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Development of empirical models for chloride binding in cementitious systems containing admixed chlorides

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HIGHLIGHTS

- Binding behavior of admixed chlorides in various cementitious systems are studied.
- Free chlorides were measured using water-soluble and pore press testing procedures.
- An interaction between *w/b, SCM, SCM level*, and admixed chloride level exists.
- Three empirical binding isotherms are developed.
- Chloride testing method influences the concentration of measured bound chlorides.

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ABSTRACT

The binding of admixed chlorides in the concrete can delay the corrosion of reinforcing steel and extend the service life of reinforced concrete structures. Although extensive research has been conducted to study the chloride binding capacity of cementitious systems subject to external chlorides, there is little information available on the chloride binding capacity of cementitious systems containing admixed chlorides. In this paper, the chloride binding capacity of several cementitious systems containing ordinary portland cement (OPC), Type C and F fly ashes, slag, and silica fume with different replacement levels is studied using acid-soluble, water-soluble, and pore-pressed testing procedures. In addition, the influence of water-to-binder ratio and admixed chloride levels on the percentages of bound chlorides is explored and discussed. The experimental results indicate that, on average, the concentration of pore-pressed chlorides is significantly lower than the concentration of water-soluble chlorides. Furthermore, the estimated bound chlorides using the pore-pressed chlorides are significantly higher than the bound chloride estimated using water-soluble chlorides. Results show that the Langmuir isotherm can be used to explain the relationship between free and bound chlorides in OPC paste samples containing admixed chlorides. Results of this study also suggest that chloride testing procedures can be very influential in quantifying the concentration of bound chlorides. Therefore, there is a need to standardize the process used for measuring the chlorides in cementitious systems for assessing chloride binding.

1. Introduction

Chlorides can be introduced into the fresh concrete by the constituent materials or by intentionally adding salts (i.e., admixed chlorides). Regardless of how chlorides enter the concrete, in sufficient quantities, these chlorides can lead to early corrosion of the reinforcing steel [1–5]. Corrosion can lead to cracking, spalling, and reduction in the cross-section of reinforcing steel, which in turn can result in the loss of serviceability and reduced service life of concrete structures. In the context of chloride-induced corrosion, the service lives of a structure can be divided into two phases, namely, corrosion initiation and propagation. The corrosion initiation phase is the time required for chlorides to reach the surface of the reinforcing steel in sufficient quantities. The quantity of chlorides that can initiate the corrosion of reinforcing steel is known as the critical chloride threshold, C_T [6]. It is important to note that there are uncertainty and debate on a single C_T value or distribution of C_T values. A comprehensive review of the challenges in measuring C_T is given in [7,8].

One of the critical factors that can delay the corrosion initiation of the reinforcing steel in concrete is the chloride binding capacity

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of the cementitious systems. As a result of chloride binding, some of the chlorides can be removed from the concrete pore solution, thereby reducing the concentration of available chlorides to initiate the corrosion process [9]. Respectively, chlorides in the cementitious systems can exist in the form of free chlorides in the concrete pore solution and bound chlorides in the hydrated cement paste, where the latter chlorides can be further categorized as either chemically bound chlorides or physically bound chlorides. Yuan et al. [9] reported that more than 80% of admixed chloride binding takes place in less than 5 h after water is introduced to the concrete. The type of chloride binding, to a large extent, depends on whether chlorides are present in the concrete during the early or late stages of cement hydration (i.e., fresh concrete vs. hardened concrete). Some researchers attribute the corrosion initiation of the reinforcing steel to only the concentration of free chlorides in the pore solution at early ages [10,11]. However, research shows that when the pH within the concrete pore solution drops below 11.5 (e.g., in case of carbonation and sulfate attack), the chloride binding mechanism can be reversed and more than 90% of bound chlorides can unbind and release into the pore solution in the form of free at later ages, increasing the risk of corrosion [12,13].

In the case where chlorides are present in the concrete from the early stages of hydration (i.e., in the form of admixed chlorides), chlorides can bind chemically with the primary cement compounds such as C_3A and C_4AF to form Friedel's salt and its iron analogue. In addition, depending on the type and concentration of chlorides in the cementitious system, other products such as Kuzel'salt and oxychlorides may be formed [14]. However, oxychlorides typically only occur at high chloride exposure concentrations of $CaCl_2$ or $MgCl_2$ salts, [15,16], well above the typical admixed chloride levels. Some of the admixed chlorides that are not chemically bound to the hydrated cement compounds can be adsorbed to the surface of the hydration products, such as the calcium silicate hydrates. This form of binding is of a physical nature [17]. It should be noted that there is currently no established method to determine what fraction of bound chlorides are physical or chemical in nature and information about the distribution of chloride binding in admixed chloride systems is scant and not well understood.

Researchers often use chloride binding isotherms to express the relationship between free and bound chlorides at a given temperature. Three common chloride binding isotherms that have been used extensively in the literature are the linear, Langmuir, and Freundlich isotherms as shown in Eq. (1) through (3).

$$Cl_{b,linear} = kCl_f \tag{1}$$

$$Cl_{b,\ Langmuir} = \frac{\alpha c_f}{1 + \beta Cl_f} \tag{2}$$

$$Cl_{b,Freundlich} = \alpha Cl_f^{\beta} \tag{3}$$

where Cl_b and Cl_f are bound and free chlorides, respectively. The coefficients k,α, and β are empirical values determined by fitting Eqs. (1) through (3) to the measured data. It is important to note that Cl_f is often expressed in terms of the number of moles of chlorides in one liter of concrete pore solution (mol/l) and Cl_b is expressed in term of unit mass of chlorides per unit mass of concrete, cement, or cementitious materials (e.g., kg/m^3 concrete, mg/g sample, percent by weight of cement or cementitious materials). Conventionally, the rate of change in bound chlorides as a function of free chlorides in the pore solution is referred to as the binding capacity of the cementitious system. This approach, however, is faced with several challenges. For example, to predict the concentration of bound chlorides, one must first determine the concentration of free chlorides in the concrete pore solution using different testing methods. These tests are time-consuming and often require a well-equipped laboratory. In addition, different test procedures could produce different estimates of "free" chlorides which adds to the uncertainty of the results.

There is currently debate over the test method used to extract the free chlorides from a cementitious sample. Free chlorides are commonly defined as the unbound and unabsorbed portion of chlorides in the concrete pore solution [18]. Using this definition, a review of the literature shows that there are three common test methods, namely equilibrium method, water-soluble, and pore press testing procedure that have been used to assess the concentration of free chlorides and determine the binding capacity of cementitious systems.

In equilibrium method, a sample (e.g., a thinly sliced disk or powdered concrete sample) is added to a chloride solution with a known concentration of chlorides and once the equilibrium is reached, the concentration of chlorides in the solution is measured and used as an indicator of free chlorides [9,19–22]. This method measures the binding capacity of cementitious systems exposed to external chlorides and therefore, ignores the possible impacts of admixed chlorides during the hydration process. Another drawback to the equilibrium method is that it ignores the influence of chloride binding products (e.g., Friedel's salt) on the structure of pores in concrete. Research shows that the products of chloride binding can reduce the porosity of concrete and as a result, can slow down the transport of chlorides into the concrete [9,23]. In addition, the equilibrium method disregards the variation in the concentration of free chlorides in the pore solution and its possible impacts on the transport properties of chlorides in concrete. It is expected that an increase in the concentration of free chlorides in the pore solution can result in a reduction in the chloride concentration gradient between the pore solution and the exposure environment which in turn can reduce the diffusion rate of chlorides in concrete.

The literature on chloride binding also shows that some researchers have used the water-soluble testing method to estimate the concentration of free chlorides and develop binding isotherms based on the water-soluble chlorides [24]. Because water-soluble test involves boiling the powdered concrete samples in water, the water-soluble test has been reported to release some of the physically bound chlorides, and therefore, the obtained values from this test may not be equivalent to the actual concentration of free chlorides. It is also important to note that there is a wide range of water-soluble tests (e.g., ASTM C1218 [25], RILEM TC 178-TMC [26], AASHTO T260 [27], ACI 222.1-96 [28]). In fact, the amount of unbinding would be expected to be very much dependent on the test procedures used.

Research indicates that among all different test methods to measure the concentration of free chlorides in the concrete, the pore press test can be the most representative test procedure for assessing these free chlorides [22]. In this test, the pore solution is extracted by applying high pressures to the hardened cementitious material samples [21]. Applying high pressures to the hardened cementitious materials could unbind some of the bound chlorides. Therefore, there may be some degree of error associated with this test per the definition of free chlorides in the pore solution. In fact, some research indicates that the pore press technique may overestimate the concentration of free chlorides by up to 20% [29]. One drawback to using pore press testing procedure is that extracting the pore solution from cementitious systems requires high pressure and high-capacity equipment, which are not commonly available. In addition, the volume of the extracted pore solution is dependent on the magnitude and the duration of the applied force to the crushed cementitious samples. Based on the authors' experience, pore press method is more suitable for young samples