



The inhibitive effect of bicarbonate and carbonate ions on carbon steel in simulated concrete pore solution



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ABSTRACT

The critical chloride threshold concentration and the polarizability of the barrier layer/outer layer (as defined by the Point Defect Model) have been determined for AISI 1020 carbon steel in simulated concrete pore solutions of pH 9, 10, 11 and 12.5 with varying chloride and bicarbonate/carbonate concentrations. It was found that bicarbonate/carbonate ions have a beneficial effect on the charge transfer resistance, the critical chloride threshold concentration and the pitting potential. When the critical chloride threshold concentration for pitting is exceeded, the inhibitive effectiveness of bicarbonate/carbonate against pitting corrosion is around one order of magnitude lower compared to hydroxide.

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1. Introduction

The benign environment that allows the carbon steel rebar to enter a passive state is one in which the pH value is high and the rebar is isolated from aggressive chemical species in the external environment by the concrete cover [1]. The pH value of concrete pore solution can be higher than 13 due to the presence of KOH, NaOH and Ca(OH)₂ dissolved in solution, with Ca(OH)₂ being one of the main hydration products of Portland cement. However, this passive state of the steel rebar can be disturbed through different means, leading to various types of corrosion. There are two main causes of rebar corrosion, namely chloride ingress and carbonation of concrete pore solution [1–3].

Chloride ingress is detrimental to the carbon steel rebar as chloride ions act as catalysts for the dissolution of the protective oxide film present on the rebar surface. The chloride ions adsorb on the passive film surface and form soluble iron complexes with Fe²⁺ ions in the passive film, which then precipitates out as loose and porous Fe(OH)₂ which is non-protective, releasing the chloride ions to repeat the dissolution process at the passive film surface again [1,3]. Previous works on this subject have identified a concept of a critical chloride threshold concentration, beyond which pitting will occur [4–10]. Different researchers have given different ways

of characterising this critical chloride threshold value, with a [Cl⁻]/[OH⁻] ratio being one that is commonly encountered. Pitting corrosion should not be disregarded as it may lead to other forms of corrosion like stress corrosion cracking and corrosion fatigue [11].

The drop in pH value due to carbonation (reaction with atmospheric CO₂) has been identified as an important factor in causing general corrosion of the carbon steel, as this causes destabilization of the passive film on the steel surface. It is commonly quoted that this critical pH value is 11.5 [4], below which the steel surface starts to depassivate. The situation is aggravated because a reduction in pH value results in a destabilization of the chloro-aluminate complexes present in concrete, thereby releasing previously bound chlorides into the concrete pore solution [9].

Bicarbonate and carbonate ions are produced in the process of carbonation. There is research indicating that HCO₃⁻ is harmful for the corrosion performance of Fe and also those that showed that bicarbonate is beneficial for inhibition of corrosion. Previous works have shown that HCO₃⁻ complexes Fe²⁺ ions, increasing Fe dissolution with increasing HCO₃⁻ concentration [12,13]. Thomas and Davies [14] reported that bicarbonate ions decreases the Flade potential for ferric oxide while increasing the Flade potential for magnetite with increasing bicarbonate concentration when the concentration is more than 10⁻² M. Deodshumukh et al. showed that the presence of 0.5 M HCO₃⁻ ions in 3.5% NaCl solution (pH 8.5) increases the pitting potential of medium strength carbon

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steel by 150 mV [15]. Moreno et al. [7] showed that carbon steel does not passivate under weak carbonation conditions (0.015 M NaHCO_3 + 0.005 M Na_2CO_3) but shows an enhanced resistance to localised corrosion at high bicarbonate and carbonate concentrations (0.3 M NaHCO_3 + 0.1 M Na_2CO_3). Brasher [16] in a survey of multiple anions, postulated that anions undergo a transition from aggressive behaviour to inhibitive behaviour at a critical concentration that is specific to each anion. For bicarbonate and carbonate, this critical concentration is on the order of 10^{-1} M and 10^{-2} M respectively. However, this critical concentration value was not supported by research carried out by Castro et al. [13] who worked with KHCO_3 – K_2CO_3 solutions up to 2.5 M HCO_3^- and found that increasing the bicarbonate concentration increases the solubility of Fe^{2+} ions.

As can be seen, the role of bicarbonate/carbonate ions in the corrosion process is a matter of some debate. The objective of this work is to elucidate the role of bicarbonate/carbonate ions on the behaviour of carbon steel in simulated concrete pore solutions affected by carbonation and chloride contamination. The Point Defect Model (Generation II) is used to analyse the pitting corrosion of carbon steel in this work as it is a model that has been applied successfully to account for passivity and passivity breakdown of metals and alloys [11,17,18].

2. Experimental

Flat metal specimens used in the electrochemical experiments were low-carbon steel of grade AISI 1020 with dimensions 20 mm × 20 mm × 2 mm and a nominal composition in wt. %: 0.20 C; 0.25 Si; 0.45 Mn; 0.04 P; 0.04 S; balance Fe. Just prior to the electrochemical experiments, each metal sample was ground with a series of SiC papers from grade P180 to P600, degreased with ethanol, washed with deionized water and blown dry with compressed air at room temperature. The polished surface was then covered with a piece of electrochemical mask fabricated from 3 M™ Electroplating Tape 470, so as to prevent crevice corrosion and expose a well-defined circular area of 1 cm² to the electrolyte.

Ordinary Portland cement concrete pore solutions are a complex mixture of $\text{Ca}(\text{OH})_2$, NaOH, KOH and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ [19,20]. In this work, a saturated $\text{Ca}(\text{OH})_2$ solution with a pH of 12.5 at room temperature was used as a simulation of an actual concrete pore solution. Chloride ingress was simulated by addition of NaCl and the pH drop caused by carbonation was simulated by diluting the saturated $\text{Ca}(\text{OH})_2$ solution (for pH 11 pore solution) or by the addition of NaHCO_3 .

Due to the low solubility of CaCO_3 (K_{sp} of calcite = 3.4×10^{-9}), on the addition of the NaHCO_3 to the initial saturated $\text{Ca}(\text{OH})_2$ solution, virtually all (>99.9%) of the calcium ions precipitate out. Therefore the total bicarbonate and carbonate concentrations remaining in each pore solution can be found by subtracting the initial calcium concentration from the amount of NaHCO_3 added to the solution, with the $[\text{HCO}_3^-]$ to $[\text{CO}_3^{2-}]$ ratio being determined by the relevant equilibrium constant ($K = 4.84 \times 10^{-11}$) [21]. Table 1 gives the hydroxide and sum of bicarbonate and carbonate concentrations present in the various simulated pore solutions tested.

Table 1
Hydroxide and the sum of bicarbonate and carbonate concentrations in pore solutions tested.

pH	$[\text{OH}^-]$ (mM)	$[\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ (mM)
12.5	31.6	0
11	1	0
11 (with NaHCO_3)	1	29.4
10 (with NaHCO_3)	0.1	47.3
9 (with NaHCO_3)	0.01	263.9

For each experiment, 100 ml of electrolyte was freshly prepared with deionized water and reagent-grade chemicals. The electrolyte was sparged with compressed N_2 gas for at least 30 min to deaerate it prior to the start of the electrochemical experiments. During the course of the electrochemical experiments the electrolyte was neither stirred nor sparged. The pH value of the electrolyte was measured immediately before and after each experiment with a pH meter to ensure that the pH change in each experiment was not more than 0.3 pH unit.

The experimental conditions utilised in this work for the metal specimen (ground steel surfaces) and the sample electrolyte (aqueous solutions) are typical of accelerated corrosion testing and are only in part representative of real conditions of reinforced concrete where the steel rebar surfaces are most likely to be even rougher and covered with a layer of corrosion products before being embedded within actual concrete.

Electrochemical experiments were conducted using a conventional three-electrode set-up in an electrochemical cell and results were registered by a Solartron Analytical SI 1287 potentiostat controlled by CorrWare software. Electrochemical impedance spectroscopy (EIS) experiments were carried out using a SI 1260 Impedance/Gain-phase Analyser in conjunction with the SI 1287. The carbon steel sample was the working electrode while a high-density graphite rod was used as the counter electrode. The reference electrode was Hg/HgO/1.0 M NaOH (XR400 from Radiometer Analytical) that has a potential of +0.140 V vs. SHE, however, potentials quoted in this work are given with respect to the saturated calomel electrode (SCE) scale for easier comparison with the bulk of the literature. The electrochemical cell was placed in a Faraday cage to minimise electromagnetic noise. All experiments were conducted at ambient temperature ($\sim 23^\circ\text{C}$).

The electrochemical experiments were carried out in a continuous sequence that consisted of: 30 min of open-circuit potential (OCP) measurement, followed by linear polarisation resistance (LPR) measurement, 5 min of OCP, EIS and finally potentiodynamic polarisation. For the LPR measurement, the metal sample was swept at 0.17 mV/s from -10 mV to $+10$ mV relative to its corrosion potential and there the sweep direction was reversed. The EIS experiment was conducted at the corrosion potential with an AC signal having an amplitude of 10 mV, from 10 kHz to 10 mHz. Potentiodynamic polarisation curves were obtained from a starting potential of -0.9 V vs. SCE to a final potential of 0.95 V vs. SCE at a scan rate of +0.67 mV/s. All the electrochemical experiments were conducted at least three times with a new AISI 1020 steel sample and fresh electrolyte each time.

Scanning electron microscope (SEM) imaging was carried out using a Philips XL30 FEG SEM in secondary electron imaging mode with an accelerating voltage between 5 kV and 25 kV.

3. Results and discussion

3.1. Corrosion potential

The purpose of the open-circuit potential monitoring was twofold: first to ensure that sufficient time had passed for the system to have reached a pseudo steady state that would allow reliable LPR and EIS measurements to be performed and; second to determine pitting potentials in those cases where the carbon steel spontaneously pitted at open-circuit, which causes a drastic decrease in the OCP.

Fig. 1 shows the corrosion potential of AISI 1020 steel at the end of the 30 min OCP experiment as a function of the chloride concentration for the different pore solutions. For the pH 12.5 pore solution, the corrosion potential measured decreased from -0.49 V to -0.58 V vs. SCE for chloride concentrations increasing from

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