Influences of chloride immersion on zeta potential and chloride concentration index of cement-based materials

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A B S T R A C T

This paper measured the zeta potential and chloride concentration index of hardened cement paste, which was defined as the ratio of chloride concentration in the expressed pore solution to that in soaking solution. A model was proposed to explain the relationship of zeta potential and concentration index of hardened cement pastes immersed in chloride solution. The results showed that with the increase of chloride concentration in soaking solution, both the chloride concentration index and zeta potential of hardened cement paste gradually decreased. The addition of slag influenced the chloride concentration index and zeta potential. The relationship between chloride concentration index, chloride concentration in soaking solution and slag replacement level, as studied by the Gouy-Chapman model was well correlated with the measured results.

1. Introduction

Corrosion of steel in concrete is one of the major causes for deterioration of reinforcement steel in concrete, especially in the presence of chloride ions and carbon dioxide [1]. For the concrete structures exposed to chloride-bearing environment, such as marine exposure or the highway structures where de-icing salt is used, the consequence caused by chloride ingress does great harm to the durability of reinforced concrete structures and gives rise to very high repair and reconstruction costs [2–4]. The high alkaline condition in cement-based materials forms a passivation film at the rebar surface to protect it from being corroded. However, the passivation film breaks when the threshold chloride content is reached at the surface of steel, consequently corrosion is initiated.

In concrete, chlorides can be presented in three forms: physically adsorbed chloride, chemically bound chloride and free chloride [5]. The physically adsorbed and chemically bound chlorides are collectively called bound chlorides. It is generally accepted that only free chloride leads to steel corrosion [6]. However, chloride binding plays extremely important role in chloride-induced corrosion. Firstly, it decreases the content of free chloride in pore solution and reduces the chloride flux into concrete. Secondly, the formation of Friedel's salt due to the chemical binding of chloride decreases the porosity up to 10–20% of total volume and improves the impermeability of pastes or concrete [7,8].

Chlorides may derive from aggregates and other constituent materials or mixing water (internal chloride), or penetrate into concrete during exposure to chloride-bearing environments (intruded chloride). Chloride ions added or penetrated into concrete will react with some of the cement constituent or hydration products [9]. Due to the differences in hydration degree, internal and intruded chlorides show different influences on properties and performance of cement-based materials [8].

The internal chlorides may participate in the hydration process of cementitious materials and affect hydration rate and the morphology and properties of hydration products. Traetteberg et al. [10] found that sodium chloride in mixing water accelerated the hydration of C_3S and chloride appeared to promote the formation of a higher Ca/Si (C/S) ratio hydrated product, the chloride ions can increase the C/S ratio of C-S-H gels from 1.8 to 2.19–2.95 [11]. It was also reported in their paper that the presence of NaCl influenced the morphological features, especially in the early stages of hydration. Both C_3A and C_4AF in cementitious materials form Friedel's salt ($C_3A \cdot CaCl_2 \cdot 10H_2O$) or its analogues [12], which may decrease the porosity of concrete [13,14].

The chloride penetrated from the surrounding into hardened cement also changes the structure and morphological features through some physical processes or chemical reactions with hydration products. Different from the internal chloride, the chemical binding of intruded

chloride ion is mainly occurring between chloride and alumina-bearing phases [8]. In cement-based materials, chloride ions can also be physically absorbed by solid, and the electrical double layer (EDL) formed at the interface of solid and liquid was regarded as the reason causing the physical adsorption. Especially, when calcium chloride was used as chlorine source, the additional calcium accelerated the formation of Friedel's salt and increased the amount of chloride ions in EDL [15].

In 1993, Nagataki et al. [16] immersed the cement paste discs in sodium chloride solution with chloride concentration equalling to seawater. After the immersion, they measured the free chloride concentrations of samples by pore solution expression method. They found that, after 91 d of immersion, the concentration of free chloride in pore solution almost upped to twice of that in the soaking solution. In their paper, "chloride condensation" was used to describe this phenomenon, and the ratio of chloride concentration in expressed pore solution to that in soaking solution was defined as "condensation index". Generally, condensation is the change of the physical state of matter from gas phase into liquid phase, mostly refers to the water cycle, or a class of an organic addition reaction that proceeds in a step-wise fashion to produce the additional product. However, the higher chloride concentration in expressed pore solution is due to physical adsorption of chloride ions in EDL formed at the solid-liquid interface. Therefore, in this paper we used chloride concentration index (N_c) instead of chloride condensation index. Li et al. [17] investigated the influences of curing age, soaking time, concentration of soaking solution, soaking temperature and pore solution expression pressure on free chloride content of cement-based materials. N_c decreased as the concentration of soaking solution and the curing time increased, and it increased with soaking time before 63 d of immersion, then decreased. Soaking temperature and pressure did not affect free chloride ion concentration.

Nagataki et al. [16] tried to interpret the higher chloride concentration in the expressed pore solution of cement-based materials by using the theory of EDL firstly. After that, Yuan [18] calculated the thickness of electrical double layer based on Debye equation, and gained the conclusion that the higher concentration of soaking solution, the thinner the thickness of EDL and the smaller N_c. Based on the results of Yuan, He [19] assumed the average concentration of chloride ion in diffuse layer and proposed a computational formula to calculate N_c caused by electrical double layer formed within pores of cement-based materials.

The EDL forms at the interface between pore walls and pore solution. The electrical double layer consists of two layers [20]: Stern layer and diffuse layer. In the Stern layer, ions are tightly adsorbed on the solid surface, while they diffusely distribute in the diffuse layer due to the simultaneous effects of attraction from solid phase and thermal motion. Zeta potential is the electrokinetic potential formed at the boundary between Stern and diffuse layer when the later moves along with the bulk pore solution.

The properties of EDL can bring some effects on the value of zeta potential. During the process of chloride penetration, surface potential of solids may attract chloride ions in pore solution and slow down the penetration of chloride into steel surface. However, under some specific conditions, the chloride in EDL may release into pore solution. This paper studies the influences of chloride ions and slag content on early hydration and N_c of hardened cement pastes by measuring the zeta potential. A model was established to investigate the relationship between zeta potential and N_c. The results of this study may help for further understanding on how EDL and physical adsorption affects chloride penetration and chloride concentration in pore solution of concrete, and provide some useful information on service life prediction of concrete structure subjected to chloride environment.

Table 1
Chemical composition of raw materials/%.

Raw material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	SO_3	C	Ignition loss
Cement	21.09	4.34	2.81	62.50	1.81	0.62	2.87	–	–
Slag	33.00	13.91	0.82	39.11	10.04	1.91	0.16	–	0.08

2. Experimental

2.1. Raw materials

PI 52.5 portland cement (PC) according to GB175-2007 and grade S95 slag powder according to GB/T18046-2000 were used in this study. The chemical compositions of the cement and slag are given in Table 1. NaCl, $Ca(OH)_2$ and $AgNO_3$ were analytical grade chemicals. De-ionized water was used to prepare solution for chemical analysis.

2.2. Specimen preparation and curing

Water to binder ratio of the pastes was 0.4. A $\Phi 50 \times 200$ mm PVC pipe was used as a mold. One end of the mold was sealed with polyvinyl chloride board. After cement pastes were cast into the mold, the other end of the mold was sealed with plastic film immediately, then placed in an oscillator for 6 h to avoid segregation. After that, the specimens with mold were left in a room at 20 °C for 24 h, then demolded and cut into thin discs of about 5 mm thickness.

Cement paste disc specimens were cured in water for another 27 d before vacuum saturation with saturated limewater, then immersed into 0.1, 0.3, 0.5, 0.7 and 1.0 mol/L of NaCl solutions respectively. The samples were stored in plastic containers covered with plastic film at 20 °C. The volume ratio of soaking solution to specimen was kept above 40 and the solution was replaced every 2 weeks to ensure the relatively constant chloride ion concentration in the soaking solution. In our previous study [17], the total chloride content of every 1 mm layers of cement paste discs was measured after 56 d of soaking. The results showed that the chloride ions within samples reached equilibrium after 28 d of bath curing and 56 d of soaking in chloride solution. In this paper, the experiments were conducted after 56 and 91 d of soaking.

2.3. Zeta potential measurements

Electrophoretic and electro-osmosis technique was widely used for zeta potential measurement. In this study, electro-acoustic technique, which has lower requirement on particle size, viscosity and content of testing samples, was applied [10]. A DT-300 instrument from Dispersion Technology was used for zeta potential measurement without dilution of samples, which to some extent avoided the differences in hydration and surface properties between diluted and original samples. For every sample, the zeta potential measurements were conducted 5 times and the average value was reported.

When the designed soaking time was reached, the samples were ground by ball mill and placed in 60 °C vacuum drying oven for 24 h. The fraction of particles with diameter between 0.025 and 0.045 mm was separated by sieving and used for zeta potential measurement. In order to ensure the same solid to liquid ratio of every testing batch, the suspension was prepared by mixing the vacuum dried powder samples with sodium chloride solution with concentration equal to that of corresponding soaking solution. In this paper, the mixed sample was kept as long as possible before measurement to ensure the EDL to reach equilibrium state. The mass ratio of solid to liquid was 1:1. The suspensions were kept stirring apparatus for 6 h, then left still for 1 min before the measurement. The zeta potential of the suspensions was measured with DT300 instrument.