



Influence of calcium leaching on chloride diffusivity in cement-based materials

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HIGHLIGHTS

- Solutions with same chloride concentration but different leaching rate were designed to carry out the coupled corrosion experiment.
- Two types of samples were prepared for macroscopic and microscopic testing, respectively.
- Influences of calcium leaching on chloride diffusivity in cement pastes were investigated.

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ABSTRACT

The coupling action of calcium leaching and chloride attack is an important durability problem for the cement-based materials served in long-termly in the environmental water like seawater or groundwater containing chloride. This paper investigates the influence of calcium leaching on the chloride diffusivity in cement-based materials by the corrosion experiment, in which the hardened cement paste (HCP) specimens are immersed into three corrosion solutions with the same chloride concentration, such as 1 M sodium chloride solution, 1 M ammonium chloride solution and the mixed solution of 1 M sodium chloride and 3 M ammonium nitrate. Some measurements, like the phenolphthalein, saturation-drying weighing, mercury intrusion porosimetry (MIP), Scanning Electron Microscopy (SEM/EDS), X-ray diffraction analysis (XRD) and rapid chloride test (RCT), are used to analyze the leaching behaviors and its influence on the chloride diffusivity of HCP, characterized by leaching depth, pore structure, morphology, calcium-silicon ratio, chloride-silicon ratio, phase composition and free chloride ion content. Results show that, in the calcium leaching process, the compactness, calcium hydroxide content and calcium-silicon ratio of C-S-H gel of HCP decreases with the leaching time. The calcium leaching causes the reduction of the physically chloride-bound ability and the chemically chloride-absorbed ability in HCP, and it results in high chloride diffusivity.

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1. Introduction

Long-termly in the environmental water like seawater or groundwater containing chloride, Concrete structures, such as dams, bridge piers, underground pipes, and radioactive waste disposal containers, are easily subjected to the coupling actions of calcium leaching and chloride attack, which result in the durability deterioration and lifetime reduction of concrete structures [1–5]. Chloride attack is due to the diffusion of chloride ions in concrete, and the accumulative chloride ions on the surface of steel bar result in its corrosion, so the diffusion of chloride ion associated with the pore structure has a significant impact on the durability of concrete structures [6,7]. Calcium leaching, caused by a

low-calcium water attack, leads to the dissolution of calcium hydroxide and the decalcification of C-S-H gel in the hydrated products and further brings about the decrease of pH value in pore solution [8,9] and the increase of porosity in concrete [10,11]. The decrease of pH value in pore solution causes the reduction of depassivation threshold of passive film on the surface of steel bar [12], while the increase of porosity not only accelerates the chloride diffusion process in concrete but also reduces the strength and stiffness of concrete [13,14], so both of them will cause the earlier rust of steel bar and the premature failure of concrete structures. Thus, the study of the leaching characteristics and its influence on chloride diffusion is helpful for revealing the deterioration mechanism of the durability of concrete structures in contact with water for a long time.

The pore structure has an influence on chloride diffusivity in concrete, and the related studies have been experimentally

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investigated [15–17]. Yang [18] investigated the relationship between the pore structure and chloride diffusivity in concrete through accelerated chloride migration test, and obtained that the chloride diffusivity is influenced by the capillary pore volume and critical pore diameter, the chloride diffusion coefficient is linearly related to not only the capillary pore volume but also the critical pore diameter of concrete. Gao et al. [19] studied the changes of the chloride diffusion coefficient with microstructural parameters of concrete, such as total porosity, capillary porosity and connected pore size. Results show that there is a good correlation between the chloride diffusivity and the total porosity and the capillary porosity, and the diffusion coefficient is almost linear with the connected pore diameter. Halamickova et al. [20] assessed the influence of pore structure on the transport properties of concrete by mercury intrusion porosimetry (MIP) and electrically-accelerated concentration cell test. Results show that, the diffusion coefficient of chloride ion has a linear increase with the critical pore radius, and there is a power-law relationship between the concrete permeability and its critical radius. At present, the relationship between pore structure and chloride diffusivity in concrete has extensively been studied but the concrete used in the experiments is non-corrosive, and its pore structure has a randomly uniform distribution. However, the environmental attack, such as calcium leaching, sulfate attack and carbonization, results in a non-uniform and time-varying distribution of pore structure, the influence of which on the chloride diffusivity has not almost been experimentally investigated.

Calcium leaching causes the microstructure evolution of concrete, which has further influence on the chloride diffusivity of concrete [21,22]. Through accelerated leaching test, the researches on the leaching-induced evolution of concrete microstructure have been extensively investigated [23–26]. Haga et al. [27] used scanning electron microscopy (SEM) and MIP to investigate the time-varied pore structure and calcium hydroxide of hardened cement paste slabs immersed in deionized water, and obtained that, the pore size caused by the dissolution of calcium hydroxide is basically greater than 0.2 μm , while the pore size formed by the decalcification of C-S-H gel is generally smaller than 0.2 μm . Choi et al. [5] utilized MIP to analyze the leaching-induced changes of porosity and pore diameter of concrete with the leaching time. With the increase of leaching time, the pore volume has a great increase for the pore size in the range of 50–500 nm, and the number of the pore with the size of greater than 200 nm has a rapid increase in the period of initial leaching, but after a period of leaching, it increases slowly for the pore size of smaller than 200 nm. Quoc et al. [28] discussed the changes in the porosity and permeability of hardened cement paste in ammonium nitrate solution with the leaching time. Results show that the accelerated leaching caused a significant degradation of microstructure in hardened cement pastes, which results in the increases of the specific surface area, total porosity and pore size, and finally led to a significant increase in the permeability of materials. Current studies mainly investigated the influence of calcium leaching on the microstructure of concrete and revealed the characteristic of leaching-induced gradient distribution of pore structure. However, in the process of calcium leaching, it produces a time-varying distribution of pore structure, which can result in the spatio-temporal variation of the chloride diffusivity in concrete. Therefore, the influence of calcium leaching on the pore structure and further on the chloride diffusivity need be further investigated.

Aiming at the degradation of concrete cover and steel bar of the structure in a water environment, and replacing concrete with hardened cement paste, this paper investigates the microstructural evolution caused by the leaching and its influence on chloride diffusivity to bridge the relationship between calcium leaching and chloride diffusivity. Firstly, three corrosion solutions with same chloride concentration but different accelerated leaching rate were prepared to carry out the immersion test of hardened cement pastes. Secondly, the pore structure, microstructure morphology, Calcium-Silicon ratio, Chloride-Silicon ratio, phase composition and free chloride concentration of the HPC in the process of immersion in three solutions were measured by using the mercury intrusion porosimetry (MIP), scanning electron microscope (SEM/EDS), X-ray diffraction (XRD) and rapid chloride test (RCT). Finally, the calcium leaching-induced degradation of microstructure and its influence on the chloride diffusivity were analyzed.

2. Experiments

2.1. Materials and specimens

The cement used in this study is the 52.5-grade ordinary Portland cement, whose chemical composition is listed in Table 1, with density of 3150 kg/m³ and specific surface area of 369.6 m²/kg. The initial and final setting times are 72 Min and 290 Min respectively, while its normal compression strength and flexural strength for 28 days curing are 60.5 MPa and 8.7 MPa respectively. Ammonium chloride reagent, ammonium nitrate reagent and sodium chloride reagent with the solubility of 37.2 g, 190.0 g and 36.0 g per 100 ml at room temperature were used to prepare the accelerated corrosion solution. Tap water and purified water were used to prepare the HPC and the corrosion solution, respectively.

The mixed cement paste with the water-cement ratio of 0.55 was first injected into the prismatic mold with the size of 40 × 40 × 160 mm. After curing for 24hrs at room temperature, the prism was demoulded, and then placed in a standard curing room with the relative humidity of 95% and the temperature of 20 ± 3 °C. Next, after 28 days curing, the cured prism was cut into the specimens with the size of 40 mm × 40 mm × 40 mm. Finally, four adjacent surfaces of the specimen were sealed with the epoxy resin, and the other two opposite surfaces were exposed to impose one-dimensional coupled diffusion of calcium and chloride ions.

2.2. Experimental method

2.2.1. Immersion

In this experiment, three solutions, including 1 M sodium chloride solution, 1 M ammonium chloride solution and the mixed solution of 1 M sodium chloride and 3 M ammonium nitrate, were used as the corrosion solution to carry out the coupled attack on the specimen with same chloride concentration but different accelerated leaching rate, and further investigate the leaching characteristic and its influence on chloride diffusivity in cement-based materials. Three solutions with the liter of 400 were respectively poured into three different sealed plastic boxes, and six specimens were placed into each plastic box so as to execute the immersion experiment, in which the volume of solution is 100 times of six specimens in the plastic box. After the immersion for 10, 20, 30, 40, 50 and 60 days in the three solutions, respectively, the six specimens were successively taken out to prepare the measured samples.

2.2.2. Sample

In order to investigate the leaching characteristics of cement-based materials and its influence on the chloride diffusivity, two types of samples, Type-I and Type-II were prepared for macroscopic and microscopic testing, respectively. Type-I samples were used for the phenolphthalein, saturation-drying weighing and rapid chloride test (RCT) [29] to obtain their temporal and spatial distribution of leaching depth, porosity and chloride content at different immersion time. Type-II samples were applied for the mercury intrusion porosimetry (MIP), scanning electron microscope (SEM/EDS) and X-ray diffraction (XRD) analysis to investigate their pore structure, morphology and phase composition at different leaching degree.

Table 1
Chemical composition of cement (% by mass).

Composition	SiO ₂	Al ₂ O ₃	CaO	MgO	SO ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O
Cement	21.10	5.56	62.48	1.76	3.59	3.98	0.94	0.20

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