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Corrosion inhibitors in concrete
Part II: Effect on chloride threshold values for corrosion of steel in synthetic pore solutions

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Abstract

The effectiveness of four commercially available corrosion inhibitors for use in cement-based materials was assessed in synthetic concrete pore solution containing chlorides. The effect of the surface topography of the sample and the composition of the pore solution was also assessed. Although in a parallel study the inhibitors were observed to delay the onset of corrosion, in these tests in pore solution they were found to be ineffective in increasing the chloride threshold value of reinforcing steel exposed to chlorides and had little influence on the progression of corrosion once initiated. This suggests that chemical reactions within the cement phase are responsible for the observed results. Metallographically polished samples proved the most resistant to corrosion regardless of electrolyte composition and samples with all surface finishes exhibited lower resistance in solutions containing only calcium hydroxide than in the higher pH synthetic concrete pore solutions.

Keywords: pH; Corrosion; Electrochemical properties; Pore solution; Inhibitors

1. Introduction

Corrosion of reinforcing steel embedded in concrete is becoming a significant structural and financial problem. A large proportion of reinforcement corrosion within North America is a direct result of the use of deicing salts during winter months to maintain ice-free highways and roads. This has led to an increased incidence of potholes, spalls, and delaminations of concrete in reinforced highway structures such as bridge decks, parking garages, and support pillars of various structures. Also affected by salt-induced corrosion are coastal structures that are exposed to seawater. As a consequence, a large effort is being made to find a means of delaying the onset of rebar corrosion. One such method is the use of chemical admixtures to act as "corrosion inhibitors."

This paper describes one portion of a four-part project, the objectives of which were to evaluate the effectiveness of those corrosion inhibitors available commercially at the onset of the project, to determine the factors influencing their effectiveness, and, where possible, to determine the mechanism of inhibition and whether or not the admixtures are consumed in the process of providing corrosion inhibition. Possible mechanisms of corrosion inhibition, as they apply to steel in concrete, have been described in Part 1 [1]. In practice, the inhibitor can delay the onset of corrosion (a) by reducing the rate of ingress of chlorides, by increasing the chemical binding of chlorides, or by raising the chloride threshold value for corrosion initiation, and/or (b) by reducing the rate of corrosion once it is initiated. Six corrosion inhibitors were identified as being available commercially and their manufacturers were invited to supply samples of their inhibitors for testing.

One manufacturer declined and, after examination of the constituents of a second product, it was decided not to include it in the investigation. Thus four products, two calcium nitrite-based, designated CN(1) and CN(2), and two organic compounds, designated ORG(1) and ORG(2), were investigated. The investigation was carried out in three parts. The first part reported here involves studies of the electrochemical behaviour of steel in synthetic concrete pore solutions to determine the chloride threshold values and subsequent rates of corrosion and whether or not the inhibitor was "consumed" in the process of providing inhibition and, thus, would lose its effectiveness over time. While all inhibitors have been shown to be effective in delaying

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the onset of corrosion, it was believed necessary to identify the mechanism in order to ascertain the long-term effects. The second study measured the time to corrosion initiation and subsequent corrosion rates of steel in mortar and in concrete and is reported separately [2]. Finally, the effect of these inhibitors on the physical and mechanical properties of the concrete was evaluated [3].

2. Experimental

2.1. Chemical identification of the inhibitors

All four inhibitors were supplied as solutions and Materials Safety Data Sheets (MSDS) were provided with each product. From the information given in the MSDS, it was assumed that the two nitrite inhibitors were essentially the same product but because of differences in the recommended dosages and subsequently observed effectiveness of these products, samples of each were oven-dried and the residue analyzed by energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The manufacturer's identification of the ORG(1) inhibitor as an amine/ester mixture was accepted as sufficient for the purposes of this project and the solution was not analyzed. The identity of the ORG(2) inhibitor could not be obtained from the manufacturer or the Materials Safety Data Sheet supplied with the product but the inhibitor was gelatinous in consistency, brown, and had the distinct odour of ammonia.

2.2. Electrochemical measurements

To determine the amount of chloride that could be tolerated by the steel without initiating active corrosion (the chloride threshold value), the following procedure was performed. Samples of reinforcing black steel bar were mounted in "bakelite" and polished metallographically to a 0.05-μm finish. Three samples were then placed in each of 15 electrochemical cells and immersed in a synthetic pore solution (a saturated calcium hydroxide solution containing NaOH, KOH, and excess $Ca(OH)_2$ with a pH of $\sim$13.3) with the recommended dose of inhibitor. For each of the four inhibitors and a control solution, there were three cells, one of which was exposed to the atmosphere (designated as naturally aerated). The other two cells were deaerated and oxygenated by bubbling nitrogen and oxygen, respectively, through the solution.

A cyclic polarization curve was obtained for each steel sample by scanning the potential at a rate of 1 mV/s and measuring the corresponding current flowing between the sample and the stainless steel counter electrode. Sodium chloride was then added to the solution providing 1% Cl^- by mass of solution and the system was allowed to stabilize for at least 1 week. A polarization curve was obtained at the end of this period and the pH of each solution was measured. The salt additions, stabilization periods, and polarization curves were repeated up to a total of 10% Cl^-. This concentration would be equivalent to 0.5% Cl^- by weight of cement assuming a water:cement ratio of 0.45 and complete hydration is achieved.

To determine the effects of surface finish of the steel and the pH of the solution on the chloride threshold values and corrosion rate, three types of specimens were tested in the synthetic pore solution of pH $\sim$13.3 and, to simulate a large number of reports in the literature, in filtered, saturated calcium hydroxide solution of pH $\sim$12.5; both solutions contained the inhibitor CN(1) at a dosage of 0.1% $Ca(NO_2)_2$ by weight. One type of specimen was mounted in bakelite and polished as in the experiments described above, the second was a 20-mm length of carbon steel bar that was ground with 600 grit paper and degreased, while the third specimen was a 20-mm length of deformed reinforcing steel that was simply degreased, leaving the mill scale intact (see Fig. 1).

The possible consumption of the inhibitors was investigated by preparing two containers of synthetic pore solutions for each inhibitor, one without chlorides and one containing 6% Cl^- as NaCl. The same known mass of steel wool was introduced into each container to provide a large surface area (approximately 1200 cm^2) of steel for the corrosion process. After 9 months of exposure to the steel wool, the solutions were used as electrolyte for polarization curves determined for 20-mm lengths of degreased deformed rebar. Control measurements were made in fresh solutions of the same initial compositions.

3. Results

3.1. Inhibitor properties

All the inhibitor admixtures except ORG(2) were sufficiently soluble to obtain a uniform mix. Even when mixed with warm water, this inhibitor proved impossible to disperse in solution.

When vacuum oven-dried, the two nitrite compounds left residues that were very different in appearance: CN(1) was white and obviously crystalline, whereas CN(2) was cream-coloured with a globular appearance giving the impression that it contained some organic matter. Analysis of the two residues by EDS with a light element detector in an environ-

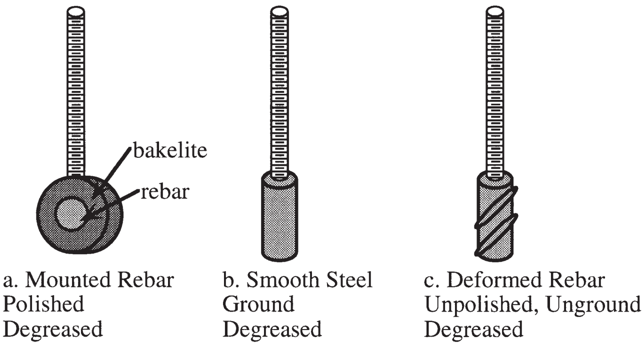

Fig. 1. Schematic representation of sample surfaces.

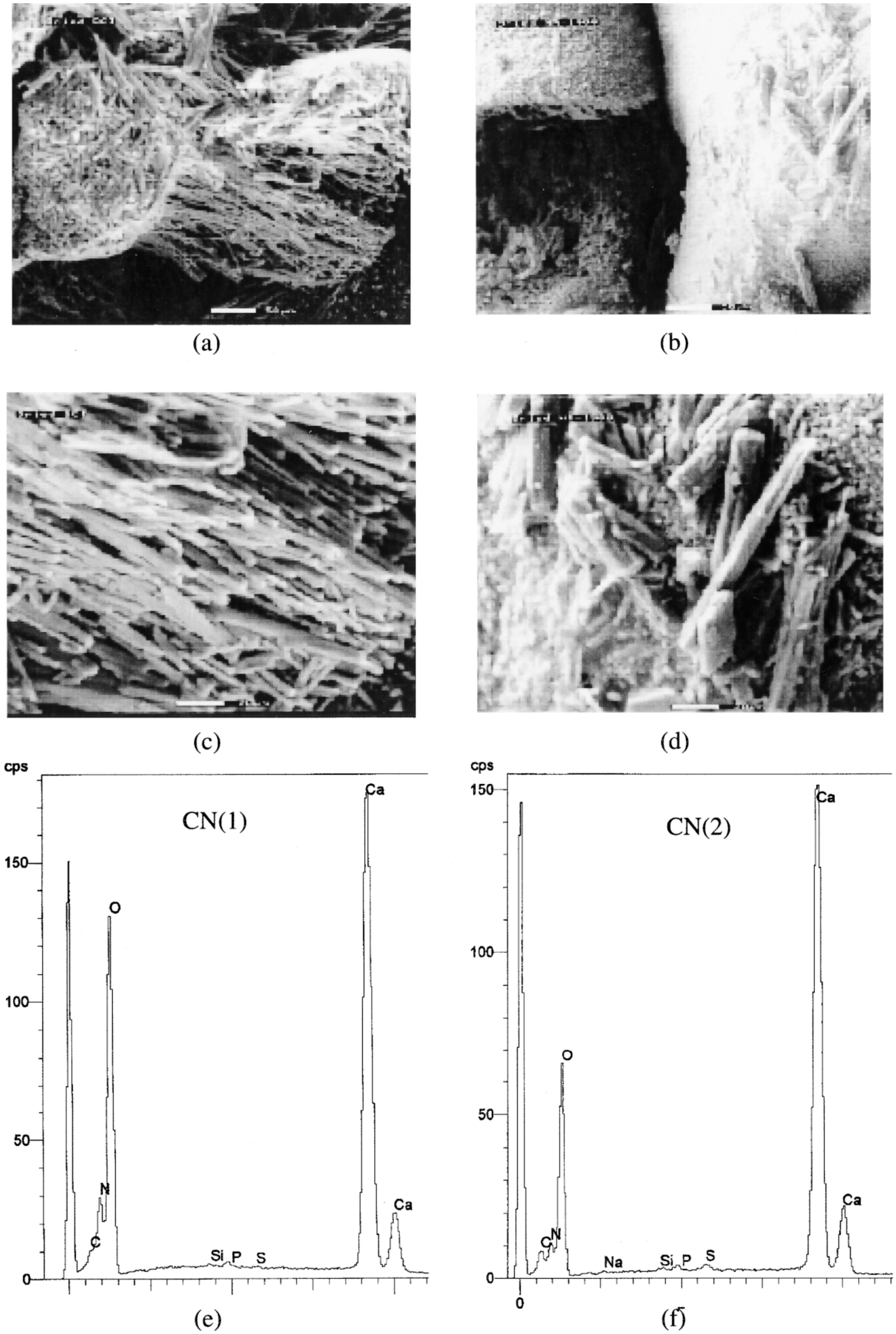

Fig. 2. ESEM micrographs and EDS spectra. (a), (c), and (e): CN(1); (b), (d), and (f): CN(2).

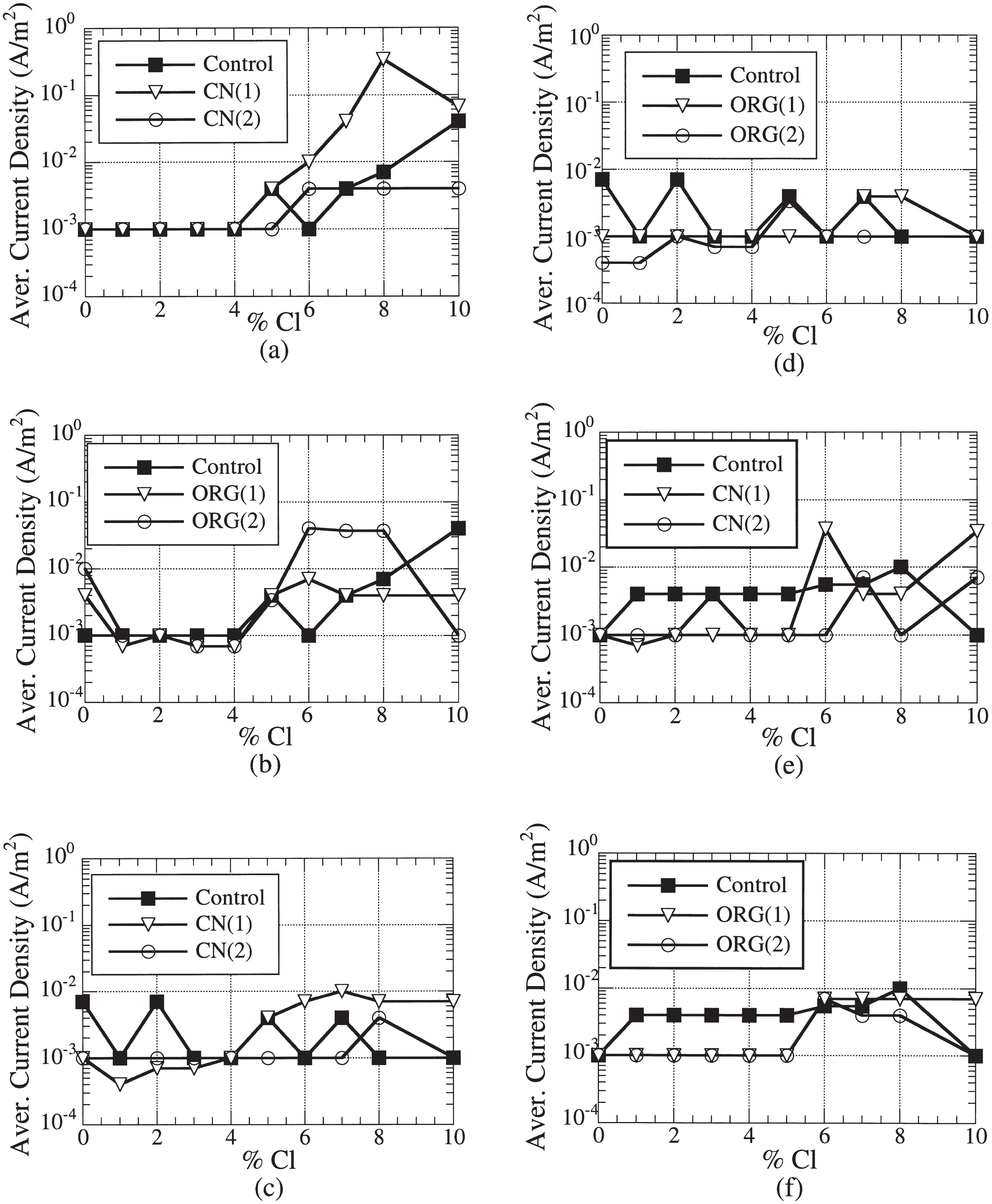

Fig. 3. Average current density vs. chloride concentration. (a) and (b): Naturally aerated states; (c) and (d): deaerated states; (e) and (f): oxygenated states.

mental scanning electron microscope (ESEM) gave no evidence of elements other than calcium, nitrogen, and oxygen and XRD showed only peaks corresponding to $Ca(NO_2)_2$, as shown in Fig. 2. It must be concluded, therefore, that any organic or other matter in the calcium nitrite inhibitors is present in quantities below the detection limit of these two techniques.

3.2. Electrochemical measurements

Figs. 3a–f display the average corrosion current densities vs. chloride content calculated from Tafel extrapolations of cyclic polarization curves for samples immersed in both inhibited and control solutions, naturally aerated, deaerated, and oxygenated. It should be noted that the values of corrosion current densities are only approximate as the polarization curves did not always exhibit clear Tafel regions. As expected, the lowest values were observed in the deaerated state, a consequence of the stifling of the cathodic reaction due to the lack of oxygen in the system. Current density values for samples immersed in the control solution also showed the greatest instability in this state, again a result of the difficulty in establishing and maintaining a homogeneous passive layer due to the lack of oxygen. The highest values were noted in the naturally aerated state, possibly a result of some degree of carbonation of the solutions. In all three states, inhibitors proved most effective at lower chloride levels ($<5\%$ Cl^-), displaying current densities comparable or lower than those exhibited by control samples. However, the inhibitors were found to be essentially ineffective at increasing the chloride threshold value and in the majority of cases, samples immersed in inhibited solutions displayed signs of passive film breakdown at lower Cl^- contents than samples exposed to control solutions.

Fig. 4 gives the measured pH values of all five solutions in the naturally aerated state. Values observed here were typical of those seen in all three states. Solutions containing CN(1) consistently gave pH values of up to one pH unit lower than its counterparts and the control solution, regardless of aeration state. At this time, the mechanism behind this drop is undetermined. However, it was noted that immediately upon adding the CN(1) inhibitor, a massive amount of a white precipitate formed. This precipitate was analyzed using EDS and found to be predominately calcium and oxygen, suggesting that it is most likely $Ca(OH)_2$.

Fig. 5 gives the cyclic polarization curves generated at a chloride level of 8.5% Cl^- in synthetic concrete pore solution of the polished, deformed, and smooth samples. The highly polished sample generally gave current density values two orders of magnitude lower than the deformed or smooth samples. This type of behaviour was evident at most chloride levels, as seen in Fig. 6. The smooth sample was the first to exhibit pitting corrosion at 2% Cl^-, followed by the deformed sample at 7% Cl^-; the polished sample never succumbed to localized attack. Fluctuations in current density are associated with the occurrence of pitting in the sample, followed by repassivation of the sample surface. Samples in the filtered lime water followed the sample corrosion sequence; that is, the smooth sample showed signs of localized corrosion first, followed by the deformed and polished samples.

Fig. 7 compares the cyclic polarization curves for polished samples in pore solution and filtered lime water, while Fig. 8 compares current density values at various chloride levels of the smooth samples in both solutions with each solution containing 0.1% $Ca(NO_2)_2$ by weight. With increasing chloride content, the samples in the filtered lime water consistently gave higher current density values than their counterparts in the pore solution. Furthermore, samples in lime water appeared more susceptible to localized corrosion (pitting at lower chloride levels) and did not exhibit any repassivation behaviour once corrosion was initiated.

With the exception of CN(2), there appeared to be little difference between the average corrosion current densities

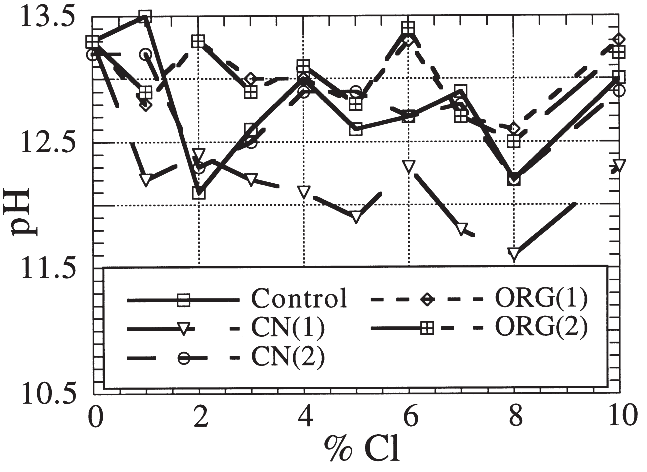

Fig. 4. pH measurements of synthetic concrete pore solutions in naturally aerated states.

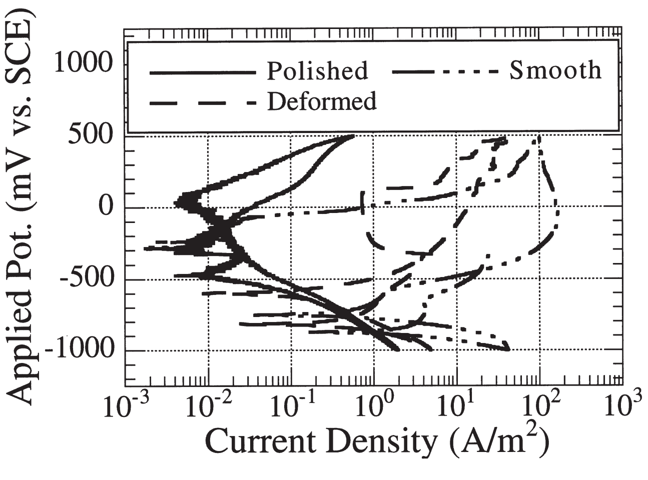

Fig. 5. Cyclic polarization curves of surface variant samples at 8.5% Cl^- in synthetic concrete pore solutions.

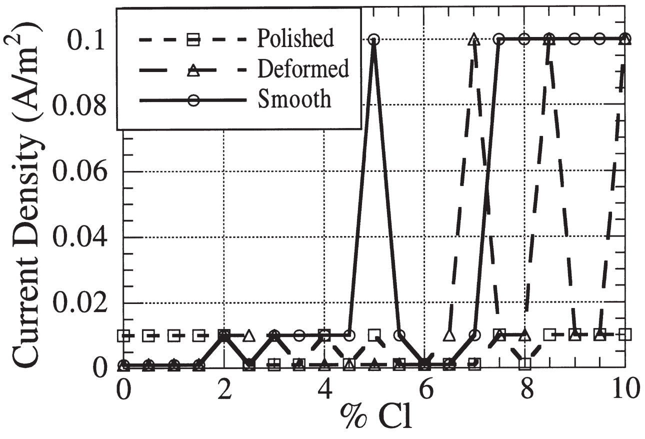

Fig. 6. Current density values for surface variant samples in synthetic concrete pore solutions.

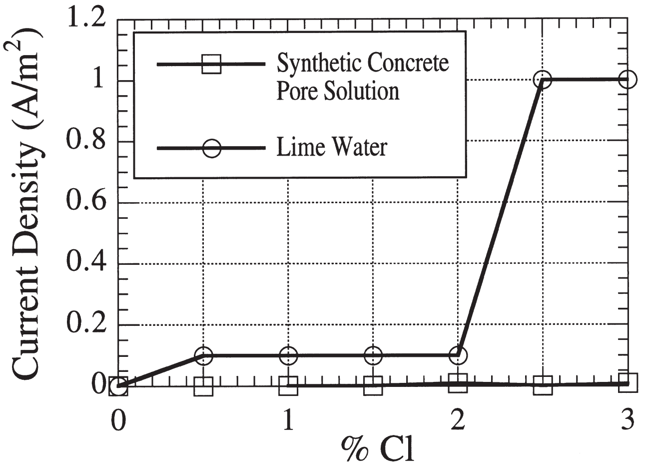

Fig. 8. Current density values of smooth samples in synthetic pore and lime water solutions.

of samples in unaged and aged solutions containing 6% Cl^-. Repassivation of samples was evident as current densities generally decreased when measured a week after the initial evaluation. Table 1 gives the pH values of aged solutions without chlorides and aged and unaged solutions containing 6% Cl^-. As observed previously, the solution containing CN(1) experienced a more significant drop in pH than the other inhibited solutions. The same observation is seen in unaged and aged solutions containing 6% Cl^-. Hence, any pH drop associated with solutions containing CN(1) can be ruled as a consequence of the constituents of the inhibitor and is not associated with the addition of chlorides.

4. Discussion

Although inhibitors have been found to delay the onset of corrosion of steel embedded in mortar or concrete [2], they were all found to be ineffective at preventing corrosion of steel in synthetic pore solution and did not increase the chloride threshold value for the steel in this study. All inhibitors were most effective at lower chlorides levels, decreasing passive corrosion rates to values slightly lower than those exhibited by control samples. Once film breakdown occurred (most often below chloride levels of breakdown in control solutions), they were incapable of reestablishing passivity with increasing chloride concentration. There also appeared to be no consumption of any inhibitor.

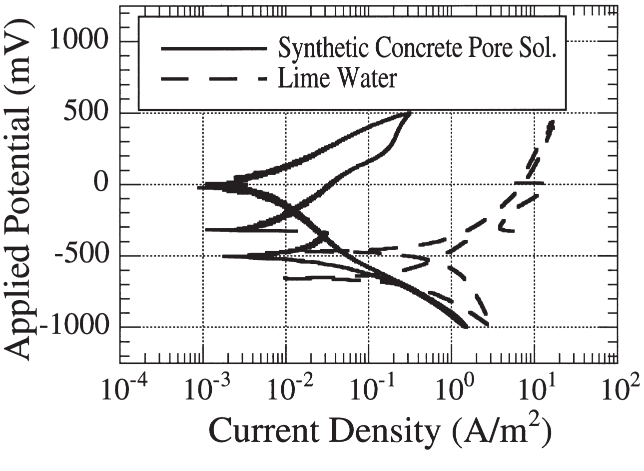

Fig. 7. Cyclic polarization curves of polished samples at 3% Cl^- in synthetic pore and lime water solutions.

The most surprising behaviour was illustrated by CN(1). Samples immersed in solutions containing this inhibitor had the highest incidences of pitting corrosion accompanied by higher current density values. Samples also had more difficulty repassivating at higher chloride levels. This behaviour is most likely attributed to the lower pH values observed in solutions containing this inhibitor. These results, however, do not support the proposed mechanism for nitrite inhibition [4,5], as shown in Eq. (1):

$$\begin{aligned}&2Fe^{2+} + 2OH^- + 2NO_2^- \rightarrow 2NO\uparrow + Fe_2O_3 + H_2O + \\ &\quad Fe^{2+} + OH^- + NO_2^- \rightarrow NO\uparrow + \gamma - FeOOH \qquad (1)\end{aligned}$$

From these equations, it was suggested that a more coherent, homogeneous passive film forms due to nitrite acting as a catalyst for film formation; however, no apparent film enhancement was observed in synthetic pore solutions.

In contrast, CN(1) was found to be the most effective inhibitor in delaying corrosion initiation in concrete and mor-

Table 1
pH values of aged solutions without $C1^-$ and aged and unaged solutions containing 6% $C1^-$

	Aged without $C1^-$	Aged 6% $C1^-$	Unaged 6% $C1^-$
CN(1)	12.0	12.1	12.3
CN(2)	12.8	12.7	13.1
ORG(1)	12.8	12.8	13.1
ORG(2)	12.9	12.7	13.1

tar samples [2], which indicates that an alternative mechanism is responsible for this behaviour. It has been reported that a decrease in the pH increases the chloride-binding capacity of concrete [6–9]. As a pH decrease was observed with use of CN(1) in synthetic pore solution, one possible mechanism is that an increase in chloride binding in concrete or mortar decreases the number of free chlorides available for film breakdown—an effect that cannot, of course, be observed in synthetic pore solutions.

White, flaky deposits were also observed on the surfaces of samples immersed in CN(1)-containing pore solutions. Similar observations have been reported by others [10,11], and this deposit is believed to be $CaCO_3$ (calcium carbonate).

The surface topography and composition of the electrolyte of the sample can have a significant effect on the both the chloride threshold value and corrosion behaviour of otherwise identical samples. Highly polished samples were found to withstand higher chloride levels than nonpolished samples, as did all samples immersed in synthetic pore solution ($pH \sim 13.3$) compared with those in filtered lime water ($pH \sim 12.5$) with all surface finishes.

5. Conclusions

Results obtained from tests performed in synthetic pore solution were contradictory to those reported in previous studies. All inhibitors were unsuccessful in increasing the chloride threshold value of steel exposed to chlorides and all had a minimal effect on corrosion rates once corrosion was initiated. CN(1) was found to be the most ineffective in pore solution but the most effective in concrete and mortar. It must be assumed that the corrosion-inhibiting mechanism is more dependent on chemical interaction with the cement/concrete than with reinforcing steel. As such, this hypothesis warrants further investigation.

Surface topography and electrolyte composition were found to have a significant influence on the corrosion behaviour of steel reinforcement. These findings are important in that they question the use of metallographically polished samples and of $Ca(OH)_2$ solutions when evaluating corrosion in concrete. Additionally, the surface topography and the electrolyte composition must be considered when comparing results among studies.

Acknowledgments

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