Anion capture and exchange by functional coatings: New routes to mitigate steel corrosion in concrete infrastructure

Gabriel Falzone[a,b], Magdalena Balonis[b,c,*], Dale Bentz[d], Scott Jones[d], Gaurav Sant[a,b,e,**]

[a] Laboratory for the Chemistry of Construction Materials (LC²), Department of Civil and Environmental Engineering, University of California, Los Angeles, CA, USA
[b] Department of Materials Science and Engineering, University of California, Los Angeles, CA, USA
[c] Institute for Technology Advancement, University of California, Los Angeles, CA, USA
[d] Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA
[e] California Nanosystems Institute (CNSI), University of California, Los Angeles, CA, USA

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ABSTRACT

Chloride-induced corrosion is a major cause of degradation of reinforced concrete infrastructure. While the binding of chloride ions (Cl^-) by cementitious phases is known to delay corrosion, this mechanism has not been systematically exploited as an approach to increase structural service life. Recently, Falzone et al. [*Cement and Concrete Research* 72, 54–68-(2015)] proposed calcium aluminate cement (CAC) formulations containing NO_3-AFm to serve as *anion exchange coatings* that are capable of binding large quantities of Cl^- ions, while simultaneously releasing corrosion-inhibiting NO_3^- species. To examine the viability of this concept, Cl^- binding isotherms and ion-diffusion coefficients of a series of hydrated CAC formulations containing admixed $Ca(NO_3)_2$ (CN) are quantified. This data is then input into a multi-species Nernst-Planck (NP) formulation, which is solved for a typical bridge-deck geometry using the finite element method (FEM). For exposure conditions corresponding to seawater, the results indicate that Cl^- scavenging CAC coatings (i.e., top-layers) can significantly delay the time to corrosion (e.g., $5 \leq d_f \leq 10$, where d_f is the steel corrosion initiation delay factor [unitless]) as compared to traditional OPC-based systems for the same cover thickness; as identified by thresholds of Cl^-/OH^- or Cl^-/NO_3^- (molar) ratios in solution. The roles of hindered ionic diffusion, and the (re)passivation of the reinforcing steel rendered by NO_3^- are also discussed.

1. Introduction and background

Chloride (Cl^-) induced corrosion of reinforcing steel is a significant cause of premature damage and degradation of concrete infrastructure [1–3]. Concrete may be subject to chloride ingress as a result of contact with de-icing salts, seawater exposure, etc. [4]. In the U.S. alone, over $8 billion is spent annually on corrosion-related repair, maintenance, and rehabilitation of bridges [5]. In addition, 11% of the 600,000 highway bridges in the U.S. are deemed to be structurally deficient [5,6]; the majority due to corrosion-related degradation.

Due to the alkalinity of cementitious pore solutions (pH > 12), steel embedded in concrete is generally covered with a passivating oxide layer (γ-Fe_2O_3 [7,8]). The ingress of Cl^- ions into the concrete is thought to initiate steel corrosion by displacing OH^- from this passivating layer [2,9]. Cl^--induced depassivation results in localized pitting and corrosion product formation, which reduces the cross-sectional area of the reinforcing steel, and, therefore, its load-bearing capacity [3,7,9]. The Cl^-/OH^- ratio (in molar units), which accounts for the passivating effects of OH^- ions, is often used to describe the risk of steel corrosion [9,10]. Although the precise value of Cl^-/OH^- required to initiate corrosion is a subject of debate [9,10], a survey of the literature suggests that corrosion initiates when $Cl^-/OH^- \geq 0.6$ [9–11].

The presence of NO_3^- and NO_2^- anions in the pore solution can counteract the corrosive actions of Cl^- ions [12–17]. These species mitigate corrosion processes by oxidizing Fe^{2+} species to Fe^{3+} ions, which precipitate and re-form passivating films [7,18]. A critical Cl^-/NO_2^- ratio for corrosion initiation has been suggested to range from 0.25-to-2.0 (unitless, molar ratio) [19,20]. While data regarding NO_3^- is lacking, indirect evidence suggests that NO_3^- provides similar corrosion inhibition as NO_2^- (i.e., for $Cl^-/NO_3^- \leq 0.25$) [21]. While the use of NO_2^- or NO_3^- is attractive, the corrosion inhibition offered by these species offer is often limited by their initial dosage into the

concrete [22]. Moreover, both $Ca(NO_3)_2$ and $Ca(NO_2)_2$ are highly soluble and, therefore, are subject to leaching, which may reduce their potential for corrosion mitigation.

The binding of Cl^- by cementitious phases can significantly suppress Cl^-/OH^- in the pore solution and thereby increase the service life of infrastructure [23–25]. For example, Cl^- binding can occur by ion exchange into alumino-ferrite monosubstituent (AFm) compounds, or by sorption onto C-S-H or other compounds [26]. AFm's are represented by $[Ca_2(Al,Fe)(OH)_6]\cdot X\cdot nH_2O$, where X is the exchangeable interlayer anion, and n is the number of water molecules. The site (i.e., anion) occupation preference within the AFm-interlayer has the ranking $Cl^- > NO_3^- > NO_2^- > CO_3^{2-} > SO_4^{2-} > OH^-$ [27], assuring that AFm's present in cementitious formulations (i.e., those containing CO_3^{2-}, SO_4^{2-}, or OH^- in their interlayers) will capture Cl^- ions from solution to form Cl-AFm (i.e., Friedel's salt) or Kuzel's salt [27,28]. Ion exchange results in the release of the anion initially present in the AFm interlayer by a process of anion capture and exchange (A-CE); a process that is guided by thermodynamic selectivity [27,28].

ACE by AFm's is significant as (i) it operates in a Cl^- concentration range relevant to typical ingress conditions (≥ 14 mmol/L [29]), (ii) it has a much larger binding capacity per unit mass than Cl^- sorption by C-S-H [25], and (iii) Cl^- species taken up by AFm's are more strongly bound into their structure (i.e., reflecting structural incorporation), than binding by the C-S-H which represents weaker physisorption. Therefore, the Cl^- binding capacity of cementitious formulations is linked to the mass fraction of AFm phases present [30]. Even though the specific binding capacity of AFm phases is high, the total binding capacity of OPC-based formulations is limited, since AFm's comprise only 5% to 15% by mass of the solids in a hydrated OPC binder, offering only limited retardation of steel corrosion [19,23–25]. The Cl^- binding capacity of OPC-based binders can be increased by the addition of supplementary cementing materials (SCMs: e.g., ground-granulated blast-furnace slag [31,32], fly ash [33]) which increases the Al_2O_3/SO_3 ratio of the mixture, leading to the enhanced formation of AFm's at the expense of AFt [19,34,35]. However, these effects are confounded with changes in the transport properties (e.g., permeability, and diffusivity) and the limited reaction of the SCMs that become relevant when OPC is replaced by SCMs at high levels [25,34,36]. As a result, while SCMs do indeed contribute reactive alumina that is required for AFm formation, they do so at a level that only slightly increases the mass of AFm's formed.

Several numerical models have been developed to describe mass transport of ions that influence the service life of reinforced concrete infrastructure [23,24,37–42]. These transport models vary in complexity from single-species models governed by Fick's laws of diffusion [23,37], to multi-species Poisson-Nernst-Planck (PNP) models which account for electric coupling between ions due to their differing mobilities [40,41]. Other models may also consider the effect of advective transport due to moisture gradients (e.g., replicating the effects of wet-dry cycles) [43,44] and/or reactions between ions and cementitious solids, which may be accounted for by mass-transport and chemical equilibrium calculations [40,41,45], or by considering sorption isotherms [23,24,37,46]. A wide-range of models especially describe the role of Cl^- binding by cementitious phases on service life predictions [23,24]. Although quantitative prediction of the service lifetime of real structures is notoriously difficult, carefully formulated transport models can illustrate the role of enhanced Cl^- binding by cementitious compounds on delaying the onset of corrosion.

Calcium aluminate cement (CAC) mixtures, when suitably formulated, can exhibit a significantly higher Cl^- binding capacity as compared to those of OPC systems [47]. However, this approach has not been studied as a pathway to mitigate corrosion due to a lack of clarity as to how AFm formation can be increased in a controlled manner to scavenge/sequester Cl^- species. Recently, Falzone et al. suggested that NO_3-AFm dominant hydrated CAC mixtures (e.g., those containing up to 60 mass% AFm) could produce ACE benefits, by

sequestering Cl^- ions while simultaneously releasing NO_3^- (or NO_2^-) species, i.e., an anodic corrosion inhibitor [28]. This *smart release* of NO_3^- and NO_2^- ions was first described by Balonis and Glasser [19]. Significantly, since volume changes accompanying NO_3^- to Cl^- exchange in the AFm's are minimal, no internal damage develops, e.g., due to deleterious shrinkage or expansion [48]. With this concept in mind, this study investigates the efficacy of CAC + $Ca(NO_3)_2$ based *top-layers* (i.e., formed by replacing a fractional thickness of the OPC concrete cover) that engender ACE as a means to delay corrosion. Besides corrosion delay, CAC-based binders are anecdotally expected to feature equivalent (or superior) durability to OPC systems as relevant to bridge deck applications (e.g., resistance to freeze-thaw damage [49], and mechanical abrasion [50]), but are restricted to a top-layer due to their high cost ($\approx 5 \times$ that of OPC). The beneficial effects of Cl^- binding (i.e., reduced Cl^- abundance around the steel reinforcement) and NO_3^- ion release are explained by considering thermodynamic and transport properties that are influential in the initiation and progression of corrosion. As such, this study explains how ACE is a robust pathway to delay corrosion degradation of infrastructure and thereby prolong service life.

2. Materials and methods

2.1. Materials

A commercially available calcium aluminate cement (Secar®51 produced by Kerneos Aluminate Technologies)[1] was used. The oxide composition of the CAC as determined by X-ray fluorescence (XRF) was (51.05 ± 0.20) % Al_2O_3, (38.94 ± 0.40) % CaO, (4.77 ± 0.40) % SiO_2, (2.23 ± 0.10) % Fe_2O_3, (2.02 ± 0.01) % TiO_2, (0.59 ± 0.10)% MgO, (0.11 ± 0.01) % P_2O_5, (0.31 ± 0.04) % K_2O and (0.07 ± 0.03) % Na_2O by mass [51]. Unless otherwise noted, the uncertainty represents one standard deviation. The mineralogy of the CAC as determined by X-ray diffraction and Rietveld refinement, was $73.3 \pm 3.3\%$ CA, $18.1 \pm 3.3\%$ C_2AS, $4.9 \pm 2.0\%$ CT with minor phases in the form of 0.8% CaO, 0.6% C_2F, 1.5% C_3FT and 0.8% Fe_3O_4 by mass [52].

CAC pastes were prepared at a fixed water-to-cement ratio ($w/c = 0.45$, mass basis) using de-ionized (DI) water, as described in ASTM C305 [53]. Calcium nitrate ($Ca(NO_3)_2$, CN) was added to the CAC mixtures in dosages of 0%, 10%, and 30% by mass of anhydrous CAC. The CN admixture was provided in the form of an aqueous solution (52 mass% CN in water). This admixture was first combined with additional water prior to mixing with the anhydrous CAC. CAC mortars were also prepared at the same CN dosages using ASTM C778 [54] compliant graded quartz sand at volume fractions $\phi_q = 0.00$, 0.25, and 0.50. To suppress the formation of metastable hydrates [49,55], the mixtures were cured under sealed conditions at $45\,°C \pm 0.2\,°C$ for a period of 28 d. Reagent grade calcium chloride dihydrate ($CaCl_2\cdot 2H_2O$, > 99% purity) was added to Milli-Q water (i.e., $18\,M\Omega$ cm deionized water) to prepare solutions at Cl^- concentrations of: 0.01, 0.05, 0.1, 0.3, 1, and 3 mol/L.

2.2. Methods

2.2.1. Thermodynamic calculations

To ascertain the phase assemblages of the CAC mixtures prepared in Section 2.1, thermodynamic calculations were carried out using the Gibbs Energy Minimization Software[1] (GEMS-PSI), version 2.1 [56–59]. Thermodynamic modeling was performed for systems containing CAC