

Improvement of Corrosion Related Durability of Steel Reinforcement in a Novel Concrete Formulation

Carolina Páez Jiménez
University of South Florida
4202 E Fowler Ave
Tampa, Florida, 33613
United States of America

Alberto Sagüés
University of South Florida
4202 E Fowler Ave
Tampa, Florida, 33613
United States of America

Jitendra Jain
Solidia Technologies Inc.
11 Colonial Dr
Piscataway, New Jersey, 08854
United States of America

Christopher L. Alexander
University of South Florida
4202 E Fowler Ave
Tampa, Florida, 33613
United States of America

ABSTRACT

This work presents experimental results comparing the corrosion durability of two formulations of a novel, non-hydraulic, calcium silicate cement (CSC) concrete to that of one type of ordinary Portland cement (OPC) concrete. Cured CSC-based concrete has a lower pore water pH (9-11) than OPC-based concrete (13-14), likely resulting in a corrosion initiation stage that is comparatively shorter. However, CSC-based concrete has a higher resistivity than OPC-based concrete, making the formation of corrosion macrocells more difficult. Corrosion experiments were performed to evaluate the corrosion-related durability of these two formulations. The array of tests included exposure to fresh water and salt water (each alternate wetting and drying regimes) and a high humidity environment. Additionally, accelerated corrosion propagation test were performed to assess the ability of each concrete formulation to accommodate corrosion products as an indicator of the duration of the corrosion propagation stage. The corrosion performance of each concrete formulation was evaluated in terms of chloride diffusivity, corrosion rate, and the critical corrosion penetration required to crack the concrete. The preliminary data were used to predict the service life of the steel reinforced concrete.

Key words: calcium silicate cement concrete, corrosion, durability, initiation, propagation

INTRODUCTION

Concrete is the second most used material in the world after water.¹ A large part of the world's civil infrastructure is built with reinforced concrete. Typical concrete materials are made by mixing ordinary Portland cement (OPC), water and aggregates. The OPC manufacturing process involves grinding and calcining and sintering of clay and limestone, which requires high temperatures and elevated energy consumption, resulting in high CO₂ emissions. The cement industry is responsible for approximately 8% of anthropogenic greenhouse gases (GHGs).² In addition, the global demand for cement is increasing at a rate of 2.5% per year.² If changes are not made to current manufacturing processes, CO₂ emissions from the cement industry could increase 260% between 1990 and 2050 based on the expected increase in demand.¹ However, the Intergovernmental Panel on Climate Change (IPCC) mitigation scenario requires the cement industry to reduce its total carbon dioxide emissions from 2.0 Gt in 2007 to 1.55 Gt by 2050.³ To overcome the challenge of an increasing demand of this high-CO₂ emitting industry, new energy-efficient production technologies along with alternative low-lime cement formulations are needed.

A promising solution is a recently introduced cement that cures by CO₂ consumption. Calcium silicate cement formulations may be produced at lower clinkerization temperatures and with less limestone than that of OPC-based cement, resulting in a decrease of kiln CO₂ emissions by 245 kg per ton of cement. This reduction corresponds to 30% less emissions in both calcination and combustion processes. Furthermore, up to 240 kg of CO₂ per ton of cement is consumed during carbonation curing, for a combined 60 to 70% reduction in CO₂ footprint compared to that of conventional OPC-based concrete.⁴ However, due to the differences between OPC-based concrete material properties and those of CSC-based concrete, comparative investigations are required to ensure high performance of this novel concrete. Specifically, steel reinforcement corrosion-related issues raise an important durability question since CSC-based concrete's mechanical, physical and chemical properties differ from that of OPC concrete.

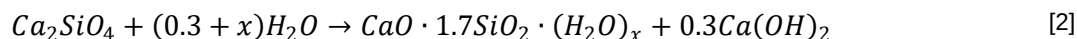
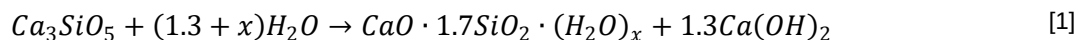
In particular, CSC-based concrete reaction products result in a different microstructure from that of OPC-based concrete. CSC-based paste, for example, has a porosity of 16%, whereas OPC-based mortar has a porosity of 9%.⁵ This would change some corrosion parameters such as chloride diffusivity and accumulation, as well as formation and dissipation of corrosion products. Similarly, the pore water pH levels at the CSC-based concrete microstructure are lower (~9-11) than those of OPC-based concrete (~13), lowering the chloride threshold needed to initiate corrosion of the steel reinforcement.⁶ CSC-based concrete resistivity, on the other hand, is higher than that of OPC-based concrete, making the formation of corrosion macrocells more difficult in the new formulation. This phenomenon potentially could produce lower corrosion rate values in the novel concrete than those of typical OPC concretes.

The corrosion related durability of OPC-based steel reinforced concrete has been extensively studied, which facilitates accurate prediction of a structure's service life.^{7,8,9} However, corrosion related durability of steel reinforced CSC-concrete has not been extensively studied. At this point there are no field performance data available—only a few laboratory scale experimental results are reported. This poses a big challenge to predict the service life of concrete structures accurately. This research assessed the concrete performance in terms of corrosion durability of CSC-based formulations in comparison to OPC-based concrete when exposed to conditions simulating aggressive marine environments. Experiments were designed to obtain material parameters that may be used to estimate the time to corrosion initiation and the rate of corrosion propagation. Preliminary estimates were used to forecast structural service life of the new concrete formulations.

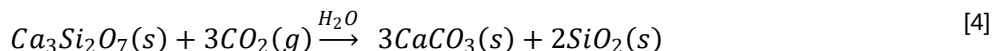
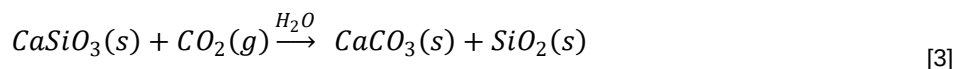
BACKGROUND

Low-calcium silicate cement material properties

The reactions involved in the curing process of CSC-based concrete formulations differ from those of typical OPC-based concrete. OPC-based concrete cures and develops most of its early age strength according to Equation 1 which represents the primary curing process. In this reaction a high-lime mineral is hydrated to form calcium silicate hydrate (CSH) gel and calcium hydroxide. A similar process, expressed as Equation 2, contributes to the long-term strength by further production of CSH and calcium hydroxide.¹⁰



Alternatively, CSC-based formulations during curing do not consume water, only using it to facilitate the curing reactions. Instead, carbon dioxide gas reacts with a low lime mineral of CSC to form calcium carbonate and silica gel as described in Equation 3 and 4, which produce the early age strength increase and the long-term strength, respectively.¹⁰



Therefore, microstructural phases of OPC-based concrete comprise CH, C-S-H, and unhydrated cement. Carbonated calcium silicate cement phases include polymerized silica gel, $CaCO_3$, and uncarbonated cement.¹¹ The resulting concrete porosity for OPC-based and CSC-based concrete formulations is ~9% and 16%, respectively. Pore sizes of low-calcium silicate cement concrete system after carbonation reaction range between 2 and 500 μm .⁵ The pH value for the two CSC-based formulations studied in this research, CSC1 and CSC2, was estimated to be 9 and 11, respectively, whereas the OPC-based concrete pH is typically around 13. Due to the differences in composition, pH, and porosity, it may be expected that differences may also arise in CSC's ability to protect steel reinforcement from corrosion. Experiments performed in this work seek to identify the ability of CSC-based concrete formulations to extend corrosion protection by quantifying corrosion durability parameters that may be used in service life models.

Reinforced concrete corrosion model

Corrosion related service life forecasting of steel reinforced concrete elements can proceed via a two-stage initiation/propagation model as shown in Figure 1.¹² The initiation stage duration (t_i) is governed by the transport of penetrating substances (chloride) into the concrete cover (C) and by the threshold concentration of those substances required to start the corrosion process (C_T). The propagation duration (t_p) is a function of the critical steel loss to cause cracking of concrete cover (X_{crit}), and corrosion rate of the steel reinforcement (CR), which is influenced by different factors such as moisture content, temperature around corroding areas, chemical composition of the concrete pore solution, concrete cover thickness, among others. A serviceability limit state, often pre-defined as some quantifiable degree of concrete cracking, bounds the end of the propagation stage. The amount of corrosion required to cause the concrete to crack (X_{crit}) is expressed as the radius loss of the reinforcement due to corrosion. The

service life of the reinforced concrete structure is given by the summation of the time to corrosion initiation and the duration of the corrosion propagation period.¹²

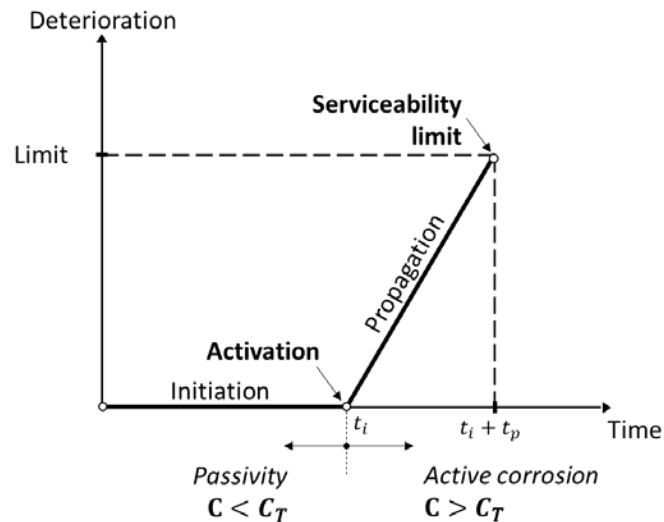


Figure 1: Two-stage corrosion modeling in reinforced concrete elements.

Initiation stage parameters

In marine environments or regions where de-icing salts are used, chlorides penetrate into the concrete and cause corrosion of the reinforcing steel, often severe¹³ This investigation will focus on that corrosion modality.

The mechanism for chloride transport depends on the degree of saturation and structure of the concrete pores. Under typical marine and highway salt exposure conditions, chlorides are predominantly transported by diffusion in the bulk of OPC concrete, with absorption prevalent only on a thin region near the surface.¹³ The situation for the novel concrete formulations will be considered in this work.

The time of chloride-induced corrosion initiation based on diffusion as the primary mechanism may be calculated according to Equation 5, derived from the solution to Fick's second law of diffusion for a simple fixed uniform surface concentration case with no initial native chloride.

$$t_i = \frac{x^2}{4D_a \left(\operatorname{erf}^{-1} \left(1 - \frac{C_t}{C_s} \right) \right)^2} \quad [5]$$

where:

t = time to initiation, s.

x = depth below exposed surface to the middle of the layer, m,

D_a = apparent chloride diffusion coefficient, m^2/s , and

C_t = chloride threshold, mass %,

C_s = chloride concentration at the surface, mass %,

x = depth below exposed surface to the middle of the layer, m.

It is assumed that the diffusion of chlorides occurs in a homogeneous material such that the diffusivity is not a function of position or time. Since this is only a rough approximation of actual concrete conditions,

the diffusivity is referred to as an apparent diffusivity. Nevertheless, this formulation provides a useful means to obtain a working estimate of the time for chloride ingress to initiate corrosion in sound concrete.

Propagation stage parameters

The corrosion propagation stage represents the period from corrosion initiation to the formation of corrosion-induced cracks in the reinforced concrete element. The stage duration is provided by the ratio of the critical corrosion penetration needed to crack the concrete (X_{crit}) and the mean corrosion rate (CR), commonly assumed to be constant over time.

The corrosion rate of steel in concrete is controlled by exposure conditions and concrete characteristics. In this sense, it depends on several factors that include the cement chemical composition, concrete microstructure, temperature and moisture content, oxygen availability, and pH of the concrete pore solution.¹⁴ During active corrosion, a macrocell may develop between actively corroding (anodic) regions and adjacent passive (cathodic) regions of the steel surface. At the same time, the anodic reaction is balanced by local cathodic activity. The total corrosion rate that describes the steel material loss is then the sum of both the macrocell and microcell corrosion current.

The critical corrosion penetration to crack the concrete cover (X_{crit}) represents the tolerance to the accumulation of expansive steel corrosion products of a concrete element. As the reinforcement bar corrodes, corrosion products penetrate into the concrete pore structure. Due to the expansive nature of corrosion products (4-7 times the consumed volume of steel^{15,16}), once the transport of the corrosion products into the pores of the concrete becomes blocked, further corrosion imposes stress on the concrete matrix which eventually leads to cracking. X_{crit} values are highly influenced by variations in cover thickness, concrete mechanical properties such as compressive and tensile strength¹⁷, and the concrete pore size distribution, the solubility of corrosion products, and connectivity.^{18,19} The average cross-sectional steel loss to cause cracking of the concrete is represented in Figure 2.

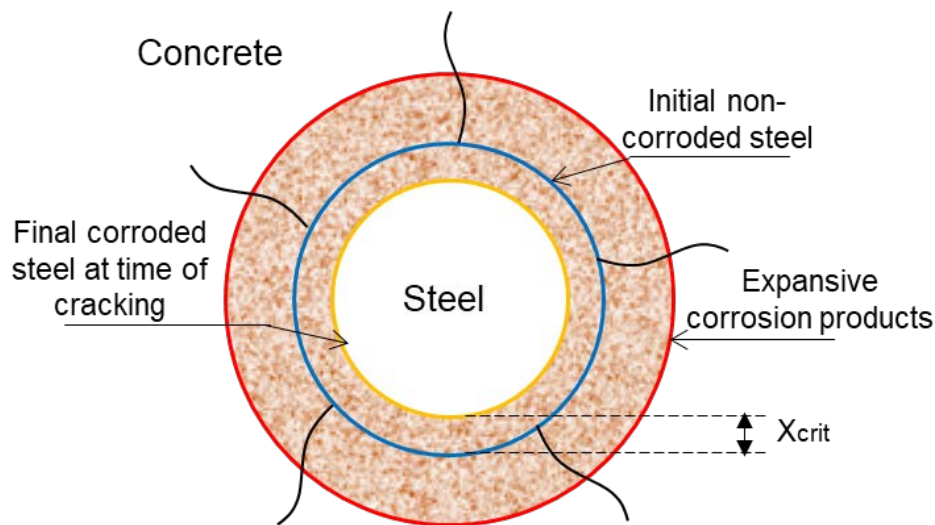


Figure 2: Average cross-sectional steel loss to cause cracking of the concrete.

Some empirical models have been proposed to determine X_{crit} for carbon steel reinforced OPC-based concrete, one of which is expressed in Equation 6 for concrete in typical unsaturated (85% relative humidity) conditions.²⁰

$$X_{crit} \sim 0.011 \text{ mm} \frac{x}{\phi} \left(1 + \frac{x}{L}\right)^n \quad [6]$$

where:

X_{crit} = critical corrosion penetration needed to cause cracking of the concrete, mm,

x = concrete cover thickness, cm,

ϕ = rebar diameter, cm,

L = length of the corroding region of steel, cm.

n = exponent between ~1.4 and ~2. ^{20,21}

In this work, experiments on laboratory-sized specimens were performed to monitor corrosion activity under cyclic chloride solution exposure. Autopsy of samples that exhibited corrosion induced damage facilitated chloride content analysis and estimation of the apparent chloride diffusivity. Accelerated corrosion experiments on small, reinforced beams partially immersed in a chloride solution were performed to measure X_{crit} when different corrosion current densities were imposed. The results obtained in this manner provide a relative indication of corrosion propagation time, and do not reflect natural exposure performance. Nevertheless, preliminary service life estimates can be made from these results.

EXPERIMENTAL METHODS

The early indications of corrosion performance of two formulations of CSC-based concrete were compared to those of a generic OPC-based concrete of modest water/binder content but no Pozzolanic admixtures. The aggregate to binder ratio and the fine aggregate were held constant for all concrete mixes. Table 1 details the concrete mixture proportions and compressive strength of the OPC-based concrete and the two CSC-based mix designs (CSC1 and CSC2). Relevant service life parameters were determined by chloride analysis of exposed concrete specimens, macrocell and microcell corrosion rates, as well as accelerated corrosion testing for estimates of X_{crit} done at various impressed current regimes.

Table 1: Concrete mixture proportions and compressive strength

Property	Concrete type		
	CSC1	CSC2	OPC
Solid component			
Binder (wt%)	17.3 ¹	17.3 ²	17.3 ³
Construction sand (wt%)	38.1	38.1	38.1
1/4" Granite aggregate (wt%)	24.3	24.3	24.3
3/8" Granite aggregate (wt%)	20.3	20.3	20.3
Water to binder ratio (wt/wt)	0.33	0.33	0.4
Liquid admixtures			
Water reducer (ml/kg binder)	7	7	7
Air entraining agent (ml/kg binder)	5	1.5	3
Set retarder (ml/kg binder)	7	5	0
Proprietary admixture (ml/kg binder)	0	20	0
Average compressive strength (psi)	8633	8376	8500

¹ CSC1: Low calcium silicate based carbonated concrete (*Cement only – no additional admixtures)

² CSC2: Low calcium silicate based carbonated concrete with partial (26 wt%) replacement of CSC with proprietary admixture

³ OPC: Ordinary Portland Cement hydrated concrete (*Cement only – no additional admixtures)

G109 Corrosion macrocell tests