methods described above, neutron radiography can be used to observe the dynamic processes of moisture movement in cement-based materials. Neutron radiography is based upon the fact that the neutron attenuation coefficient changes abruptly according to the atomic number of the element. Elements with the highest attenuation coefficient are boron, hydrogen, lithium and dysprosium, which are, except for hydrogen, very rare in nature. Aggregate and the cement matrix, which are the dominant ingredients of concrete, mostly consist of calcium, silicon, aluminium, iron, magnesium, oxygen and carbon, so cement-based materials evidently have low attenuation coefficient for neutrons. The water present in the hydrate structure certainly also contribute to the attenuation of neutrons. But in the case of measuring the water movement in cement-based materials, the initial water existing in hydrate structure will be eliminated during the quantification analysis. Therefore, high sensitivity to small amounts of moisture movement can be expected. Thanks to this unique characteristic, neutron radiography has been identified as a most appropriate and powerful method for the observation and quantification of moisture movement inside the cement-based materials.

In this contribution, the processes of water penetration and chloride ions migration into porous cementitious mortar have been investigated. The water movement and moisture distributions in two types of mortar has been visualized and quantified by means of neutron radiography. The spatial distributions of chloride ions in the materials have been measured both by the conventional titration method and the EPMA (Electron Probe Micro-Analysis) method. The relationship between the water penetration and chloride ions migration has been investigated in particular. Additionally, to further provide the insights on the transport mechanism, molecular dynamics has been employed to study the molecular structure and dynamics nature of water and ions diffusing in the nanometer calcium silicate hydrate gel pore.

2. Experimental method

2.1. Materials and preparation of specimens

The specimens were prepared with two types of cement mortar. Portland cement type 52.5 and river sand with a maximum grain size of 5 mm were used. Cubes with the side length of 100 mm were produced. All the specimens were demolded after 24 h and then stored in a humid room with RH ≥ 95% and temperature of 20 ± 2 °C until they reached an age of 28 days. The compositions of the two types of mortar used in this project are given in Table 1.

Table 1
Compositions of the mortar used in this project, kg/m^3.

	W/C	Cement	Sand	Water
M1	0.6	500	1350	300
M2	0.4	562	1350	225

2.2. Water and chloride penetration

Before the test the samples were dried at 50 °C until constant weight was achieved. Then the specimens were taken out of the oven and put in the sealed box at 20 °C for one day until cooling down. After that four surfaces were sealed with aluminium foil, leaving two opposite surfaces remained free. Then the specimens were placed in contact with water (or 3% NaCl solution). In this way, it is assumed that the concrete specimens were dry and there was no free water in capillary pores before water and chloride penetration. Water (or chloride ions) entered the specimens in one dimension. At the contact time of 0.5 h, 1 h, 2 h, 4 h, 8 h, 12 h, 24 h, 48 h, 3 d, 7 d and 28 d, the specimens were taken out and split into two halves. From the fracture surfaces, the water front can be distinguished from the colour difference. In the meantime, the chloride penetration depth was measured by spraying 0.1 mol/L $AgNO_3$ on the surface [16]. Then, thin layers of 1 mm thickness were milled consecutively from the surface which was in contact with the salt solution. The chloride profiles along the penetration depth in concrete were then determined by titration method. In addition, some specimens were also selected for EPMA analysis. In this way, the spatial distributions of chloride ions in specimens were measured in two dimensions.

2.3. Neutron radiography

Furthermore, some specimens were cut into slices with thickness of 20 mm for neutron radiography test. Neutron radiography is a powerful tool for non-destructive testing of materials for scientific research and industrial applications. The neutron beamlines have been extensively and successfully installed both from reactor-based facilities and spallation sources over the last few decades. The special features of neutron interaction with matter make it possible to inspect bulk of specimen and to produce images of components containing light elements such as hydrogen in particular. The neutron radiography (NR) tests have been performed at the beamline NEUTRA at Paul Scherrer Institute, Switzerland [17]. The basic experimental set-up of NR is shown in Fig. 1. The principle of NR in general terms is recording of the radiation passing through an object by a position sensitive detector, a 6Lif/ZnS scintillator screen in this test. In the neutron beam images were taken serially by a cooled slow-scan CCD camera system. The pixel size was 60 μm in this test.

The specimens were placed on two knife supports in a shallow aluminium container and positioned in front of the neutron beam. After the first image had been taken in the dry state the specimens were put in contact with water. Then neutron images were taken serially up to 48 h. The obtained data were then analysed to determine the time-dependent moisture distributions in the mortar specimens.

2.4. Quantitative analysis of the moisture content in mortar

As the neutron beam is attenuated depending on the sample material and geometry according to the radiation law, attenuation can be described in first order approximation as the following equation.

$$I(x,y,z) = I_0(x,y,z)\cdot\exp(-\sum N_i\cdot\tau_i) \tag{1}$$

where I (x, y, z) is the flux density transmitting through the object and reaching the detector, $I_0(x, y, E)$ is the flux density leaving the collimator and penetrating the object, N_i and τ_i are the mass attenuation coefficient and mass thickness of the component (such as water) in material, respectively.

Then the transmission value of the sample by neutron beam can be calculated as the ratio between I and I_0, as written in Eq. (2).

$$T(\tau,E) = \frac{I(x,y,z)}{I_0(x,y,E)} = \exp(-\sum N_i\cdot\tau_i) \tag{2}$$