

Electrochemical Studies of Rebar Corrosion and Inhibition in Simulated Pore Solution

L. A. WEBSTER, T. OSIROFF, J. G. DILLARD, J. O. GLANVILLE, AND
R. E. WEYERS

Measurements of electrochemical potential have been used to evaluate relative inhibitor effectiveness in controlling the corrosion of rebar in chloride-doped simulated pore solution. The rates at which inhibitors bring the corrosion potential into the passive region provide a comparison of inhibitor effectiveness and serve as a screening test. Degreased rebar specimens were immersed in aerated solutions and their electrode potential was measured against a standard calomel electrode over several months. Measurements were made of corrosion potentials as a function of time both in the presence and in the absence of inhibitors and at various inhibitor concentrations. Results of the test procedure are described and comparisons are made with parallel tests of inhibition using visual methods and surface analytical techniques.

Spalling has been recognized as a major contributing factor to the deterioration of reinforced concrete structures (1,2). Spalling occurs when an iron oxide (or rust) on the steel reinforcement (rebar) occupies a volume greater than the metallic iron from which it is formed (3). Rebar corrosion occurs at an accelerated rate in concrete structures exposed to deicing salts or sea water (3,4). Typically, chloride-induced corrosion takes place at local points along the length of the bar, forming severe pitting (3-5). Thus, the load-carrying capacity of the bar is decreased at that point and, along with spalling, leads to gross deterioration of the concrete structure.

The treatment of corroded structures with inhibitors is a possible solution to the corrosion problem (4,6-8). In order to identify, evaluate, and compare the corrosion protection afforded by various inhibitors, rapid and nondestructive techniques are necessary (9-11). In this study, the measurement of electrochemical potential has been examined as a method of quickly evaluating relative inhibitor effectiveness for rebar specimens immersed in simulated pore solution. Rebar samples whose surfaces had been cleaned to remove surface contaminants and rebar specimens whose surfaces had been prepared to contain chloride-induced corrosion products were exposed to simulated pore solutions containing chloride ions and inhibitors. Electrochemical potential measurements were made as a function of time both in the presence and in the absence of inhibitors and at various concentrations. Materials

that are found to be effective inhibitors under these experimental test conditions would be candidates for treatment of bridge decks without removal of concrete. The electrochemical measurement results are presented and comparisons are made with the findings from corrosion studies in which the effectiveness of inhibitors was determined using surface analytical techniques and visual inspection procedures (Dillard et al. and Dressman et al., companion papers in this Record).

EXPERIMENTAL

Electrochemical measurements were made to determine the corrosion potential of rebar immersed in test solutions. For all experiments, a standard calomel electrode was used as the reference electrode. The potentials were measured using a Fisher Accumet Model 910 pH/voltmeter and Fisher calomel electrode. ASTM Standard C876-87 relates potential ranges [relative to a copper sulfate electrode (CSE)] to the probability of corrosion. These values were converted from a CSE scale to a saturated calomel electrode (SCE) scale. The potential ranges (relative to SCE) and the probabilities are presented in Table 1.

Cylindrical reinforcement steel rods 6 ft long and 1/2 in. in diameter were obtained from Roanoke Electric Steel Co., Roanoke, Virginia. The composition of this material was formulated to be similar to that used 20 to 30 years ago. Bulk and surface analyses (Dillard et al., a companion paper in this Record) of the rods are presented in Table 2. Test specimens were prepared by cutting the rods into 3 1/2-in. segments. One end of each segment was drilled and tapped to permit making electrical connections. The segments were cleaned in hexane and allowed to dry. Tru-Bond TB-700 epoxy paste was used to cover the wire connections. The cut end of the rebar was also covered with epoxy paste.

These cylindrical rebar samples were immersed in simulated pore solution, pH = 13.9 ± 0.1 [KOH (0.600 M); NaOH (0.300 M); saturated with $\text{Ca}(\text{OH})_2$], containing NaCl (3.5 wt percent) (control); and pore solution containing NaCl (3.5 wt percent) and the following concentrations of inhibitor: 0.00200, 0.0100, 0.0500, and 0.100 M. The inhibitors studied were sodium nitrite (NaNO_2), sodium monofluorophosphate ($\text{Na}_2\text{PO}_3\text{F}$) (MFP), and sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$). The test solutions were aerated for 2 hr before rebar immersion. Samples of rebar were maintained at 60°C. In order to min-

L. A. Webster, T. Osiroff, J. G. Dillard, and J. O. Glanville, Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Va. 24061-0212. R. E. Weyers, Department of Civil Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Va. 24061-0105.

TABLE 1 CORROSION SCALE (ASTM C876-87)

| Probability of Corrosion | E (corr); SCE Scale |
|--------------------------|----------------------------|
| greater than 90% | more negative than -290 mV |
| uncertain | -140 mV to -290 mV |
| less than 10% | more positive than -140 mV |

imize evaporation of solution, the bottles were covered. The test solutions were replaced every 2 to 3 weeks to maintain proper aeration, volume, concentration, and pH. Potential measurements were taken at regular time intervals.

Flat stock steel (A36, 1 in. wide \times $\frac{1}{4}$ in. thick), with a composition similar to that of cylindrical rebar, was cut from material obtained from Roanoke Electric Steel Co., Roanoke, Virginia. The bulk and surface analyses for this material are presented in Table 3. The bars were drilled and tapped in one end to enable electrical connection. Bars were cleaned in hexane and allowed to dry. Additional bars were cleaned in a 1:1 (v/v) solution of concentrated sulfuric acid and deionized water. The latter bars were also scrubbed with a ScotchBrite pad, rinsed with deionized water, allowed to dry, cleaned with hexane, and allowed to dry. Two coats of Nybco epoxy paint were applied to each end of the rebar and allowed to cure according to the manufacturer's specifications.

These flat stock rebar specimens were immersed in simulated pore solution, pore solution containing NaCl (3.5 wt percent), pore solution containing NaCl (3.5 wt percent) and NaNO_2 (0.300 M), and pore solution containing NaCl (3.5 wt percent) and NaNO_2 (0.670 M). The test solutions were aerated for 2 hr before use. Samples were maintained in solution at 60°C and the samples bottles were covered to prevent evaporation of solution. The test solutions were replaced every

2 weeks. Potential measurements were taken at regular time intervals.

In experiments in which corroded rebar samples were prepared to investigate the effectiveness of compounds to inhibit active corrosion, flat stock rebar was maintained at 60°C in a solution of deionized water containing NaCl (10 wt percent) for a time sufficient to achieve an active corrosion potential. These corroded bars were then placed in the test solutions: pore solution, pore solution containing NaCl (3.5 wt percent), and pore solution containing NaCl (3.5 wt percent), and sodium tetraborate inhibitor at the concentrations 0.00200, 0.0100, 0.0500, and 0.100 M. The solutions were aerated for 2 hr before rebar immersion. The test samples were prepared in duplicate and maintained at 60°C. The test solutions were replaced every 2 weeks. Potential measurements were taken several times weekly and then at selected intervals.

In studies to evaluate the effectiveness of inhibitors toward active corrosion at different pH values, flat stock rebar specimens were cleaned in hexane, dried, and placed in aerated deionized water containing NaCl (10 wt percent) at pH 8.5 to 8.6 and 60°C for a time sufficient to obtain an active corrosion potential. The bars were subsequently placed in the solutions: NaCl (10 wt percent) (control), and NaCl (10 wt percent) containing 0.100 M inhibitor. The inhibitors were sodium nitrite, sodium tetraborate, MFP, and tetra-n-butylphosphonium bromide $\{[\text{CH}_3(\text{CH}_2)_3\text{PBr}]\}$. The pH values of the solutions were adjusted to 8, 10, and 12, respectively, with HCl, NaOH, or NaHCO_3 . The samples were maintained at 60°C.

Potential and pH measurements were taken after 1, 3, 6, 9, and 18 days. The solutions were replaced after 18 days. At this time (18 days), the NaCl concentration was decreased to 1.75 wt percent and the inhibitor concentration was increased to 0.600 M, except for the concentration of tetra-n-butylphosphonium bromide, which was maintained at 0.100 M. At

TABLE 2 ESCA ANALYSIS OF REBAR ROD BEFORE AND AFTER HEXANE CLEANING AND MANUFACTURER'S BULK ANALYSIS

| | ESCA Element (atomic percent) | | Bulk Analysis (visible spectroscopic) | |
|-------|----------------------------------|-----------------------|--|----------|
| | as received | after hexane cleaning | mass % | atomic % |
| C | 58.4 | 56.4 | 0.22 | 1.00 |
| O | 28.7 | 31.6 | nd | nd |
| Fe | 3.68 | 4.64 | 97.2 | 95.8 |
| Si | 3.26 | 2.56 | 0.59 | 1.16 |
| Cu | 2.06 | 1.70 | 0.26 | 0.23 |
| N | 1.41 | 1.09 | nd | |
| Na | 0.97 | 0.68 | nd | |
| S | 0.90 | 0.62 | 0.036 | 0.062 |
| Ca | 0.45 | 0.59 | nd | |
| Zn | 0.18 | 0.10 | nd | |
| Al | <0.1 | <0.1 | 0.006 | 0.01 |
| P | <0.1 | <0.1 | 0.018 | 0.032 |
| Mn | nd | nd | 1.00 | 1.00 |
| Cr | nd | nd | 0.50 | 0.52 |
| Ni | nd | nd | 0.11 | 0.10 |
| V | nd | nd | 0.04 | 0.04 |
| Mo | nd | nd | 0.02 | 0.01 |
| Total | 100.0 | 100.0 | 100 | |

ESCA = Electron spectroscopy for chemical analysis - surface composition

nd = not determined

TABLE 3 ESCA ANALYSIS OF REBAR (FLAT) BEFORE CLEANING, AFTER HEXANE CLEANING, AFTER ACID WASHING, AND MANUFACTURER'S BULK ANALYSIS

| | ESCA | | | Bulk Analysis | |
|----|--------------------------|-----------------------|-----------------|-------------------------|----------|
| | Element (atomic percent) | | | (visible spectroscopic) | |
| | as received | after hexane cleaning | after acid wash | mass % | atomic % |
| C | 39.5 | 58.0 | 54.4 | 0.11 | 0.51 |
| O | 45.0 | 28.0 | 25.2 | nd | |
| Fe | 6.67 | 4.09 | 4.17 | 98.0 | 97.5 |
| Si | 5.05 | 1.45 | 1.04 | 0.24 | 0.47 |
| Cu | nd | 0.68 | 0.07 | 0.31 | 0.27 |
| N | 0.82 | 2.34 | 2.32 | nd | |
| Na | 0.79 | 2.21 | 0.51 | nd | |
| S | 1.37 | 0.99 | 1.01 | 0.036 | 0.062 |
| Ca | 0.76 | 0.29 | 0.23 | nd | |
| Zn | nd | nd | 0.16 | nd | |
| Al | nd | nd | 2.25 | 0.004 | 0.008 |
| P | <0.1 | 0.39 | <0.1 | 0.022 | 0.004 |
| Mn | <0.1 | nd | 8.74 | 0.65 | 0.66 |
| Cr | nd | nd | nd | 0.25 | 0.27 |
| Ni | nd | nd | nd | 0.26 | 0.25 |
| V | nd | nd | nd | 0.003 | 0.003 |
| Mo | nd | nd | nd | 0.05 | 0.29 |

ESCA = Electron spectroscopy for chemical analysis; nd = not determined

this time (18 days), additional rebar specimens and solutions [NaCl (1.75 wt percent) containing 0.600 M inhibitor] were prepared to permit studies at pH 12.5 and 13.0. Potential and pH measurements were made after 3 and 6 days at the new conditions, and the pH value of each solution was adjusted to maintain a fixed pH value.

RESULTS AND DISCUSSION

The first series of experiments was carried out using rebar to determine the manner in which the electrochemical potential changed for specimens immersed in chloride-containing pore solution containing inhibitor anions that are known to be effective agents, namely nitrite (9-11) and monofluorophosphate (Domtar Corp., Mississauga, Ontario) salts, and to compare the results with other potential inhibitors, e.g., borate and alkylphosphonium salts. The potential measurement results for cylindrical rebar, maintained in chloride-containing pore solution (control) or in chloride-containing pore solution including the inhibitors sodium nitrite, MFP, or sodium tetraborate, each at 0.0100 M concentrations, are shown in Figure 1. At the beginning of the experiments, the measured potential for all specimens is approximately -450 mvolt, a potential that indicates active corrosion.

As time passes, the potential for the control sample remains in the active corrosion region. In contrast, the potentials for rebar in solutions containing inhibitors become more positive with time and reach values of about -312 mvolt, nitrite; -315 mvolt, MFP; -282 mvolt, tetraborate; compared with -420 mvolt, control; after 16 weeks. The important result is that these three inhibitors are effective in making the corrosion potential more positive. Under the experimental conditions, the time at which the potential begins to become more positive

(see Figure 1) is nitrite, 12 weeks; MFP, 10 weeks; and borate, 4 weeks.

For studies in which the concentration of inhibitor was greater than 0.010 M, the respective maximum values for the potentials were not greater than those measured for the 0.0100 M solutions, but the potentials began to increase at shorter times. The times at which the potential increased at concentrations of inhibitor other than 0.0100 M were also in the relative order borate < MFP < nitrite.

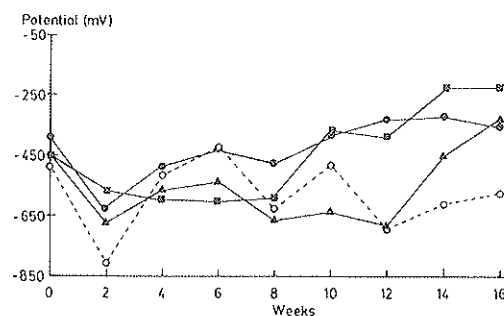


FIGURE 1 Electrochemical potential (SCE) as a function of time for hexane-cleaned cylindrical rebar immersed in chloride-containing pore solution [NaCl (3.5 wt%)], and in chloride-containing pore solution [NaCl (3.5 wt%) and 0.0100 M inhibitor solutions.

○—Control solution: NaCl (3.5 wt%) in pore solution
 Test solutions: NaCl (3.5 wt%) in pore solution containing 0.0100 M inhibitor.
 ▲—Sodium nitrite (NaNO_2)
 ■—Sodium monofluorophosphate ($\text{Na}_2\text{PO}_3\text{F}$)
 ●—Sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$)

The preceding discussion indicates that potential measurements can be used to screen potential inhibitors; however, there are aspects of the approach that are undesirable for a rapid screening test; the effect of inhibitors at concentrations less than 0.0100 M is revealed only after several weeks into the test and if there is significant variation (± 50 mV) in the measured potential from week to week. Furthermore, over this period of time complications were introduced by deterioration of rebar under the epoxy coating, and by degradation of the electrical connections and the epoxy that covers them. It is likely that chemical heterogeneity among the rebar specimens accounts for the variability in potential measurements.

In an effort to combat these problems, A36 flat rebar was used in all subsequent experiments and the method of making connections was modified. To determine the electrochemical behavior of the flat stock material, experiments were carried out (a) to determine whether flat stock rebar exhibited less variability in potential measurements than cylindrical rebar; (b) to examine the influence of an effective inhibitor, sodium nitrite, at selected concentrations, on electrochemical potential; and (c) to determine whether the method of cleaning (acid-washing plus cleaning in hexane compared with cleaning only in hexane) influenced the potential measurements using flat stock material.

That flat stock rebar (cleaned in acid and washed in hexane) exhibited less variability in potential is evident from the plot of potential (Figure 2) as a function of time for rebar immersed in pore solution containing no chloride. The effect of inhibitor on electrochemical potential is also shown in Figure 2. The potential for rebar maintained in chloride-containing pore solution containing NaNO_2 (0.300 M) becomes more negative during the first 2 weeks of immersion, indicating that severe corrosion occurs within 2 weeks of initiating the test. However, the potential increases for measurement taken at 4 weeks and continues to increase during the 12-week test, approaching a potential characteristic of reduced corrosion. The effect of increased NaNO_2 concentration is also shown in Figure 2, in which more positive potentials are obtained in a shorter

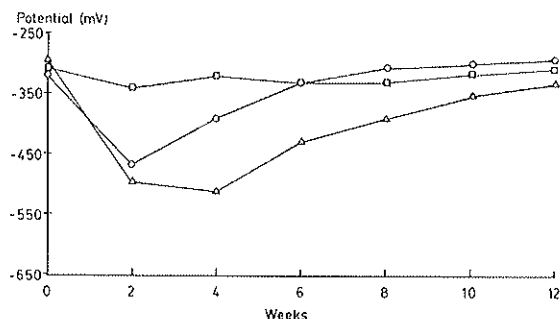


FIGURE 2 Electrochemical potential (SCE) as a function of time for acid-washed, hexane-cleaned flat stock rebar immersed in pore solution, and in chloride-containing pore solution [NaCl (3.5 wt%)] and containing NaNO_2 (0.300 and 0.670 M).

□—Pore solution
 △—Chloride-containing pore solution— NaNO_2 (0.300 M)
 ○—Chloride-containing pore solution— NaNO_2 (0.670 M)

time for the more concentrated inhibitor solution. Although not shown in the figure, the magnitude of the measured potential and the change with time for rebar cleaned only in cyclohexane was equivalent to that for the acid-cleaned, hexane-washed rebar.

The principal results from these measurements with flat stock rebar are as follows: (a) flat stock rebar gives less variability in potential measurements than cylindrical rebar, (b) the method of rebar cleaning does not appear to influence the measured potential, (c) the higher concentration (0.670 M) of sodium nitrite produces a slightly more positive potential than that measured for sodium nitrite (0.300 M), and (d) the time to recovery of a corroded rebar surface is more rapid for more concentrated solutions.

Once it was demonstrated that measurement of electrode potential could be used to evaluate the performance of a given inhibitor, the change of potential for rebar immersed in sodium tetraborate, a potentially effective inhibitor, could be examined. Corroded A36 flat rebar specimens were immersed in pore solution containing NaCl (3.5 wt percent) and sodium tetraborate (0.00200, 0.0100, 0.0500, and 0.100 M). The potentials, measured as a function of time, are shown in Figure 3 for the borate (0.0100 M) solution. The variation of potential with time for rebar in other concentrations of borate was similar to that shown in Figure 3. Also plotted in Figure 3 is the variation in potential for a flat rebar sample immersed in pore solution containing NaCl (3.5 wt percent).

The potentials for the specimens maintained in the chloride-containing pore solution plus borate increased dramatically after only 12 hr in the test solution, whereas the potential for

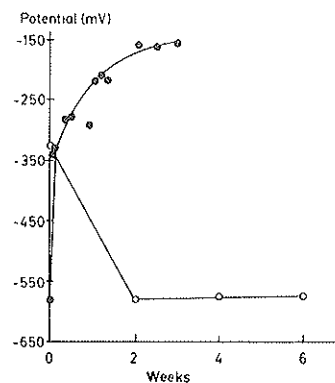


FIGURE 3 Electrochemical potential (SCE) as a function of time for acid-washed, hexane-cleaned flat stock rebar immersed in chloride-containing pore solution [NaCl (3.5 wt%)], and for corroded flat stock rebar immersed in chloride-containing pore solution [NaCl (3.5 wt%)] and 0.0100 M $\text{Na}_2\text{B}_4\text{O}_7$.

○—Chloride-containing pore solution
 ●—Corroded rebar in chloride-containing pore solution— $\text{Na}_2\text{B}_4\text{O}_7$ (0.0100 M)

rebar in the solution containing no borate remained in the active corrosion region. By the end of the experiments, the potentials for all samples immersed in chloride-containing pore solution *with* borate had increased to values in the range -190 to -160 mvolt. On comparing potentials at different borate concentrations, no significant difference was noted. The potentials for the bars in pore solution containing chloride and no inhibitor remained in the active corrosion region, about -550 mvolt. The findings indicate that the potential for actively corroding rebar specimens can be increased to be in the region corresponding to uncertain probability of corrosion (see Table 1). From the data shown in Figure 3, prolonged immersion of rebar samples in borate inhibitor could eventually result in a potential more positive than -140 mvolt, the region of inactive corrosion, i.e., <10 percent probability of corrosion.

The question of the ability of inhibitors to function at pH values less than highly alkaline was of interest for the situations in which rebar might be exposed to more acidic environmental conditions. Corroded flat rebar samples were immersed in NaCl (10 wt percent) and 0.100 M inhibitor at selected pH values for 18 days and then subsequently placed in NaCl (1.75 wt percent) and 0.600 M inhibitor for additional

time. The results are presented in Table 4. On comparing the control and inhibitor solutions during the first 18 days, there was no substantial difference in potential. In order to permit an evaluation of the performance of the inhibitors, the salt concentration was lowered and the inhibitor content was increased. With decreased salt concentration and increased inhibitor concentration, differences in inhibitor performance were revealed, as presented in Table 4. This procedure enables the parameters of the screening test to be optimized.

The performance of the various inhibitors is indicated by comparing the potential for test specimens maintained in chloride-containing solutions *with* inhibitor to those for control specimens, i.e., rebar immersed in chloride-containing solutions *without* inhibitor. An inhibitor is taken as being effective if the potential, ΔV , is more positive by at least 90 to 100 mvolt when comparing potentials for inhibitor-containing solutions with those for solutions containing no inhibitor. The comparison indicates that borate is ineffective at pH 8; marginally effective at pH values 10, 12, and 12.5; and significantly effective at pH 13. Nitrite is effective at all pH values investigated. MFP is active at the intermediate pH values but is marginally effective at pH 8 and ineffective at pH 13. Tetra-n-butylphosphonium bromide is effective only at pH 13.

TABLE 4 ELECTROCHEMICAL POTENTIAL MEASUREMENTS FROM SCREENING TESTS

| | A | B | del V* | C | del V* |
|-----------------------------------|------|------|--------|------|--------|
| control | | | | | |
| pH 8 | -634 | -486 | | -431 | |
| pH 10 | -649 | -520 | | -508 | |
| pH 12 | -642 | -500 | | -428 | |
| pH 12.5 | -627 | | | -341 | |
| pH 13.0 | -651 | | | -652 | |
| sodium tetraborate | | | | | |
| pH 8 | -628 | -473 | +13 | -442 | -11 |
| pH 10 | -649 | -462 | +58 | -409 | +99 |
| pH 12 | -647 | -424 | +76 | -334 | +94 |
| pH 12.5 | -651 | | | -246 | +95 |
| pH 13.0 | -639 | | | -211 | +441 |
| sodium nitrite | | | | | |
| pH 8 | -645 | -481 | +5 | -27 | +404 |
| pH 10 | -630 | -445 | +75 | -61 | +447 |
| pH 12 | -646 | -406 | +94 | -79 | +349 |
| pH 12.5 | -648 | | | -114 | +227 |
| pH 13.0 | -621 | | | -266 | +386 |
| sodium monofluorophosphate | | | | | |
| pH 8 | -635 | -467 | +19 | -344 | +87 |
| pH 10 | -645 | -452 | +68 | -308 | +200 |
| pH 12 | -636 | -459 | +41 | -290 | +138 |
| pH 12.5 | -635 | | | -161 | +180 |
| pH 13.0 | -647 | | | -619 | +33 |
| tetra-n-butyl phosphonium bromide | | | | | |
| pH 8 | -635 | -482 | +4 | -443 | -12 |
| pH 10 | -632 | -549 | +29 | -502 | +6 |
| pH 12 | -636 | -517 | -17 | -505 | -77 |
| pH 12.5 | -623 | | | -367 | -26 |
| pH 13.0 | -631 | | | -317 | +335 |

* del V = potential of control minus potential of inhibitor under equivalent solution conditions.

A = Potential of corroded specimen before immersion in inhibitor solution.

B = Potential after 18 day immersion in 10(wt)% NaCl including 0.100M inhibitor.

C = Potential after 6 day immersion in 1.75(wt)% NaCl including 0.600M inhibitor of samples from B. (phosphonium bromide = 0.100M)

In summary, sodium nitrite, containing the anion common to other corrosion inhibitors (9–11), performed the best over the wide range of pH values. It produced the highest increase in potential for pH values 8, 10, 12, and 12.5. MFP, another known corrosion inhibitor (Domtar Corp., Mississauga, Ontario), performed second best, except at pH 13.0, where it ranked relatively poorly. Sodium tetraborate exhibited excellent behavior and ranked as the best inhibitor at pH 13.0, which most accurately simulates the macrolevel conditions in concrete.

During the experiments, there were noticeable changes in pH (1 to 2 units) that required addition of reagents to restore the solution to constant pH conditions. For the sodium nitrite solutions, there was a general increase in pH value for initial pH values 8 and 10. This can possibly be attributed to the formation of OH^- anions in solution from hydrolysis involving NO_2^- with H_2O . For MFP solutions, there was a decrease in pH value for solutions at initial pH values of 10 and 12. A possible process to account for this observation is hydrolysis of MFP in solution to produce HF and hydrogen phosphate species. No significant change was noted in the pH value of the borate solutions during the experiments.

COMPARISON OF VISUAL INSPECTION WITH SURFACE ANALYSIS

In related studies using a screening test based on the visual estimation of corrosion (Dressman et al., a companion paper in this Record), it was found that sodium nitrite, MFP, and sodium tetraborate all exhibit good corrosion-inhibiting properties for rebar in chloride-doped pore solution. The twin procedures of visual and electrochemical screening provide complementary results, and together suggest that rapid laboratory screening of candidate inhibitors is a worthwhile endeavor. Surface analysis measurements (Dillard et al., a companion paper in this Record) suggest that sodium tetraborate reacts to form a coating on the rebar surface. This coating could possibly function as a barrier layer to inhibit chloride-induced corrosion, thereby increasing the electrochemical potential values as noted in the present experiments. Surface analysis of MFP-treated rebar suggests that hydrolysis of MFP is a likely cause of the resultant phosphorus-to-fluorine atomic ratio of nonunity on the rebar surface. This idea is supported by the decrease in pH value noted for specimens at initial pH values 10 and 12.

CONCLUSIONS

The effect of corrosion inhibitors for rebar under highly alkaline conditions can be directly studied by electrochemical methods. Specifically, side-by-side measurements of the electrochemical potentials of rebar in chloride-doped pore solutions exhibit the protective effect of added inhibitors compared with uninhibited solutions. The effect is manifested by the corrosion potential becoming progressively more positive over a period of weeks when inhibitor is present, or has been added.

Therefore, controlled electrochemical studies under specified conditions can serve as screening tests for candidate

corrosion inhibitors. This latter conclusion is substantially validated by the fact that known corrosion inhibitors performed well in the test procedure. Sodium nitrite and MFP caused the corrosion potential to become more positive under the selected test conditions. Sodium tetraborate performs similarly—a significant result, because it has recently been demonstrated by visual inspection corrosion evaluation techniques (Dressman et al., a companion paper in this Record) that sodium tetraborate is a promising inhibitor.

Having two complementary screening tests available for studies of candidate inhibitors means that the selection of the most promising materials can be expedited. Thus, sodium tetraborate is a good candidate as a practical corrosion inhibitor for rebar corrosion. The coating-forming properties of sodium tetraborate (Dillard et al., a companion paper in this Record) on rebar may provide the mechanism by which it works. Furthermore, this inhibitor can be expected to diffuse through concrete cover to rebar at depth in a reinforced structure (Dillard et al., a companion paper in this Record).

The present results confirm the well-known fact that corrosion potentials are dependent on the solution pH value. Beyond that, different inhibitors have different relative effectiveness at varying pH values. Thus, sodium nitrite is an effective inhibitor over the pH range 8 to 13. In contrast, sodium tetraborate is most effective at pH 13, and there is some evidence to suggest that it is the best of the tested inhibitors at that pH value.

The precise properties of the rebar, either its configuration or chemical composition, are not critical in comparing inhibitors. Providing side-by-side testing is carried out with all parameters except inhibitor held constant, a fair measure of relative effectiveness can be obtained.

The results demonstrate that corrosion inhibition is a function of the inhibitor concentration. Experiments at higher inhibitor concentrations indicate that the electrochemical potential more rapidly reverts to the voltage range of low corrosion probability.

This work deserves extension to a wide range of inhibitors at various concentrations. Scaled-up tests of promising materials have already been initiated on the basis of the data reported in this work.

ACKNOWLEDGMENTS

Thanks are expressed to Frank Cromer, who helped in the surface analysis measurements; to the National Science Foundation and the Commonwealth of Virginia for surface analysis equipment grants; and to the Strategic Highway Research Program, Project C-103, for support of this work. The authors are grateful to a referee who carefully read and provided valuable comments on this manuscript.

REFERENCES

1. *Durability of Concrete Bridge Decks*. Report 5. Portland Cement Association and U.S. Bureau of Public Roads, 1969, 46 pp.
2. *Durability of Concrete Bridge Decks*. Final Report. Portland Cement Association and U.S. Bureau of Public Roads, 1970, 33 pp.
3. *Corrosion of Reinforcement in Concrete Construction*. (Alan P. Crane, ed.) Ellis Horwood Ltd., Chichester, England, 1983, 437 pp.

4. *Corrosion of Steel in Concrete*. Report of the Technical Committee 60-CSC, RILEM (The International Union of Testing Research Laboratories for Materials Structures), P. Schiessl, ed., Chapman and Hall, London, 1988, 102 pp.
5. K. Tuutti. *Corrosion of Steel in Concrete*. Swedish Cement and Concrete Research Institute, Stockholm, pp. 17–101, 1982.
6. M. G. Fontana and N. D. Greene. *Corrosion Engineering*. McGraw-Hill, New York, 1967, pp. 198–204.
7. H. H. Uhlig and R. W. Revie. *Corrosion and Corrosion Control*. John Wiley, New York, 1985, pp. 263–277.
8. J. M. West. *Electrodeposition and Corrosion Processes*. Van Nostrand-Reinhold, New York, 1971, pp. 138–148.
9. J. T. Lundquist, A. M. Rosenberg, and J. M. Gaidis. Calcium Nitrite as an Inhibitor of Rebar Corrosion in Chloride Containing Concrete. *Materials Performance*, Vol. 18, 1979, pp. 36–40.
10. A. M. Rosenberg and J. M. Gaidis. The Mechanism of Nitrite Inhibition of Chloride Attack on Reinforcing Steel in Alkaline Aqueous Environments. *Materials Performance*, Vol. 18, 1979, pp. 45–48.
11. N. S. Berke and P. Stark. Calcium Nitrite as an Inhibitor: Evaluating and Testing for Corrosion Resistance. *Concrete International: Design and Construction*, Vol. 7, 1985, pp. 42–47.

The opinions, findings, and conclusions herein are those of the authors and not necessarily those of the sponsoring agencies.

Publication of this paper sponsored by Committee on Corrosion.