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Cement and Concrete Research 36 (2006) 492 – 503

Cement and Concrete Research

In situ leaching method for determination of chloride in concrete pore water

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Received 13 July 2005; accepted 13 December 2005

Abstract

In the in situ leaching (ISL) method, pore water ionic content is determined in small cavities drilled in mortar/concrete specimens. Prior investigations have demonstrated the ISL applicability to obtain pH and nitrite ion concentration in concrete/mortar pore water. The application of the method is extended here to determine pore water chloride ion concentration (and pH) within practical test times in mortars and concretes prepared in the laboratory and in concrete cores extracted from a bridge deck in deicing salt service. Spatial resolution for the determination of composition profiles is also illustrated. Modeling of the ISL process indicates that chloride binding accelerates the approach toward a terminal cavity concentration, reducing test duration to practical lengths for moderate permeability concretes. This acceleration can be attributed to maintaining a higher gradient of free chloride near the cavity wall due to the release, during leaching, of previously bound chloride. Consequently, there is a faster chloride buildup in the cavity water compared with the no-binding case. Experimental chloride and pH results obtained by the ISL test in mortar samples show good agreement with those from the pore water expression (PWE) method. Also, examples are presented of application of ISL data to obtain chloride binding isotherms, and pore water chloride to hydroxide ratio relevant to assessing conditions for corrosion of steel reinforcement. The ISL method presents a less costly and less disruptive alternative to PWE for pore water analysis. It is noted, however, that in a few instances ISL could not be implemented because of excessive absorption of cavity water by the surrounding medium.

Keywords: Chloride; Leaching; Binding; Corrosion; Pore water

1. Introduction

Significant interest exists in assessing concrete pore water composition, particularly for chloride content as a source of corrosion of reinforcing steel. The most common procedure for assessment of cement paste/mortar pore water composition is by the use of the pore water extraction (PWE) technique, although it may be subject to errors, especially when applied to concrete samples [1–4]. Moreover, the PWE method requires special safety precautions and is highly mechanically disruptive of the concrete/mortar sample.

As an alternative to the PWE method, Castellote et al. [5] developed an alkaline leaching technique for free chloride analysis of a crushed concrete/mortar specimen in about 24 h of testing. However, this method is also highly disruptive of the sample. Glass and Buenfeld [2] determined free chloride content of a thin cement paste disk immersed in a NaCl–NaOH solution placed in an ultrasonic bath. The chloride concentration was determined measuring the external solution concentration evolution with time until an apparent terminal chloride value was reached, typically after 14 days. The practical implementation of this method with actual concrete samples has yet to be demonstrated.

The in situ leaching (ISL) technique represents another attractive practical alternative to determine pore water chloride content, but its applicability needed to be explored. ISL was initially developed to measure pH of the concrete/mortar pore water [6], and later implemented to examine nitrite concentration in concrete pore water [7]. In the ISL technique a mortar/concrete specimen is allowed to reach near water saturation in a closed 100% relative humidity chamber, periodically mist spraying the specimen surface with distilled water. Fresh lime is placed inside the chamber to act as a CO_2 trap. After 30–40 days of conditioning, small equidistant cavities (typically 3–5

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doi:10.1016/j.cemconres.2005.12.013

mm diameter, 30–40 mm deep and at least 20 mm apart) are drilled with minimum disruption of the specimen using a masonry drill bit. Concrete dust is carefully removed from cavities. An acrylic washer is then affixed to the rim of each drilled cavity with a fast curing epoxy. Subsequently, a small volume (typically 0.25 mL) of distilled water is injected. The cavity-to-water volume ratio is made as large as practicable to shorten the test period. A rubber stopper is firmly pushed into the acrylic washer to isolate the cavity water. The cavity water is then allowed to evolve toward equilibrium with the surrounding pore water over a sufficiently period of time. Periodically, a small amount of cavity water (10–30 mg) is extracted and analyzed for dissolved species.

The ISL method is inexpensive, simple to implement in concretes (of high and moderate permeability) and mortars, and causes minimum disruption. Loss of cavity water into the surrounding concrete and a potentially lengthy required time toward cavity water equilibration are limitations of the technique.

This investigation was conducted to evaluate the applicability of the ISL method for the determination of chloride in mortar/concrete pore water. Of interest was whether test times could be kept within reasonable limits in view of the often moderate diffusivity of chloride ion in concrete [8,9], and how chloride binding [10,11] may affect the cavity water equilibration kinetics. These issues were addressed by detailed modeling to examine equilibration kinetics. Results using the ISL technique are compared with those obtained by the well-established PWE method applied to mortar samples. The applicability of the ISL technique to obtain a chloride distribution and binding information pertinent to durability forecasting is demonstrated.

1.1. Modeling of chloride transport into small concrete cavities

The success of the ISL method depends on the development within the cavity, in a reasonable timeframe, of a chemical composition representative of that of the surrounding pore water. Early modeling work [6] of the approach to equilibration addressed only simple diffusion with no binding of the type often encountered for chloride transport in concrete. Those results indicated that the time needed to achieve near equilibrium is proportional to $D^{-1}r_c^2$ and roughly proportional to $\varepsilon^{-2}V_r^{-2}$, where r_c is the cavity radius, D the diffusion coefficient (binding absent) of the leached species, ε the porosity (pore volume fraction) of the material, and V_r is the ratio of the cavity volume V_C to the volume of water in the cavity V_W. This analysis permitted semi-quantitative projections of the time for equilibration in the more complex systems of interest. Those projections together with experimental results showed encouragingly short times (e.g. one week) for equilibration for ions responsible for pH development [6]. Additional work with nitrite ions showed also reasonable short times to approach equilibrium [7]. The present paper extends the model to the transport of chloride ions including linear and non-linear binding.

For modeling purposes, the following assumptions are made:

1. The concrete cavity is treated as a long cylinder of length L and a radius r_c centered in a cylindrical specimen also of length L (thus, chloride transport beneath the cavity is ignored for simplicity) and radius $r_e \gg r_c$ (see Fig. 1). The chloride concentration at $r = r_e$ is assumed to be unaffected by leaching within the time frame of the experiment. Chloride is initially uniformly distributed in the concrete matrix.
2. The concrete pores are assumed to be always filled with water so that cavity water depletion is negligible (limitations for the applicability of this assumption are discussed later).
3. The concrete is considered as a homogeneously porous medium with porosity invariant with time.
4. The cavity is assumed to be partially filled with water but with walls efficiently wetted by capillarity.
5. Transport inside the cavity is assumed to be fast enough so as to have the same chloride concentration in the water at the bottom and on the moist cavity walls.
6. Equilibrium between the cavity and concrete pore water is reached at the cavity wall at all times.
7. The total chloride content as mass per unit volume of concrete can be expressed as $C_{TOT} = C_B + C_F$, where C_B is the bound chloride and C_F is the free chloride. The free chloride is present only in the pore water at concentration C_f (in mass per unit volume of pore water), so that:

$$C_F = \varepsilon \cdot C_f \tag{1}$$

8. There is instantaneous equilibration between bound and free chlorides so that C_B and C_F are related by a time-invariant isotherm function.
9. Chloride transport in the bulk of the concrete is by diffusion, forced only by gradient of the free chloride concentration.

In one-dimensional cylindrical coordinates, the mass conservation equation for chloride transport in the concrete bulk is then given by [10,12]:

$$\frac{\partial C_F}{\partial t} = \frac{D_F}{\left(1 + \frac{dC_B}{dC_F}\right)} \left[\frac{\partial^2 C_F}{\partial r^2} + \frac{1}{r} \frac{\partial C_F}{\partial r} \right] \tag{2}$$

where r is the distance from the center of the cavity, D_F is the diffusion coefficient for free chloride, dC_B/dC_F is given by the binding isotherm, and t is the leaching time.

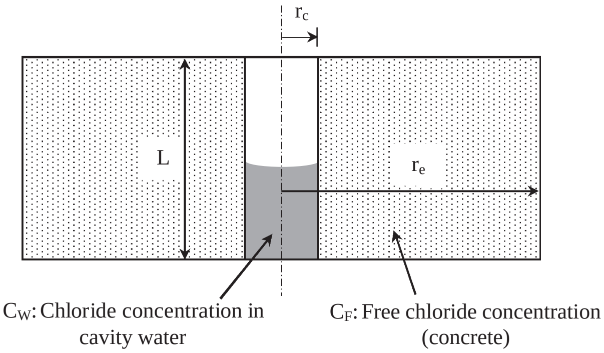

Fig. 1. Schematic for simplified modeling of chloride transport — only radial transport considered.