



# Chloride-induced corrosion of steel rebars in simulated pore solutions of alkali-activated concretes



Shishir Mundra<sup>a</sup>, Maria Criado<sup>a</sup>, Susan A. Bernal<sup>b</sup>, John L. Provis<sup>a,\*</sup>

<sup>a</sup> Department of Materials Science and Engineering, The University of Sheffield, Sir Robert Hadfield Building, Sheffield S1 3JD, United Kingdom

<sup>b</sup> Department of Civil and Structural Engineering, The University of Sheffield, Sir Frederick Mappin Building, Sheffield S1 3JD, United Kingdom

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## ABSTRACT

The passivation and chloride-induced depassivation of steel rebars immersed in varying alkaline environments (0.80 M, 1.12 M and 1.36 M NaOH solutions), simulating the pore solutions of low-Ca alkali-activated concretes, were investigated using a range of electrochemical techniques. The passive film on the steel rebars was complex in chemical makeup, composed of Fe-hydroxides, oxy-hydroxides and oxides. An increased degree of passivation of the rebars was observed when exposed to solutions with higher hydroxide concentrations. The critical chloride level ( $[\text{Cl}^-]/[\text{OH}^-]$  ratio) required to induce depassivation of steel was strongly dependent on the alkalinity of the pore solution, and was found to be 0.90, 1.70 and 2.40 for 0.80 M, 1.12 M and 1.36 M NaOH solutions, respectively. These values all correspond to a constant value of  $[\text{Cl}^-]/[\text{OH}^-]^3 = 1.25$ , which is a novel relationship to predict the onset of pitting, interlinking chloride concentration and the solubility of the passive film.

## 1. Introduction

In hydrated cement pastes, where the pore solution is characterised by high alkalinity (pH between 12.5 and 14), a thermodynamically stable passive film [1,2] is formed on the steel rebars, protecting the underlying metal from the action of aggressive species such as chloride, and slow the growth of corrosion products [3]. The passive film formed on the surface of the reinforcement comprises iron oxides such as  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , and iron hydroxides and oxy-hydroxides such as  $\text{Fe}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ ,  $\alpha\text{-FeOOH}$ ,  $\gamma\text{-FeOOH}$  and  $\beta\text{-FeOOH}$ , with a layered microstructure [4–9]. The chemistry of the passive film is governed by the oxygen availability, pH and chemistry of the surrounding environment, and the redox potential of the steel [4–8]. In concrete environment, breakdown of the passive film or ‘depassivation’ can be initiated by two common mechanisms: the lowering of pH, e.g. due to carbonation, and by the localised attack of aggressive species such as chloride.

The breakdown of passivation due to the action of chloride is often associated with the concept of critical chloride value or chloride ‘threshold’ value ( $C_{\text{crit}}$ ); defined as the minimum amount of chloride at the steel-concrete interface which is required to initiate depassivation of the reinforcement [10]. The  $C_{\text{crit}}$  value is influenced by a large number of factors, including: the chemistry and alkalinity of the pore solution [8,11–17], chloride binding in the cement hydrates [18–20],

the steel-concrete interface [21], the availability of oxygen at the steel-concrete interface [22] and the surface condition and chemical composition of the reinforcement [11,14]. Given the number of confounding variables, there exists no general consensus on a precise chloride ‘threshold’ value [10]. In an extensive review, Angst et al. [10] summarised the  $C_{\text{crit}}$  values obtained by several authors to be between 0.04 wt% and 8.34 wt% of the binder, and between 0.01 and 45 in terms of the molar ratio  $[\text{Cl}^-]/[\text{OH}^-]$ . These values correspond to systems based primarily on Portland cement (PC), and were determined through electrochemical measurements conducted on in-service structures, simulated pore solutions and laboratory specimens.

Alkali-activated materials (AAMs) are a class of cementitious binders that have gained significant academic and industrial interest over the past decades as an alternative to PC for production of concretes. These materials have the potential to achieve significant reductions in greenhouse emissions and present performance advantages, in some applications, compared to PC [23–25]. AAMs are defined as the product of the reaction between solid aluminosilicate powders (generally industrial by-products such as fly ash or blast furnace slag; or calcined clays) and alkaline activators (often an aqueous solution of alkali metal silicate or hydroxide) [25,26]. AAMs can be characterised, according to the calcium content in the binding material, into two broad categories: high-calcium systems such as alkali-activated slags where the reaction product is dominated by a calcium-aluminosilicate hydrate (C-A-S-H)

\* Corresponding author.

E-mail address: [j.provis@sheffield.ac.uk](mailto:j.provis@sheffield.ac.uk) (J.L. Provis).

gel; and low-Ca systems such as alkali-activated fly-ash/metakaolin where the main reaction product is a poorly crystalline three dimensional alkali-aluminosilicate hydrate (N-A-S-H) gel. The composition of the pore solution at the steel-concrete interface in AAMs is significantly different from that of PC-based concretes, due to differences between the composition and mineralogy of these binders.

This study focuses on low-Ca AAMs, and specifically the simulation of pore solutions present within these binders. In the pore solutions associated with neat PC hydrates [27], alkali and hydroxide concentrations are about 0.70 M, while concentrations of calcium and sulfate are around 2 mM and 7 mM respectively, with Si and Al each present at levels of less than 1 mM [27]. However, this composition would vary with time and composition of the precursors. The pore solutions of low-Ca AAMs are more alkaline than those of PC pore solutions. Lloyd et al. [28] measured the concentrations of different species in pore solutions extracted from alkali-activated fly ashes and observed concentrations of  $\text{Na}^+$  and  $\text{OH}^-$  between 0.60 M and 1.60 M, respectively. Sulfate was not detected, and the concentrations of Ca, Si and Al were close to 1 mM [28,29]. These differences in the hydration products and pore solution of low-Ca AAMs in contact with the reinforcement, compared to PC based concretes, could lead to dissimilar mechanisms of passivation (and passivation breakdown) due to the ingress of chloride.

There are limited published data on the chloride induced corrosion of reinforcement in low-Ca AAMs. Miranda et al. [30] and Bastidas et al. [31] reported similar passivation behaviours for alkali-activated fly ash and PC mortars, however upon addition of chloride (2 wt% of binder), increased corrosion current density and lower corrosion resistance were observed for alkali activated fly ash mortars than PC mortars. Criado et al. [32] indicated that depassivation of carbon steel rebar in alkali-activated fly ash mortars could be initiated at a chloride content of around 0.4 wt% of binder, but this value depended on the activator used. However, Monticelli et al. [33] reported  $C_{\text{crit}}$  values for alkali-activated fly ash mortars to be about 1–1.7 wt% of binder, much higher than previously reported. With such limited and varying data in the literature related to degradation of the reinforcement in AAMs, and considering the significant differences from reinforced PC concretes (as shown by Babaee and Castel [34]), it is important to gain an understanding of the mechanisms responsible for passivation of the reinforcement and its breakdown due to chloride.

This study investigated the passivation behaviour of steel and the phenomena of localised corrosion due to chlorides in highly alkaline electrolyte solutions (0.80 M, 1.12 M and 1.36 M NaOH) representing the pore solutions of low-Ca AAMs, with the aim of probing the chloride ‘threshold’ values for such systems. This was achieved by employing electrochemical techniques such as cyclic voltammetry (CV), open circuit potential (OCP), alternating current electrochemical impedance spectroscopy (EIS), linear polarisation resistance (LPR) and anodic polarisation.

## 2. Experimental programme

### 2.1. Materials

Mild steel rebars ( $\varphi = 12$  mm) were obtained from a local supplier in Sheffield, UK. The rebars were sectioned into small pellets, thickness 5.5–6.5 mm, using an abrasive disc. Before electrochemical testing, the pellet surfaces were polished using SiC abrasive paper with 240 to 600 grit sizes and degreased using acetone. The chemical composition of the rebar, measured by X-ray fluorescence (XRF), is shown in Table 1.

The compositions of the simulated pore solutions were based on the work of Lloyd et al. [28] who analysed the pore solution chemistry of alkali-activated fly ashes. The concentrations of dissolved Al, Si, Ca and sulfur species in that study were close to or less than 1 mM, therefore were not considered here. In addition, preliminary tests with pore solutions containing Al, Si and Ca in concentrations of 3 mM, 0.9 mM and

**Table 1**  
Composition of mild steel rebar measured using XRF (standard deviation =  $\pm 0.03$ ).

Elements	Fe	C	Cr	Ni	Cu	Si	Mn	S	Mo	P
wt%	97.91	0.21	0.13	0.20	0.47	0.23	0.76	0.03	0.02	0.04

0.45 mM respectively [35], showed negligible or no differences in the electrochemical response of the system. Alkali hydroxide solutions were used to simulate the pore solution chemistry of these binders: sodium hydroxide solutions with  $[\text{OH}^-]$  concentrations of 0.80 M, 1.12 M and 1.36 M were prepared using ACS reagent grade NaOH pellets (Sigma Aldrich). To investigate the effect of chloride on corrosion initiation, commercial grade NaCl (EMD Chemicals) was added to the representative pore solutions; the molar ratio  $[\text{Cl}^-]/[\text{OH}^-]$  was varied between 0 and 3 for each of the three NaOH concentrations assessed. Table 2 lists the aqueous compositions considered in this study.

### 2.2. Electrochemical techniques

All electrochemical tests were conducted in a 400 mL corrosion cell using a PGSTAT 204 potentiostat/galvanostat (Metrohm Autolab B.V.). Measurements were conducted using a conventional three electrode setup (electrolyte volume 250 mL), comprising a stainless steel counter electrode, an Ag/AgCl (filled with 3 M KCl) reference electrode and the steel surface (surface area: 0.287 cm<sup>2</sup>) acting as the working electrode. The reference electrode was positioned near the surface of the working electrode by means of a Luggin capillary. All measurements were conducted at room temperature ( $22 \pm 2$  °C) at least on two samples to ensure reproducibility.

#### 2.2.1. Cyclic voltammetry

Potentiostatic cyclic voltammetry (CV) was conducted to electrochemically characterise the passive film formed on the steel surface when exposed to the three NaOH concentrations without chlorides (0.80 M, 1.12 M and 1.36 M NaOH solutions). Before starting each test, the steel was maintained at  $-1.50$  V vs. Ag/AgCl (cathodic limit:  $E_{\lambda,c}$ ) in the hydrogen evolution region for 10 min to remove the pre-existing oxide layers on the surface of steel. The electrochemical response of the system was recorded when the potential was cycled from  $-1.50$  V ( $E_{\lambda,c}$ ) to 0.65 V (anodic limit:  $E_{\lambda,a}$ ), at a scan rate of 2.5 mV/s over 10 cycles, taking into account hydrogen and oxygen evolution at the cathodic and anodic limits respectively.

#### 2.2.2. Open circuit potential, electrochemical impedance spectroscopy, linear polarisation resistance and anodic polarisation

To investigate the role of chloride on corrosion initiation, the following electrochemical techniques were employed (in the order described) on the same steel specimen, which was distinct from the specimen used for CV, in each of the solutions listed in Table 2: (i) OCP or  $E_{\text{corr}}$ ; (ii) EIS; (iii) LPR; and (iv) anodic polarisation.

Prior to testing, each sample was allowed to stabilise in the electrolyte for 15 min inside the corrosion cell. The OCP was recorded for 30 min in the beginning of the experiment, unless the change in potential with time ( $dV/dt$ ) reached  $\leq 1$   $\mu\text{V/s}$  before 30 min. The OCP value reported in each case is the mean potential recorded during the last 20 s of the test.

EIS measurements were conducted for selected specimens in galvanostatic mode, where the net current in the system was maintained at 0.00 A. The galvanostatic mode was chosen primarily to address any variation in the OCP due to the interaction of chloride with steel during the course of EIS measurements. The tests were carried out in the frequency range of  $10^5$  Hz– $10^{-2}$  Hz, with a logarithmic sweeping frequency of 50 points per decade and a current amplitude of  $10^{-5}$  A (RMS), to ensure that the corresponding potential variation did not exceed 10 mV. The results were analysed only for impedance

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