RILEM Technical Letters (2018) 3: 75-83
DOI: http://dx.doi.org/10.21809/rilemtechlett.2018.70

Detection of the critical chloride threshold of carbon steel rebar in synthetic concrete pore solutions

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Received: 26 October 2018 / Accepted: 10 January 2019 / Published online: 16 January 2019

Abstract

Knowledge of the critical chloride content in concrete required to initiate corrosion of reinforcing steel is economically beneficial for the assessment and maintenance of existing structures. Also, many building codes now specify a service life of 75 – 100 years for highway bridges and the critical chloride content is an essential input parameter in the models used in design of structures. There have been numerous studies aimed at determining this parameter but there is no consensus because of the many factors influencing the corrosion. The current standard methods, e.g. ASTM G109, require many weeks or months of testing and are not appropriate for testing large numbers of specimens in different conditions.

This project has demonstrated that a fairly rapid potentiodynamic polarization technique can be applied to carbon steel reinforcing bars in synthetic concrete pore solution to determine the critical value. The importance of selecting the appropriate synthetic concrete pore solution for this application is demonstrated by the different critical values obtained for different solutions.

Keywords: Carbon steel rebar; Concrete pore solution; Critical chloride threshold; Potentiodynamic polarization; Pitting potential

1 Introduction

Chloride-induced corrosion of reinforcing steel bars (rebar) is one of the most common causes of deterioration of reinforced structure because of marine exposure and the increasing use of de-icing and anti-icing brines employed on reinforced structures (bridges, parking lots, etc.) during the harsh winter season experienced in many countries. Chlorides diffuse through the pores of concrete structures to the reinforcement and, in sufficient quantity, they initiate active corrosion on the rebar that was initially passivated due to the high pH solution in the pores of the concrete. The amount of chlorides the steel can withstand before the initiation of active corrosion is generally referred to as the chloride threshold level or critical chloride level, C_{crit}. The knowledge of the threshold is economically beneficial for the assessment and maintenance of existing structures, so that remediation steps can be taken prior to the deterioration of structure. Also, most building codes now specify a service live of 75 – 100 years for highway bridges and the C_{crit} is a critical input parameter in the models used in design of structures to be exposed to chloride environments.

A great amount of effort has been expended to determine the C_{CRIT} of a reinforcement, but the values obtained vary significantly. As described by Tang et al. [1], this can be attributed to many factors. The first is the external environment: outdoor, with its variable temperature, relative humidity and precipitation, or constant laboratory conditions. The second is the test environment: simulated pore solution, mortar or concrete. The chloride threshold of bars in concrete or mortar will be influenced by cement type, any supplementary cementitious materials and/or chemical admixtures, the total cementitious content of the mix, the water-to-cementitious ratio and the age of the mortar or concrete. The third is the surface condition of the bars and the fourth is the measurement technique. For example, previous studies have employed corrosion potential monitoring, potentiostatic polarization, macrocell corrosion tests, and microcell corrosion tests. Many of these studies have been reviewed in references [2]–[4]. The decision on the methodology employed is often influenced by the time available to obtain results, but any accelerated technique has an effect on the result [5].

An additional factor is the method of introduction of the chloride. Some investigations have employed admixed chlorides in the concrete [6]–[9], while others have allowed chloride diffusion from outside of the concrete [10]–[12]. Although the former method takes less time, both methods can still take weeks to obtain results unless accelerated by other means. To reduce the time to obtain results and allow

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more control in testing, synthetic pore solutions have been widely employed as the test medium. Laboratory reagents are used to simulate the pore solutions inside of concrete and chlorides are added incrementally over time until active corrosion is observed electrochemically and/or visually. This way the chloride content at the surface of the bars is accurately known and the bars can be observed for immediate initiation of active corrosion. The disadvantage is that the same chloride concentrations exists over the whole bar, unlike the highly inhomogeneous concentrations existing in concrete structures.

In this paper, a method of determining the chloride threshold concentration was adapted from that of Williams et al. [13] who carried out tests on magnesium alloys in acid solution. It should be noted that these authors found the method to be successful for commercially pure magnesium but was less so for some magnesium alloys. This method, discussed in more detail in the next section, involves using anodic potentiodynamic polarization scans to determine the corrosion potential (E_{CORR}) and pitting potentials (E_{PIT}) of same grade of bars in chloride solutions. The E_{CORR} and E_{PIT} values are then plotted on the same graph against the increasing chloride concentration and both curves are extrapolated until they intersect. This intersection point represents the chloride concentration needed to initiate active corrosion on that particular grade of steel at its corrosion potential without any application of an anodic stimulus. It is important to mention that some authors have employed a similar method but plotting only the pitting potentials against chloride concentration without extrapolation [14], [15]. The goal in those papers was not to determine the C_{CRIT} of the bars, but to provide a relative comparison between different bars. The overall objective of the current work is to demonstrate this relatively rapid method of determining the threshold can be used for reinforcing bars in simulated concrete pore solution.

Many authors have tested rebar in saturated calcium hydroxide pH ~ 12.6 and some have used a synthetic pore solution based on KOH, NaOH and $Ca(OH)_2$ with pH ~ 13.6. Clearly, however, the pore solution composition must be representative of that in the specific concrete mix of interest. A recent study of the influence of the water/cementitious materials (w/cm) ratio and supplementary cementitious materials (SCM) content on the pore solution composition [16] has shown that, with increasing admixed chloride, there is an increased sulphate content in the pore solution. Yet only few authors have incorporated sulphate in their synthetic pore solution testing [17]–[20], and only at the beginning of their test without further additions with increasing chlorides. Therefore, the second objective of the current work was to employ the anodic potentiodynamic polarization method to determine the chloride threshold of reinforcing bars rebar in different "pore solutions".

2 Materials and methods

Carbon steel reinforcing bars (rebar), with composition shown in Table 1 were cut to 127 mm (5.0 in) in length, drilled on one end, soldered with a solid copper wire and lacquer was applied to both ends to allow an exposed length of 76 mm (3.0 in) The specimens were cleaned with alcohol to remove contaminations from handling. The specimens were then placed in their respective testing solutions in a three-probe electrochemical cell shown in Figure 1. The reference electrode was a saturated calomel electrode (SCE) and the cylindrical counter electrode was a mixed metal oxide coated titanium mesh.

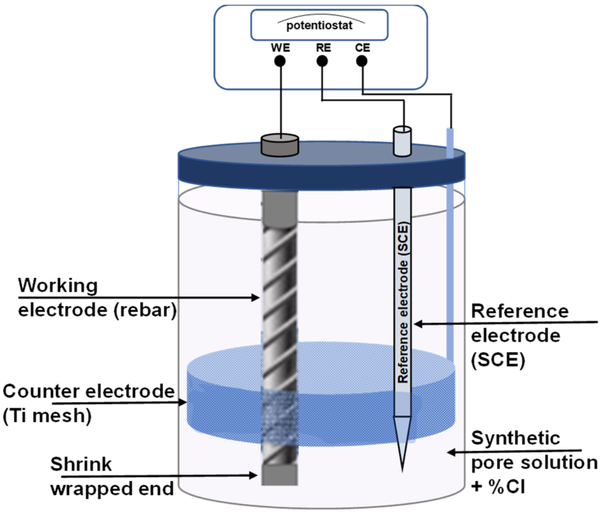

Figure 1. Three-probe electrochemical cell with a mixed metal-oxide titanium mesh counter electrode and a saturated calomel reference electrode (SCE).

Three testing solutions were employed in total as presented in Table 2. One solution (designated as PS+S) was based on the composition of the expressed solutions from a specific 75%Portland cement/25% ground granulated blast furnace slag mixture with a w/cm of 0.40 and different NaCl additions. The second solution (designated as PS) was based on the same solution but omitted the sulphates and the third solution was saturated $Ca(OH)_2$ solution (designated as CH). The percentages shown in Table 2 correspond to the amount of analytical reagent grade compound added to deionized water to make 100 mL of solution. Excess solid $Ca(OH)_2$ was present at all times in all solutions during testing. Each solution was stirred to ensure complete dissolution of all the salts and pH measurements were taken afterwards.

In the work of [16], increasing sulphates were found with increasing chlorides in the pore solutions expressed from cement pastes with increasing admixed chlorides after 28 days as shown in Figure 2. The equivalent amount of sulphate added at each chloride addition is shown Table 3.

Table 1. The mill certificate composition of tested carbon steel rebar.

	Composition (wt. %)												
Constituent	C	Mn	P	S	Si	Cu	Ni	Cr	Mo	V	N	Sn	Fe
Amount	0.210	1.310	0.008	0.018	0.180	0.260	0.060	0.090	0.013	0.050	0.010	0.021	balance

Table 2. Testing solutions.

Testing solution (denotations)	Composition (%)				pH
	$Ca(OH)_2$	KOH	NaOH	$CaSO_4 \cdot 2H_2O$	
Calcium hydroxide (CH)	Saturated				~12.5
Pore solution (PS)	0.01	2.68	0.51		~13.6
Pore solution plus sulphate (PS+S)	0.01	2.68	0.51	0.23	~13.5

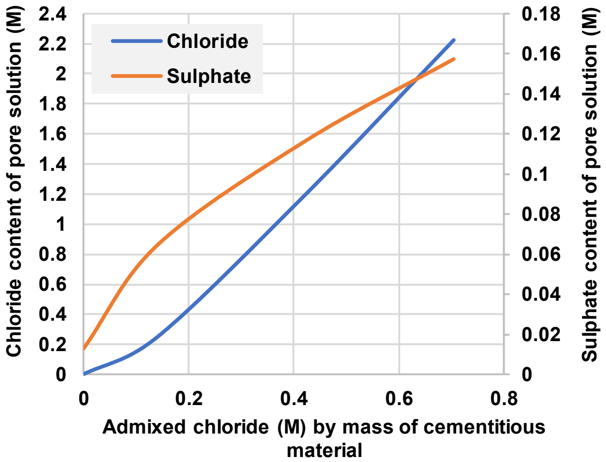

Figure 2. The chloride and sulphate contents of the pore solution expressed from 75% Portland cement/25% slag pastes 0.4 w/cm ratio and the admixed chlorides, as NaCl, in the 28 days old paste. Adapted from [16].

The bars were allowed to passivate in their respective testing solutions for two weeks before any chloride and sulphate was added and before any testing was carried out. After the bars have reached full passivation (determined by a non-varying corrosion potential), chlorides and sulphates (in the PS+S solution) were added as NaCl and $CaSO_4.2H_2O$ and the solutions were stirred for one minute with a magnetic stirrer to completely dissolve the solutes. After the corrosion potential of the steel bars stabilized, indicating equilibrium had been reached, an anodic potentiodynamic polarization test was performed on each bar in its respective solution with a scan rate of 0.01 mV/s as suggested by [5] using the BioLogic potentiostat Model VSP. Each bar was scanned from its corrosion potential in the anodic direction to 0.5 V_{SCE} (or to the current limit of 5 mA) and, if the bar did not display any pitting potential, reversed in the cathodic direction to observe any hysteresis loop. The values of the corrosion potential, E_{CORR}, pitting potential, E_{PIT}, were noted. The E_{CORR} and E_{PIT} values from each polarization curve were then plotted against the chloride content of the solution.

3 Results

Figure 3 shows examples of the corrosion potentials of the bars allowed to passivate in their different testing solutions without chlorides. It can be seen that the E_{CORR} values were relatively similar after 200 hrs, indicating that the bars had reached equilibrium with the testing solution. After the addition of chlorides, a longer wait time before the application of anodic polarization was attempted but, due to the inhomogeneity of the mill scale on the rebar, the potential values of some bars in the solutions with higher chloride contents, became more negative after ~30 mins and then remained approximately constant thereafter. This suggests initiation of pitting corrosion and repassivation on some regions on those bars. When anodic polarization was applied to these bars, some showed curves with defined pitting potentials, while others exhibited general corrosion behaviour. Therefore, for consistency, 30 minutes "wait time" was chosen for all bars in solution at all chloride concentrations.

Table 3. Chlorides and sulphate additions to testing solutions.

Chloride and sulphate content as molar ion in solution and as mass % of compound in solution								
In CH solution								
M Cl- (NaCl, %)	0.028 (0.17)	0.056 (0.34)	0.085 (0.51)	0.113 (0.68)	0.141 (0.85)	0.310 (1.87)	0.338 (2.04)	0.366 (2.21)
In PS solutions								
M Cl- (NaCl, %)	0.451 (2.72)	0.507 (3.06)	0.563 (3.40)	0.620 (3.74)				
In PS + S Solution								
M Cl- (NaCl, %)	0.451 (2.72)	0.507 (3.06)	0.535 (3.23)	0.563 (3.40)	0.620 (3.74)			
M SO_4^{2-} ($CaSO_4.2H_2O$, %)	0.080 (1.44)	0.084 (1.52)	0.086 (1.56)	0.089 (1.59)	0.091 (1.63)			

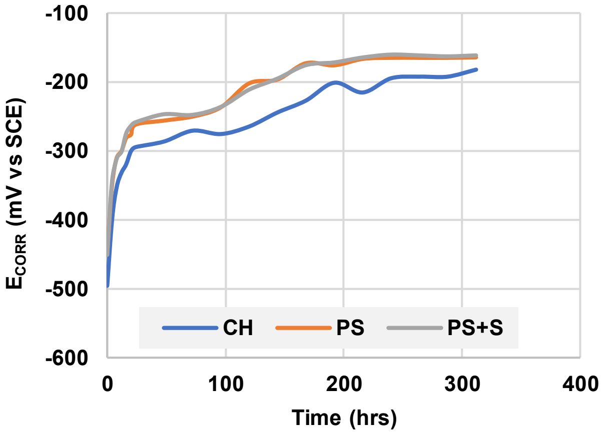

Figure 3. Corrosion potentials of bars in solution over the course of passivation.

An important point to mention is the success rate of obtaining pitting potentials from the anodic scans of these carbon steel bars. Although plots with data point of three replicates of bars tested in each solution are presented in the figures below, about five specimens were tested to obtain each data point. Some results were discarded because the tested bars showed crevice corrosion underneath the lacquer in addition to exhibiting pitting corrosion in the exposed area, as shown in Figure 4. As also evident in Figure 4, there was generally good bonding between the bar and the lacquer, although crevice corrosion did occur in some cases. A few other potentiodynamic scans exhibited the behaviour of general corrosion with no clear onset of pitting and, examination of their pre-test photographs revealed a mill scale that was characterised with several pits along the length of the specimen, Figure 5. Again, such results were discarded. In general, as observed by [13], the success rate of obtaining C_{CRIT} results using the potentiodynamic scans is dependent on the type and/or surface condition of the material. Particularly in this work, it was mostly due to the nature of the mill scale (a complex iron oxide layer) that forms on these bars during the hot rolling process of their steel fabrication which affects the behaviour of the steel in solution. The variation in mill scale between manufacturers, the inhomogeneity along the length of a specimen to be tested, the non-uniformity in thickness and microstructure, and the influence of these factors on electrochemical test results in the presence of chlorides is well documented in the work of Ghods et al. [21].

The initial tests in the PS and PS+S solutions were in the same chloride range as those in the CH solution, that is, from 0.014 to 0.423 M by mass of solution in 0.014 M increments. However, all of the curves indicated passive behaviour, with the return sweep at lower current densities than exhibited in the forward sweep, as shown for the PS solution with 0.423 M Cl in Figure 6. In contrast, it was difficult to obtain a defined pitting onset from the polarization curves obtained from specimens in PS solution with chloride contents greater than 0.62 M by mass of solution because of the high rate of corrosion.

Figures 7 – 9 shows the polarization curves obtained from specimens tested in the CH, PS and PS+S solutions with chlorides respectively. The potential value before the sharp increase in current is known as the breakdown or pitting potential (E_{PIT}). A general observation is the more negative E_{CORR} values and decreasing passivity range with increasing chlorides, as found in other work [14], [15], [22], [23]. A decreasing E_{CORR} value of carbon steel rebar has been observed in both tests carried out in chloride-contaminated pore solution [14], [22], and in cracked concrete exposed to chlorides [23]–[25]. This behaviour is mainly influenced by the surface finish of the bar, particularly the mill scale. At the higher chloride levels, the passive current density increased gradually up to the pitting potential in Figures 7 - 9.

The polarization curves from bars in the PS and PS+S solutions are similar, but the presence of sulphates results in more anodic E_{PIT} values. The passive current densities of bars in these solutions are similar and lower than those in the CH solution, which is consistent with past findings [26], [27]. A current density value with the order of magnitude of 10^{-3} A/m^2 is typically considered passive [28].

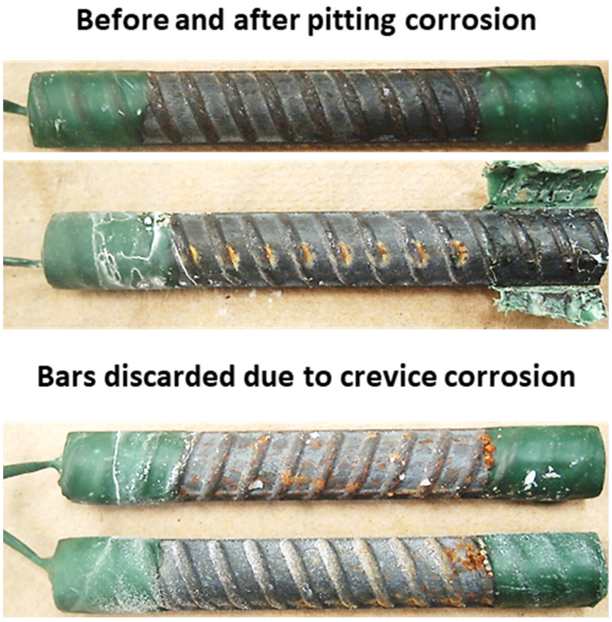

Figure 4. An example of before and after testing for pitting potential is shown at the top of the figure. The after tested bar showed clear pitting corrosion underneath the side rib with no crevice corrosion underneath the lacquer. Bars at the bottom, tested for similar purpose but showed crevice corrosion, albeit pitting corrosion in some case, were discarded.

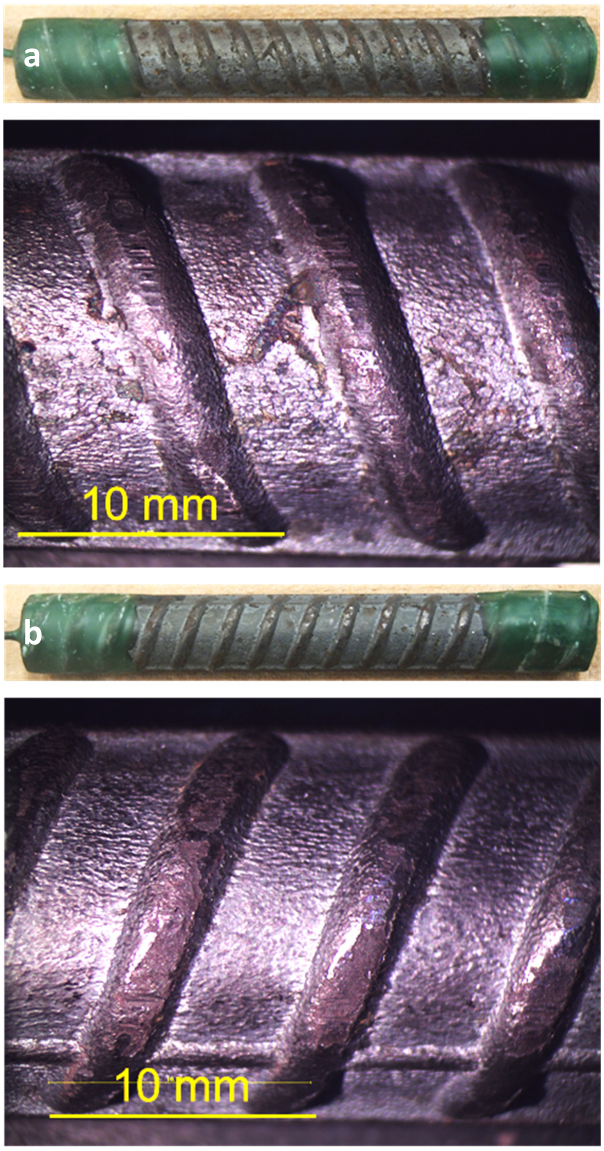

Figure 5. An example of as-received bars (a and b) prepared for testing (top photos) and their micrographs showing the condition of their mill scales (bottom photos). The bar on image a shows a rough mill scale with several pits than those on the image b, which in turn resulted in general corrosion when tested.

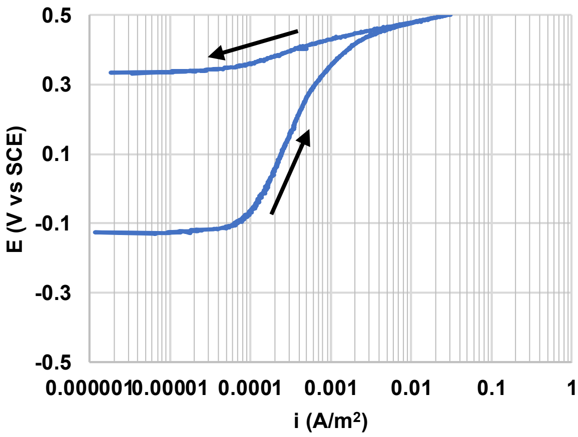

Figure 6. Polarization curves of specimens in PS solution with 1.5% Cl- by mass of solution showing no pitting potentials.

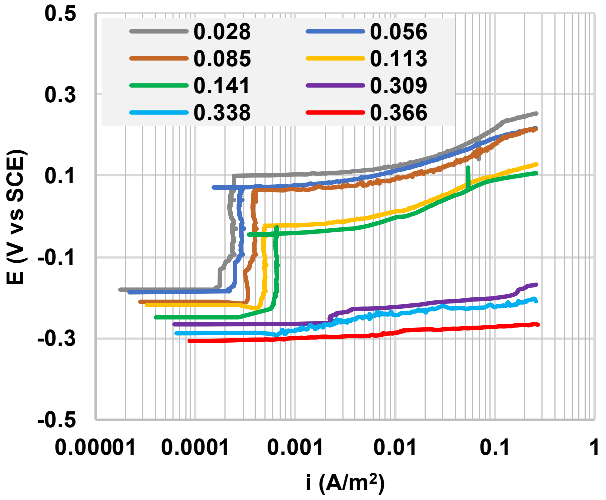

Figure 7. Polarization curves of specimens in CH solution with chlorides from 0.028 to 0.366 M by mass of solution showing pitting corrosion.

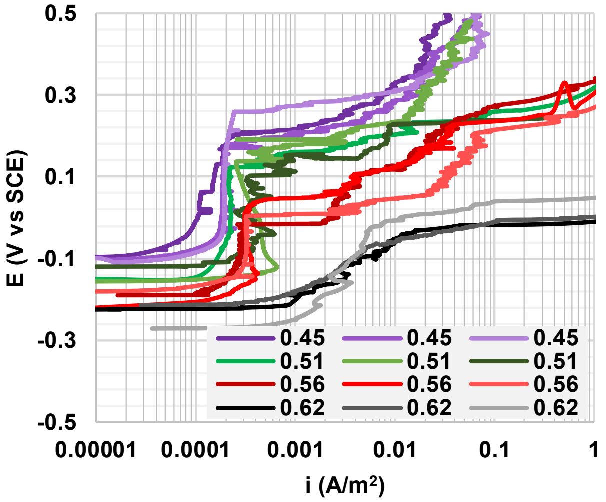

Figure 8. Polarization curves of specimens in PS solution with chlorides from 0.45 to 0.62 M by mass of solution showing pitting corrosion.

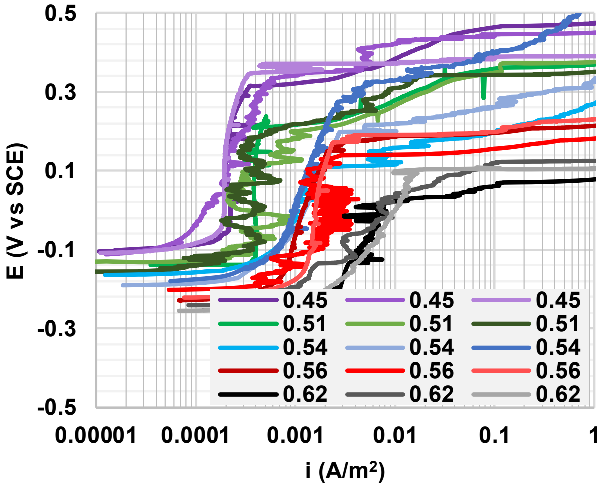

Figure 9. Polarization curves of specimens in PS+S solution with chlorides from 0.45 to 0.62 M by mass of solution showing pitting corrosion.

4 Discussion

Figures 10 to 12 show the potential versus chloride plots that summarise the passivity and pitting behaviour and, allows prediction of the chloride thresholds of carbon steel rebar in the CH, PS and PS+S solutions, respectively. Each figure shows the data for the corrosion potentials (E_{CORR}) and pitting potentials (E_{PIT}) obtained from the polarization curves above, as a function of the chloride content of the solution. Trendlines for the E_{CORR} and E_{PIT} data are extrapolated to their intersection point which, as described above, represents the chloride content of the solution at which corrosion is initiated without the application of an external stimulus, that is the chloride threshold value, C_{CRIT}.

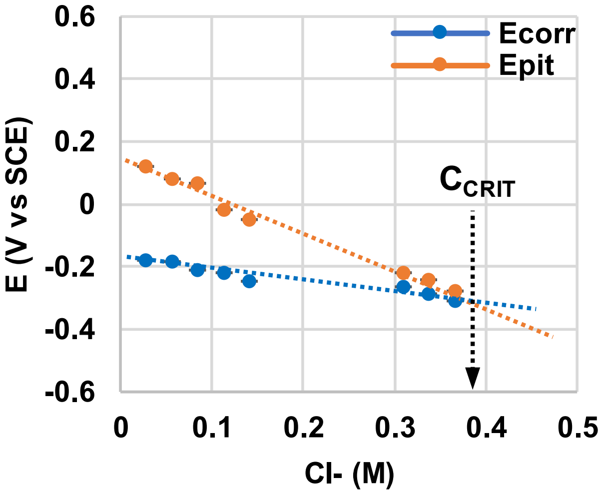

Figure 10. ECORR and EPIT versus chlorides extrapolated to predict the chloride threshold of carbon steel in CH solution. Note the difference in scale from Figures 10 and 11.

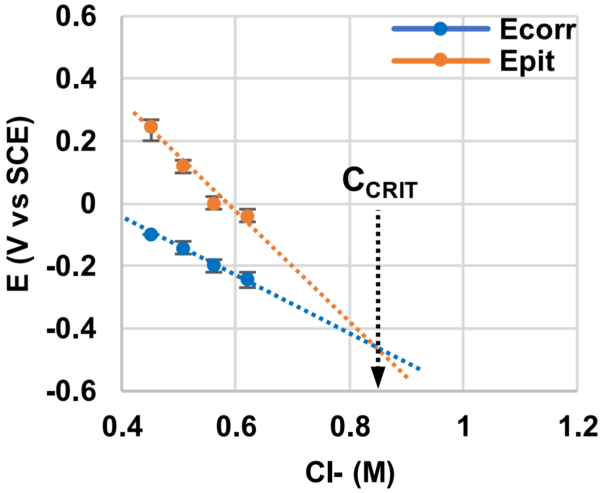

Figure 11. The average and maximum and minimum of three replicates of ECORR and EPIT versus chlorides extrapolated to predict the chloride threshold of carbon steel in PS solution.

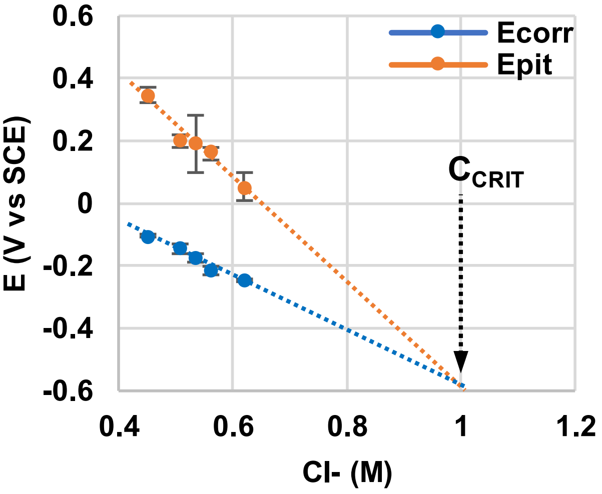

Figure 12. The average and maximum and minimum of three replicates of ECORR and EPIT versus chlorides extrapolated to predict the chloride threshold of carbon steel in PS+S solution.

The critical chloride threshold obtained for bars in the CH, PS and PS+S solutions were found to be approximately 0.38 M, 0.85 M and 1 M by mass of testing solution respectively. Using the data for the expressed pore solutions shown in Figure 2, these values translate to approximately 0.17 M, 0.34 M and 0.37 M Cl- by mass of cementitious material in cement or concrete. The C_{CRIT} values of bars in CH and PS solutions fall within the range (0.07 – 0.56 M by mass of cementitious) of those observed by [8], [9], [26], [29]–[34] using different methodology. No comparison for C_{CRIT} value could be made for bars in the PS+S solution because there does not appear to be any literature using similar solutions. However, Leckie and Uhlig [35] showed in their work in the 60's that sulphate increment in acid solution improved the pitting resistance of stainless steel bar.

The pH of the solutions was determined only at the start of the tests and it is clear that the concept of a constant Cl^-/OH ratio does not hold for these solutions, based on the initial pH values. This observation is in agreement with the results of a parallel study of expressed pore solution from cement pastes with admixed NaCl for which the pH varied with chloride content between 13.2 and 13.5 and molar ratios of Cl/OH in solution varied from 0.077 to 1.44.

To confirm that the C_{CRIT} values obtained in this work can initiate active corrosion on the carbon steel rebar tested in all three solutions, a test was carried out to monitor the corrosion potentials of bars in solution before and after the addition of chlorides and sulphates.

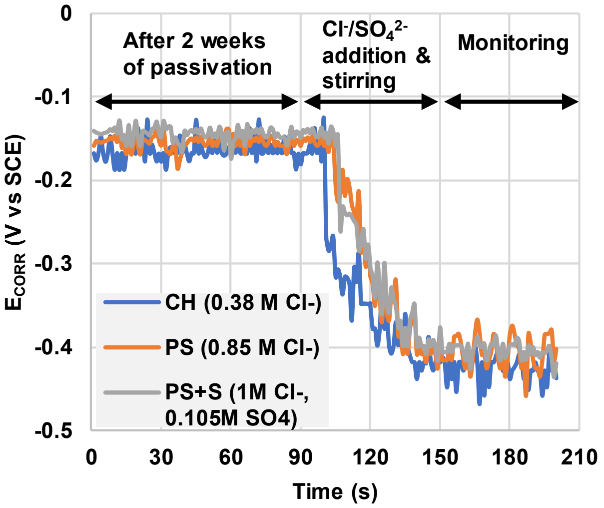

Figure 13. Corrosion potentials of bars in each of the three solutions containing the “critical chloride concentration” for each.

Similar to other bars being tested, these bars were passivated for 2 weeks in their respective containers and then placed on a stirrer. Each cell was hooked up to a potentiostat to monitor the E_{CORR} values for 90 seconds before the addition of salt. After 90 seconds, salts were added and, each solution was stirred using a magnetic stirrer for a minute. The E_{CORR} values were then monitored to observe any subsequent changes and the data are shown in Figure 13.

It is important to emphasize that the PS and PS+S solutions employed in this work were prepared based on composition of expressed solution from a particular cementitious mixture type (75%Portland cement/25% ground granulated blast furnace slag mixture with a w/cm of 0.40) at 0% admixed chloride. This same base mixture was prepared for each chloride (and sulphate) level.

On the question of applicability of these results to chlorides penetrating into concrete from the environment, it is generally accepted that it is the highly concentrated ionic solution in the pores of the concrete, not the solid phases, which is responsible for the passivation of the steel in the non-contaminated concrete, and for the corrosion once the concrete is contaminated. Ideally, therefore, one should determine the composition of the pore solution in the close vicinity of the rebar. Unfortunately, this is not feasible because there is insufficient cementitious material to be able to express and analyse the pore solution. Moreover, as discussed in detail by Tang et. al [1], the chloride content in concrete exposed to saline conditions is highly inhomogeneous, both through the depth of the concrete cover and along the length of the interface between the concrete and the rebar. Determining the critical chloride concentration of structures in service is fraught with even more difficulties including: selection of the most appropriate locations for sampling; the lack of knowledge of the corrosion initiation time and, hence the chloride concentration at that time and the inclusion of possible carbonation effects [36].

The sulphates in cement paste are known to be concentrated in the aluminate phases, ettringite and monosulphate and, therefore, it may be assumed that these phases are the source of the sulphates found in the pore solution [37]. Friedel and Kuzel [38] salts are major solid phases formed during chloride binding and their formation process requires ion exchange of the sulphates in the aluminate phases into the pore solution [39]. The formation of these salts has been found to occur for both admixed and ingressed chlorides [36]. Therefore, this work considers the PS+S solution close to the scenario found in field concrete and, therefore, it is deemed important to determine the effect of the sulphate release on the corrosion resistance of the embedded rebar.

5 Potential applications and developments

The test procedure is currently being applied to five different stainless steel rebar grades in a synthetic pore solution of the same composition as the PS+S used in the current tests, in order to assess their relative resistance to chloride attack. It is also being used to evaluate the relative effects of different chloride salts, namely $CaCl_2$, $MgCl_2$ in comparison to the commonly used NaCl.

Future developments of the test method will focus on the critical chloride levels of steel in mortar. Rebar will be cast in cylindrical mortar specimens with a small cover and, after curing, will be exposed to chlorides for different time periods prior to the cyclic potentiostatic polarization. Details of the procedure require “trial and error” determination. If successful, this procedure will lend itself to assessment of the effect of mortar mixture design, rebar surface finish, environmental conditions etc. A comparison of the results of these tests with those presented here will also clarify the relevance of testing corrosion in synthetic pore solution.

6 Summary and Conclusions

- The potentiodynamic polarization scan method of determining chloride threshold level was successful in determining the C_{CRIT} of carbon steel rebar in three different synthetic pore solutions. Obtaining results through this method is shown to be dependent on the surface condition of the carbon steel rebar. On average, five specimens were tested before three replicates in each data point in Figures 11 and 12 were obtained. Furthermore, at chloride concentrations close to the C_{CRIT} value of the bar in solution, it was difficult to obtain a polarization curve with defined pitting onset.
- The threshold level determined by this method increased from 0.38 M in the CH solution to 1 M in the synthetic pore solution containing sulphates. Using the data in Figure 2 obtained from expressed pore solution at 28 days of slag cementitious mix with admixed chloride, the latter value would be equivalent to 0.37 M by mass of cementitious materials in cement paste, mortar or concrete with the same cementitious mix.
- Corrosion potential monitoring test confirms that the C_{CRIT} values obtained in this work for each of the three

solutions is sufficient to initiate active corrosion on the carbon steel rebar tested.

- The addition of sulphate to pore solution at levels corresponding to those measured in expressed pore solution increased the C_{CRIT} of bars from 0.85 M to 1.00 M Cl^- by mass of pore solution. This is approximately 18% and equivalent to 0.03 M by mass of cementitious material.
- Sulphate increments, which were shown to improve the pitting resistance in acid solution in a past research [35], are also shown here to have positive impact on the C_{CRIT} value obtained from the extrapolation of E_{CORR} and E_{PIT} obtained from the potentiodynamic polarization curves of bars tested in alkaline solution.
- As mentioned above, there are numerous factors influencing the critical chloride concentration for rebar in concrete, including environmental conditions, rebar surface state, concrete mixture design and chloride cation type. However, by replicating the pore solution composition of the specific concrete of interest, and using the applicable chloride salt, this potentiodynamic scan method can be used to determine the influence of the last two factors.

7 Acknowledgments

The authors appreciate the funding and support provided for this project by the Natural Sciences and Engineering Research Council of Canada.

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