

Voltammetric behaviour of iron in cement II: effect of sodium chloride and corrosion inhibitor additions

J. T. HINATSU, W. F. GRAYDON, F. R. FOULKES*

Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario M5S 1A4, Canada

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A method for studying the behaviour of iron reinforcement in cured Portland cement paste using linear sweep cyclic voltammetry is described. The use of this method is demonstrated for the *in situ* study of: (i) the formation of passive films on iron embedded in cement; (ii) the NaCl-induced disruption of these passive films; and, (iii) the protection of passive films on iron in salt-contaminated cement pastes by corrosion inhibitors. Disruption of the passivity was observed upon potential cycling following immersion of cement-embedded iron electrodes for 24 h in solutions containing as little as 0.1 M NaCl. Corrosion inhibitors such as sodium nitrite, potassium chromate and sodium benzoate all had some beneficial effect in maintaining the passivity of the iron electrodes in the presence of potentially damaging concentrations of NaCl. Of these inhibitors, sodium nitrite was the most effective at the levels used in this study.

1. Introduction

The chloride-induced corrosion of concrete reinforcing steel currently is a problem of great importance, not least because the cost associated with corrosion-related damage to concrete structures, such as bridges and parking garages, in North America runs into billions of dollars. A stable, passivating film normally forms on the surface of reinforcing steel in the highly alkaline environment of Portland cement. Corrosion of the embedded steel occurs if this protective film is disrupted, as in the presence of chlorides from deicing salts.

The addition of corrosion inhibitors to the cement mix is one of several methods used to protect metals embedded in salt-contaminated concrete from corrosion [1]. An effective inhibitor must stabilize the passive films in the presence of otherwise damaging concentrations of chloride ions. It has been recommended that the effectiveness of corrosion inhibitors should be evaluated *in situ* [2]. In this regard, we have developed a reliable procedure for conducting cyclic linear sweep voltammetric measurements with iron in hardened Portland cement paste [3]. This voltammetric method enables the study of the electrode response over a wide range of electrode potentials in a single experiment. In particular, the formation and effectiveness of the passive film is readily and reliably studied under different conditions. Furthermore, non-representative behaviour is easily identified and circumvented, for example, by repeated cycling. Consequently, we have found our voltammetric method to be useful when

investigating the differences in the effects of chlorides and corrosion inhibitors on the passivation behaviour of iron in cured cement pastes.

Accordingly, in the present paper, we describe the application of the cyclic voltammetric method to the *in situ* study of (i) the formation of stable passive films on iron embedded in cement, (ii) the chloride-induced disruption of these passive films, and (iii) the protection of passive films on iron in NaCl-contaminated cement pastes by the use of corrosion inhibitors such as sodium nitrite, potassium chromate and sodium benzoate.

2. Experimental details

A method for obtaining voltammograms for iron in cured normal Portland cement pastes has been described in detail [3]. The same method, equipment and materials were used in the present study, except for the modifications described below. Briefly, the method involves embedding iron wire (Johnson-Matthey, 99.999% Fe, 0.25 mm diameter) in cement paste having a water-to-cement ratio (W:C) of 0.45. The resulting cement-embedded iron electrodes are cured for three days at 100% relative humidity. *IR*-compensated cyclic voltammograms then are run at 0.050 V s^{-1} from -1.4 V to $+0.4 \text{ V}$ (all potentials quoted herein were measured with respect to the saturated calomel electrode (sce)). The cell essentially was of a standard three-electrode design, except that four counter electrodes were used in order to maintain cylindrical geometry. Saturated $\text{Ca}(\text{OH})_2$ was used as the cell electrolyte.

* Author to whom correspondence should be addressed.

In order that the effects of contaminating the cement pore solution with chloride ions could be investigated, the cement electrodes were immersed in 'external solutions' composed of saturated $\text{Ca}(\text{OH})_2 + \text{NaCl}$ (various concentrations) for 24 h, following the 3 day air cure, and before potential cycling. Each electrode was tightly sealed into a 40 ml pyrex test tube containing the external solution, which was maintained at $25 \pm 0.2^\circ\text{C}$ by means of a recirculating water bath. Momentary exposure to the atmosphere was necessary in order to transfer the electrode to the cell.

This immersion method was deemed to better approximate the contamination of reinforced concrete by chloride ions from deicing salts than would addition of NaCl directly to the cement mix water (admixing). It has been reported that chlorides which diffuse from an external solution into concrete are more aggressive than admixed chlorides [4].

Conversely, the inhibitors (sodium nitrite, potassium chromate and sodium benzoate) were introduced as admixtures, as in actual practice. Therefore, we have expressed the inhibitor concentrations in the conventional manner as weight percents with respect to the dry cement in the mix. Although some admixed inhibitors have been reported to affect the setting time of concrete, in the case of sodium nitrite, admixing 2% of the inhibitor has been shown to exert only a slight effect on the setting time of various mortars [5]. In this regard, curing times as short as one day have reportedly been used successfully in electrochemical testing of reinforced mortar and concrete containing various admixed inhibitors and chlorides [6, 7]. However, we recommend a curing time of three days, since our results for samples cured for one day were significantly different from our results for samples cured for 3–50 days [3]. Similarly, conclusions from corrosion potential measurements on samples cured for three days have been reported to correspond with those for samples cured for 90 days [5].

Admixture solutions (containing NaNO_2 , K_2CrO_4 or sodium benzoate) were prepared from analytical grade chemicals (BDH) and de-ionized water ($\sim 18 \text{ M}\Omega\text{cm}$ resistivity). Cement pastes were prepared by weight using either de-ionized water or admixture solution. The cell electrolyte was of the same composition as the 'external solution' in which a cement electrode had been immersed, and was sparged with pre-saturated, 'O₂-free' N₂ for at least 30 min before a run, and also blanketed with N₂ during a run. All experiments were performed at $25 \pm 0.2^\circ\text{C}$. Further experimental details such as cement composition and working electrode construction have been described in Part I of these studies [3].

3. Results and discussion

Anodically-formed films resulting from potential cycling do not duplicate naturally-formed passive films found on reinforcement steel in concrete. However, although potential sweeping can affect the

passive layer characteristics, the passivation produced during the voltammetric procedure is subject to reproducible and sensitive electrochemical measurement. Care has been taken to develop a reliable experimental procedure [3], in order that the differences in behaviour caused by chlorides and corrosion inhibitors can be noted with confidence. For example, repeated cycling was performed on each sample, in order to obtain reproducible behaviour between different electrodes, and to enhance the size and definition of the voltammetric peaks. Furthermore, the voltammetric results obtained using our method correspond well with those reported by previous workers, who used steady-state methods such as galvanostatic polarization. Thus, the cyclic voltammetric method represents a complementary means of studying phenomena related to the actual passivation and corrosion processes of interest.

3.1. Voltammograms for iron in cured Portland cement paste

A typical voltammogram for iron in cured Portland cement paste is shown in Fig. 1. Two well-defined anodic peaks (peaks 1 and 3) and two well-defined cathodic peaks (peaks 4 and 5) are observed over the course of 200 cycles. The electrochemical reactions corresponding to the various peaks have been discussed previously but have not been unequivocally identified (see [3] and references therein). In the

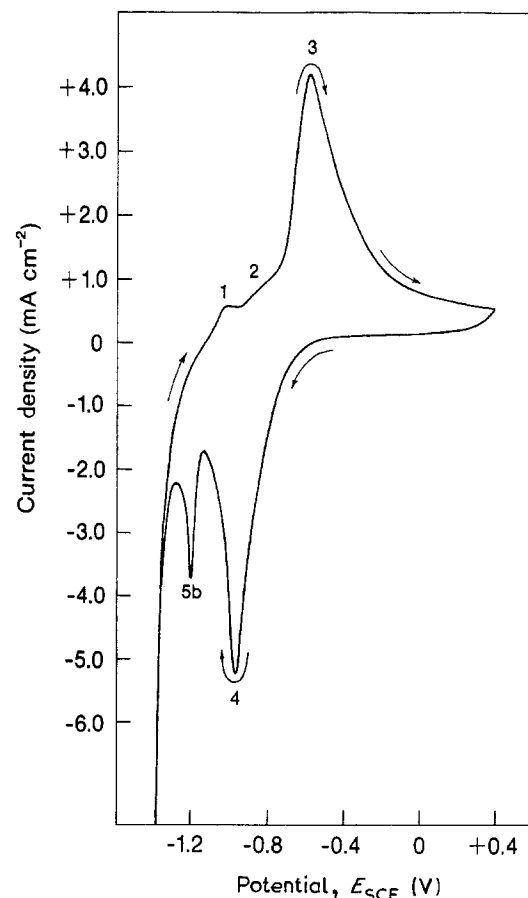


Fig. 1. Voltammogram for cement-embedded iron wire electrode after 24 h immersion in saturated $\text{Ca}(\text{OH})_2$ and 100 prior cycles $\text{W:C} = 0.45$, 25°C , 0.050 V s^{-1} .

present study, however, our main interest is the formation and stability of the passive film on each cycle. Thus, we have focused our attention on the current densities in the passivation region at peak 3 and potentials anodic to peak 3 ($-0.6\text{ V} \sim +0.6\text{ V}$). The current densities at peak 3 are characteristic of the onset of passivation, at which point Fe(II) is being oxidized to insoluble Fe(III). At the peak the increasing rate of oxidation to form the coherent passivating film of compounds of Fe(III) (possibly CaFe_2O_4 [3]) is overtaken by the increasing impermeability of the passivating layer. The current densities at potentials anodic to peak 3 are representative of the permeability of the anodic film on each cycle. The behaviour of the other peaks will only be mentioned in passing. Peak 4 is the reduction peak corresponding to peak 3. Peak 1 and the poorly-defined peak 2 usually are attributed to the formation of ferrous hydroxide from the base metal, and peak 5 has been identified with the associated reduction peaks. Peak 5 initially appears at about -1.3 V (peak 5a), but shifts to about -1.2 V after 30–50 cycles (peak 5b). Peak 5a has been ascribed to reduction of a compact, anhydrous inner layer, and peak 5b to reduction of both this inner layer and also a hydrous outer layer.

3.2. Effect of NaCl additions on the voltammetric behaviour of uncoated iron in 0.1 M KOH and saturated $\text{Ca}(\text{OH})_2$ solutions

Studies of the voltammetric behaviour of iron and steel in simple solutions such as saturated $\text{Ca}(\text{OH})_2$ and aqueous KOH are a useful basis for comparison with the corresponding behaviour of iron in the relatively complex medium of Portland cement [3, 5, 8–12]. While a solution containing small amounts of $\text{Ca}(\text{OH})_2$ in 0.1 M KOH was found to simulate the cement environment well [3], single component solutions of 0.1 M KOH or saturated $\text{Ca}(\text{OH})_2$ were used in this study, in order to provide a simple comparison for the cement measurements.

3.2.1. Voltammetric behaviour in aqueous 0.1 M KOH solution. Voltammograms for iron in 0.1 M KOH + 0.2 M NaCl during early cycles and after 200 cycles, are shown in Fig. 2. The first few cycles yield voltammograms that are more transient and less well-defined than those obtained after 200 cycles. The relatively high currents at potentials anodic to peak 3 during the first several cycles provide evidence of film breakdown followed by iron dissolution, although stable passivation was re-established and maintained on each cycle after about 30 cycles. Thus, the instability of the passivation during early cycles was a transient phenomenon, and was not indicative of the stable passivation that eventually was achieved on each cycle upon repeated cycling. This behaviour illustrates the importance of following the previously recommended procedure of extensive repeated cycling (e.g., 200 cycles) [3]. Similar erratic behaviour during early cycles also was observed in the presence of 0.1 M NaCl

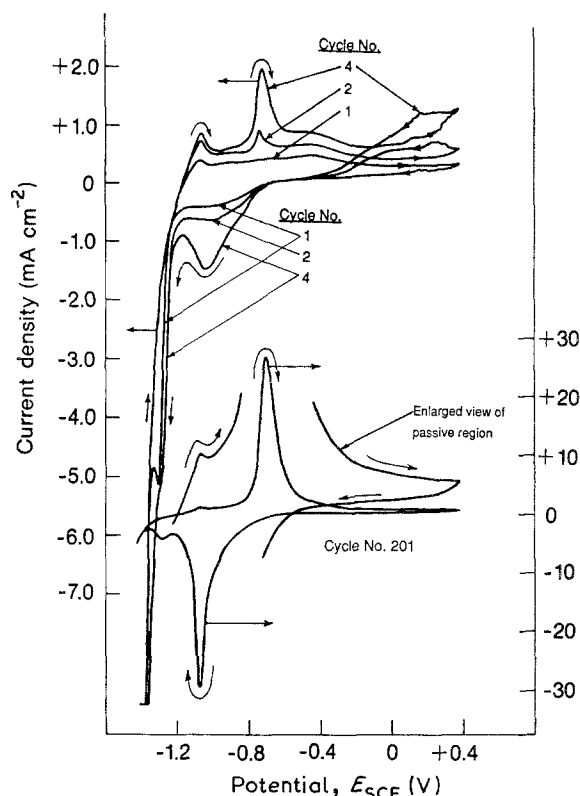


Fig. 2. Voltammograms for uncoated iron wire electrodes in 0.1 M aqueous KOH + 0.2 M NaCl at different cycle numbers. 25°C , 0.050 V s^{-1} .

and 0.25 M NaCl, although with slightly smaller or much larger oxidation currents, respectively.

3.2.2. Behaviour in saturated $\text{Ca}(\text{OH})_2$ solution. The results for iron in saturated $\text{Ca}(\text{OH})_2$ were similar to those described above for 0.1 M KOH, but disruption of the passivity was observed at much lower NaCl concentrations (as low as 0.03 M). Since saturated $\text{Ca}(\text{OH})_2$ solution involves both a lower pH and a different cation, both the pH [11] and the differing influences of the different cations (Ca^{2+} against K^+) [3, 13, 14] may have been of some importance.

3.3. Effect of exposure to NaCl on the voltammetric behaviour of iron in cured Portland cement paste

As can be seen from Fig. 3, significant depassivation is readily observed for cement-embedded iron electrodes exposed for 24 h to as little as 0.1 M NaCl in the external $\text{Ca}(\text{OH})_2$ solution. Extensive depassivation upon exposure to 0.2 M NaCl in the external solution is clearly evident, the voltammogram being extremely distorted with very large currents flowing throughout, especially in the normally passive region at potentials anodic to peak 3. (The instability of the currents at high anodic peaks might be the result of localized corrosion.) Thus, as with iron in simple alkaline solutions, increasing interference with the passivation upon exposure to increasing concentrations of NaCl is evident by inspection of the voltammograms for iron embedded in cement.

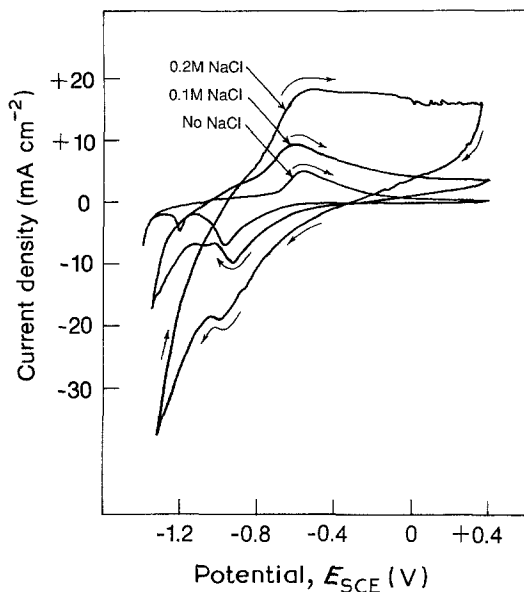


Fig. 3. Effect of external NaCl concentration on voltammograms for iron in cured cement paste. Cycle no. 201, W:C = 0.45, 25°C, 0.050 V s⁻¹. External solution: saturated Ca(OH)₂ + various concentrations of NaCl.

3.4. Effect of external solution composition

While the cement environment undoubtedly is saturated in Ca(OH)₂, the pH of cement pore solutions has been reported to be 13 or greater, which is considerably higher than that of saturated Ca(OH)₂ solutions (pH = 12.4) [9]. Thus, trials with external solutions of 0.04 M KOH (pH = 12.4), 0.1 M KOH (pH = 12.9), or saturated Ca(OH)₂ (with 0.2 M or 0.4 M NaCl added) were conducted in order to determine the effect of the external solution composition.

As described above, the voltammograms for an external solution of saturated Ca(OH)₂ + 0.2 M NaCl (pH = 12.4) were extremely distorted, with very large currents in the normally passive region following peak 3. However, much less salt-induced damage of the passive films was observed with an external solution of 0.1 M KOH + 0.2 M NaCl (pH = 12.9), as indicated by the relative magnitudes of the current densities in the normally passive region at 0 V, shown in Table 1. While the higher pH of 0.1 M KOH most likely exerted a significant protective influence, it is noteworthy that the sodium chloride attack on the passive film for an external solution of 0.04 M KOH + 0.2 M NaCl (as measured by the current density at 0 V, also shown in Table 1) also was significantly less than that for saturated Ca(OH)₂ + 0.2 M NaCl. Since these latter two external solutions were of the same pH, the observed difference in the stability of the passivity may be attributed to the respective influences of the different cations, Ca²⁺ against K⁺. Furthermore, since the cement used in this study contained 62% CaO, the cement pore solution was undoubtedly saturated with Ca(OH)₂ for external solutions of 0.04 M KOH as well as for those of saturated Ca(OH)₂.

Potassium ions penetrating to the embedded iron

may possibly have interfered with the chloride-induced destruction of the passive film. This apparent inhibition of the sodium chloride attack on the passivating film is interesting. Opinions in the literature as to the existence of such cation effects are divided, some workers citing evidence for differences in susceptibility to chloride breakdown caused by the incorporation of different cations into passive films on iron [14], and others claiming no significant role for cations in the oxidation or corrosion of steel in alkaline media, citing pH as the dominant factor [10]. In this study, we chose to use saturated Ca(OH)₂ (with various NaCl additions) as the external solution to avoid possible interference caused by the introduction of potassium ions. Saturated Ca(OH)₂ also has been used elsewhere [5–8] as the cell electrolyte for electrochemical measurements with steel in concrete or mortar.

On the other hand, elimination of the introduction of significant amounts of cations, in this case of sodium ions through the NaCl in the external solution was not possible. Separation of the anion and cation effects for various chloride salts has not yet been completed.

3.5. Effect of admixed inhibitors on the voltammetric behaviour of iron in chloride-contaminated cement paste

The introduction of corrosion inhibitors as additions to the concrete mix (admixtures) has been used to prevent, or at least delay, the onset of corrosion of reinforcing steel [5–8, 10, 12, 15–23].

Nitrites are the most commonly used inhibitors, both sodium nitrite and calcium nitrite having been shown to be effective in protecting reinforcing steel

Table 1. Current densities* at 0 V on anodic sweep for cement-embedded iron wire after immersion for 24 h in external solutions consisting of 0.2 M NaCl + either saturated Ca(OH)₂, 0.04 M KOH or 0.1 M KOH†

Cycle No.	Current density at 0 V (mA cm ⁻²)		
	Saturated Ca(OH) ₂ + 0.2 M NaCl (pH = 12.4)	0.04 M KOH + 0.2 M NaCl (pH = 12.4)	0.1 M KOH + 0.2 M NaCl (pH = 12.9)
1	0.33	0.33	0.33
2	0.53	0.44	0.42
5	0.64	0.53	0.47
11	0.85	0.61	0.52
21	1.3	0.67	0.59
51	5.6	1.8	0.79
101	14.5	6.0	1.1
151	18	7.5	1.7
201	17	7.8	2.7

* All current densities in the present study were calculated on the basis of the nominal iron surface area of about 0.08 cm², the accurately measured areas being in the range 0.080 ± 0.005 cm². No baseline corrections were applied in this study. Although potential sweeping can affect the metal surface area, extreme accuracy in the reported current densities is not of great significance in the present study.

† 25°C, W:C = 0.45, 0.050 V s⁻¹.

in chloride-contaminated concrete [5–8, 12, 17–23]. Nitrite ions are thought to rapidly oxidize the ferrous ions formed during active corrosion to ferric oxides. These ferric oxides in turn are thought to precipitate on the anode surface, thereby preventing the migration of ferrous ions away from the metal surface, and repairing the disrupted passivity of the film [19–21].

Potassium chromate and sodium benzoate also have been shown to be effective in reducing the chloride-induced corrosion of steel in concrete and $\text{Ca}(\text{OH})_2$ solutions [6, 18]. While the action of nitrites is thought to be non-localized [20, 21], CrO_4^{2-} ions are strongly adsorbed on the iron surface [24]. The mechanism of the inhibitive effect of chromates is probably complex. Theories regarding the role of CrO_4^{2-} in the passivation of stainless steels have recently been discussed [24, 25]. One possibility is that CrO_4^{2-} ions are reduced to protective Cr_2O_3 , perhaps by the sequence $\text{CrO}_4^{2-} \rightarrow \text{Cr}(\text{OH})_3 \rightarrow \text{CrOOH} \rightarrow \text{Cr}_2\text{O}_3$. There is substantial evidence for the existence of 'bipolar' passive films on stainless steels; the anion-selective inner layer prevents migration of ferrous ions to the solution, and the cation-selective outer layer stops ingress of chloride ions. Furthermore, deprotonation of hydroxyl ions is thought to occur in these bipolar films, resulting in migration of O^{2-} to the metal surface, where Cr_2O_3 is formed (presumably, Fe_2O_3 would be formed in the absence of Cr in the metal alloy); H^+ ions are simultaneously expelled into the solution. Alternatively, chromates may act as electron acceptors, thereby reducing the electronic conductivity and increasing the metal-oxygen bond strengths of the anodic films. Conversely, sodium benzoate is thought simply to be adsorbed on the iron surface, thereby diminishing the iron surface area that must be passivated by oxide films, or that is accessible to adsorbing chloride ions [26].

Extension of the voltammetric method to the study of the inhibition of NaCl-induced depassivation of iron in cement pastes through the use of admixed sodium nitrite, potassium chromate and sodium benzoate is described below.

3.5.1. Effect of sodium nitrite additions. The admixing of 0.75%–1.0% sodium nitrite (by weight of the dry cement in the mix) has been shown to suppress passivation breakdown on reinforcing steel in concrete containing admixtures of 2% NaCl or 2% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. The addition of as little as 0.5% sodium nitrite has been found to have some beneficial effect [6, 18]. Accordingly, sodium nitrite additions of 0.6% and 1.0% were chosen to demonstrate the efficacy of the cyclic voltammetric method for evaluating sodium nitrite as a corrosion inhibitor for iron in cement.

The voltammograms for iron embedded in cement with 0.6% admixed sodium nitrite, after immersion for 24 h in external solutions containing 0 to 0.4 M NaCl and 0.6 M NaCl, are shown in Fig. 4. The results clearly show that the level of protection is increased significantly upon addition of 0.6% sodium nitrite to

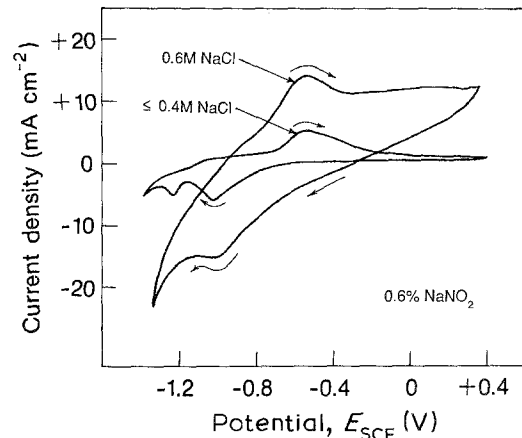


Fig. 4. Effect of 0.6% admixed NaNO_2 (by weight of the dry cement in the mix) on the voltammograms for iron in cured cement paste with external NaCl concentrations of 0–0.4 M and 0.6 M. W:C = 0.45, 25°C, 0.050 V s^{-1} .

the cement mix. For external NaCl concentrations of less than about 0.4 M, the voltammograms were similar to those obtained for iron in cement with no NaCl or inhibitor added, especially in the passive region of interest (-0.6 V to $+0.6\text{ V}$), although the peak 5 current densities with 0.6% NaNO_2 were more than double those found for cement with no added sodium chloride or inhibitor during the first ~ 30 cycles. Thus, the addition of as little as 0.6% NaNO_2 to the cement allowed for fairly normal development of protective films in the presence of as much as 0.4 M NaCl in the external solution; that is, the maximum tolerable amount of chloride in the external solution was increased by a factor of about 4 (from about 0.1 M to about 0.4 M). However, as can be seen from Fig. 4, striking deviations from the normally observed development of the passive layer occurred when the external salt concentration was increased to 0.6 M NaCl, and 0.6% NaNO_2 clearly was insufficient to prevent disruption of the passive films at this relatively high concentration of NaCl.

The protective influence of 0.6% admixed NaNO_2 and the limits of this protection are clearly illustrated by plots of the progression of the current density in the normally passive region at 0 V with cycle number (Fig. 5). With 0.6% NaNO_2 , even when the external

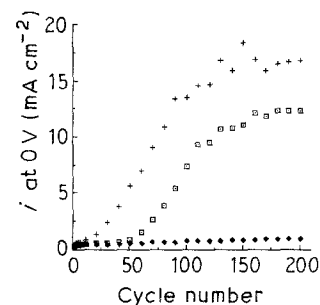


Fig. 5. Effect of external NaCl concentration in the progression of the current density at 0 V (anodic sweep) with cycle number for iron embedded in cement with 0.6% admixed NaNO_2 . Electrodes were exposed to saturated $\text{Ca}(\text{OH})_2 + \text{NaCl}$ for 24 h before potential cycling. W:C = 0.45, 25°C, 0.050 V s^{-1} . (+ + +) no inhibitor, 0.2 M NaCl; (□ □ □) 0.6% NaNO_2 , 0.6 M NaCl; (◆ ◆ ◆) 0.6% NaNO_2 , 0–0.4 M NaCl.

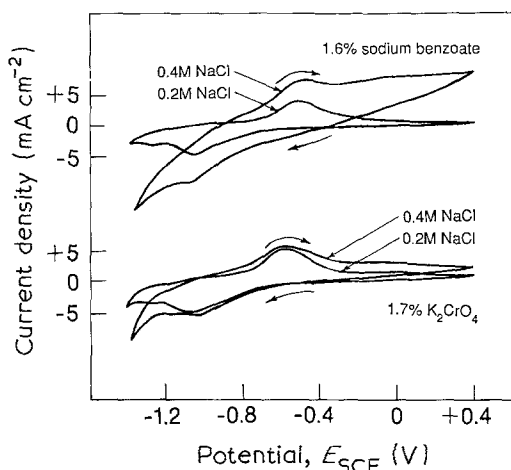


Fig. 6. Effect of admixing 1.6% sodium benzoate and 1.7% potassium chromate (by weight of the dry cement in the mix) on the voltammograms for iron in cured cement paste with external NaCl concentrations of 0.2 M and 0.4 M. W:C = 0.45, 25°C, 0.050 V s⁻¹.

NaCl concentration was increased to 0.6 M, fairly stable passivation was established during the first 40–50 cycles (although there was some evidence of instability and film breakdown during the first 5 cycles). However, the current densities increased sharply upon continued cycling, levelling off after 150–200 cycles at a value about 12 times greater than that obtained with NaCl concentrations of 0–0.4 M. This once again illustrates the value of repetitive cycling (typically 200 cycles), since the disruptive effect with 0.6 M NaCl in the external solution would not be clear at less than about 50 cycles, and even then, the magnitude of the depassivating effect would be underestimated at less than about 150 cycles.

Analogous voltammetric results were obtained with 1.0% admixed sodium nitrite. In this case, normal passivation during cycling was observed with NaCl concentrations as high as about 1.6 M NaCl in the external solution. Disruption of the passivity was observed almost immediately, however, with 1.8 M NaCl in the external solution.

The voltammetric results obtained with 0.6% and 1.0% admixed sodium nitrite are in agreement with the results of galvanostatic tests (potential-time curves and polarization curves) reported in the literature for comparable specimens [6, 18]. The voltammetric results show that for an external chloride ion concentration of between 0.4 M–0.6 M NaCl, 1.0% admixed sodium nitrite suppresses breakdown of the passive films; however, while 0.6% admixed sodium nitrite provides some beneficial effect, film breakdown is observed with 0.6 M NaCl. Similarly, galvanostatic results [6] for samples containing 2% admixed CaCl₂·2H₂O indicate that the addition of 1.0% sodium nitrite prevents passive film breakdown, while 0.5% admixed sodium nitrite delays and moderates, but does not prevent, passive film breakdown. Furthermore, chloride ion concentrations in the range of about 0.4 M–0.6 M have been measured in the pore solutions of 1–5 day-old cement pastes containing 2% admixed calcium chloride [27]. These measured

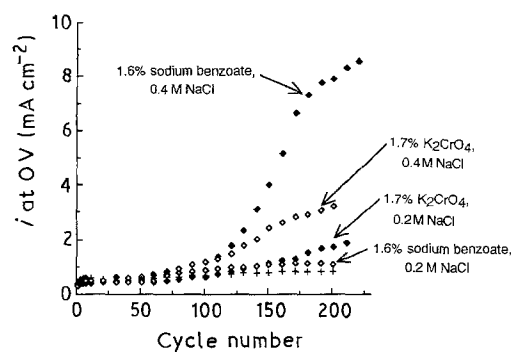


Fig. 7. Effect of external NaCl concentration and admixing of 1.6% sodium benzoate and 1.7% potassium chromate on the progression of the current densities at 0 V (anodic sweep) with cycle number. W:C = 0.45, 25°C, 0.050 V s⁻¹. The lower curve (+ + +), for no added inhibitor or NaCl, is shown as a reference.

chloride ion concentrations are similar to the external NaCl concentrations of 0.4 M–0.6 M used in the present voltammetric experiments. While the actual internal chloride ion concentration for an external chloride ion concentration of 0.4 M–0.6 M is not known exactly, the good agreement between the voltammetric and literature results gives rise to further confidence in the validity of the cyclic voltammetric procedures as a method of evaluating corrosion inhibitors for reinforced concrete.

3.5.2. Effect of potassium chromate and sodium benzoate additions. The voltammetric method was also used to evaluate the effectiveness of potassium chromate and sodium benzoate admixed at molar levels comparable to that of 0.6% sodium nitrite (0.06 mol kg⁻¹ of cement mix). The voltammograms for Fe embedded in cement having 1.7% potassium chromate (0.06 mol kg⁻¹ of cement mix) or 1.6% sodium benzoate (0.08 mol kg⁻¹ of cement mix) admixed, and with external solutions containing 0.2 M or 0.4 M NaCl, are shown in Fig. 6. Comparison of the voltammograms of Fig. 6 with those of Fig. 3 shows that 1.7% potassium chromate and 1.6% sodium benzoate both have some beneficial effect in maintaining passivity in the presence of NaCl concentrations of 0.2 M and 0.4 M. However, neither 1.7% potassium chromate nor 1.6% sodium benzoate was as effective as 0.6% sodium nitrite in preventing film depassivation. These results are in qualitative agreement with those of previous researchers who reported that potassium chromate and sodium benzoate are somewhat less effective than sodium nitrite in preventing film breakdown in the presence of high chloride concentrations [6, 8, 18]. Interestingly, reference to Table 2 shows that at low external NaCl concentrations of less than about 0.1 M, the protective influence of the films formed in the presence of 1.7% potassium chromate (as indicated by plateau current densities of ~0.7 mA cm⁻²) was somewhat greater than that obtained with 0.6% sodium nitrite or 1.6% sodium benzoate (current densities of ~0.8–0.9 mA cm⁻²). One explanation for this result is that chromate ions are able to successfully compete for

Table 2. Effect of admixed inhibitors on current density at 0 V after 200 cycles for various external NaCl concentrations*

[NaCl] (mol l ⁻¹)	Current density at 0 V (mA cm ⁻²)								
	0	0.05	0.10	0.20	0.40	0.60	0.80	1.6	1.8
No inhibitor	0.9	1.1	4.3	17	28				
1.7% K ₂ CrO ₄	0.7	0.7	0.7	1.8	2.9	8.0‡			
1.6% NaB†	0.8	0.9	0.9	1.1	7.9				
0.6% NaNO ₂	0.9	0.9	0.9	0.95	1.1	12‡			
1.0% NaNO ₂	0.9						0.9	0.9	22‡

* The line in Table 3 separates regions of passivity from regions of film breakdown. All inhibitor concentrations are expressed as weight percents with respect to the weight of dry cement in the mix.

† 'NaB' = Sodium benzoate.

‡ These points are less well defined.

adsorption sites at relatively low chloride concentrations, thereby allowing for the subsequent incorporation of chromium into the anodic film.

Plots of the progression of the current densities at 0 V with cycle number (Fig. 7) clearly illustrate some further points worth noting. First, repeated cycling clearly is required to fully ascertain the relative effects of NaCl additions. Second, the current densities in the normally passive potential regime increases more sharply with increasing NaCl concentration with 1.6% sodium benzoate than with 1.7% potassium chromate.

4. Summary

The results are summarized in Table 2, which shows the effect of the admixed inhibitors on the current at 0 V after 200 cycles for several external NaCl concentrations. The efficacy of the cyclic voltammetric method for the evaluation of corrosion inhibitors for reinforced concrete is clear from Table 2. Attack by chlorides on the passive films is marked by sharp increases in the currents. The function of the inhibitors is to maintain the films in a condition similar to that observed without sodium chloride (first column in Table 2). The zig-zag line in Table 2 separates regions in which low current densities of about 1 mA cm⁻² or less indicate the presence of stable passive films, from regions in which high current densities indicate disruption of the films by the NaCl. Additions of 1.0% and 0.6% sodium nitrite, 1.6% sodium benzoate, and 1.7% potassium chromate pro-

tect the passive films from external NaCl concentrations of up to about 1.6 M, 0.4 M, 0.2 M and 0.1 M, respectively. The inhibitors are less effective at NaCl concentrations higher than the limits stated above, but still have some beneficial effect in the cases that were investigated.

Acknowledgement

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