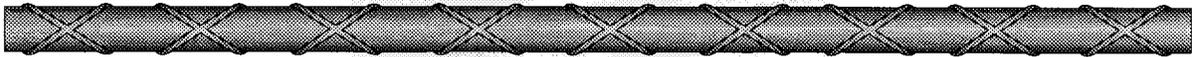
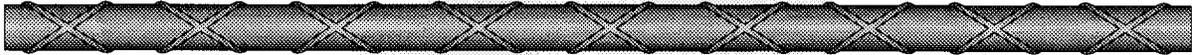


FINAL REPORT

**AN INVESTIGATION  
OF NEW INHIBITORS TO MITIGATE  
REBAR CORROSION IN CONCRETE**



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## ABSTRACT

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## **INTRODUCTION**

The corrosion of reinforcing steel (rebar) in concrete has become one of the most costly and performance-limiting problems facing the nation's infrastructure. More than 50% of the 575,000 bridges in the United States are affected by corrosion, and approximately 20% have been deemed structurally deficient.<sup>1</sup> Rebar corrosion can be mitigated through several approaches. In concrete bridges, the damaged area can be periodically repaired. However, the cost of periodic rehabilitation over the design life of a structure can often exceed the cost of total replacement. Another approach is cathodic protection. Cathodic protection can be very effective but requires long-term maintenance and a continual supply of electrical power or sacrificial anodes, depending on the selected mode.

In the opinion of these investigators, the most practical and economical approach to eliminate or minimize this costly maintenance problem is to use better materials in new construction, which slows both the initiation and growth rates of rebar corrosion. This can be effectively accomplished through the addition of corrosion inhibitors to a quality concrete mix. By combining this preventive approach with providing sufficient concrete cover over the rebars, corrosion problems in a structure will be considerably reduced if not eliminated.

Although hundreds of known chemical compounds can inhibit the corrosion of steel in aqueous environments, only about four are commercially available. One of the more widely used is calcium nitrite, although it has several deficiencies.<sup>2-5</sup> Calcium nitrite is an anodic inhibitor, which means that it polarizes the metal as an anode to develop a protective oxide. This also means that its concentration must be maintained above a critical level. If the concentration falls below this level, the corrosion rate can actually be increased. This is quite possible because of the high water solubility of calcium nitrite. The leaching of calcium nitrite from concrete over time has precluded its use in road structures in Germany and Switzerland.<sup>6-8</sup>

Although there are many documented corrosion inhibitors for steel, only a small number have been seriously examined for use in concrete.<sup>9-27</sup> More recently, the corrosion research community has launched an extensive search for new environmentally compatible inhibitors having a range of solubilities to replace the numerous chromate compounds that have been the mainstay of the inhibitor industry. Thus, the pool of low-solubility inhibitor candidates for concrete application is expanding.

This laboratory recently screened more than 30 compounds to replace chromate pigments in aerospace paints.<sup>28,29</sup> As a pigment, these compounds must have a very low solubility and a high inhibitor efficiency at very low inhibitor concentrations. These are precisely the qualities desired for an inhibitive admixture for concrete. However, to date, these compounds have been extensively screened for application to aluminum substrates, not steel.

## **PURPOSE AND SCOPE**

Concomitant with the need for new and better inhibitors of rebar corrosion is the need for improved and standardized methods for assessing the performance of inhibitive admixtures. At present, there are no universally accepted standard procedures for this assessment. Thus, a secondary but extremely important issue associated with the search for new inhibitors is the dilemma of what screening method to use. In addition to seeking alternative corrosion inhibitors, this research also examined some of the important criteria needed in the accurate assessment of prospective compounds for concrete application.

This study had the following objectives:

1. Conduct a state-of-the-art literature survey of effective compounds for inhibiting steel rebar corrosion in concrete. Expand the search for inhibitors of steel in the presence of chloride.
2. Screen identified candidate inhibitors in a simulated pore solution (SPS) so the best performers can be used in long-term concrete experiments.

## **EXPERIMENTAL APPROACH**

The first step in this study was to select good candidates for corrosion inhibitors that could be used as admixtures in concrete mixes. Then, the efficiency of the candidates and a few selected commercial inhibitors was assessed by using electrochemical testing, which involved exposing rebars to solutions of these inhibitors in SPS containing chloride ions and nondestructively measuring the rebar corrosion rate. In addition, the exposed rebars were visually examined after the electrochemical testing.

## Selection of Candidate Inhibitors

Because of the large number of possible inhibitor compounds, the candidate inhibitors were tested in two groups or phases. The phases differed in both the compounds tested and the test protocol used.

### Phase 1

Based on a survey of the literature, four compounds were selected for testing in this phase:

- sodium tetraborate
- zinc borate
- disodium fluorophosphate
- disodium  $\beta$ -glycerophosphate.

Two commercial inhibitors were also evaluated. Because of the preliminary nature of these tests and the sensitivity associated with comparing commercial products, these inhibitors were designated CI-1 and CI-2. A control sample was also examined in which the rebar was tested in SPS with no inhibitor.

### Phase 2

Based on tests of non-chromate inhibitive pigments for aluminum and a more expansive literature survey, the following eight compounds were used in Phase 2:

- monobasic sodium phosphate
- nitrolotris-triphosphonate
- dibasic sodium phosphate
- sodium hexa-metaphosphate
- strontium chromate
- disodium  $\beta$ -glycerophosphate
- barium metaborate

- sodium metavanadate.

Three commercial inhibitors were also tested: CI-1 and CI-2 (as in Phase 1) and a third designated CI-3. A control sample containing only SPS was also tested.

### **Electrochemical Testing**

Inhibitor performance was monitored using electrochemical impedance spectroscopy, an electrochemical method that allows the nondestructive determination of the corrosion rate under steady-state conditions. This noninvasive approach for the determination of the polarization resistance was needed to monitor the time course of inhibitor performance continuously.

Electrochemical impedance spectroscopy was performed using the three-electrode configuration under potentiostatic control. The open circuit potential was monitored with a saturated calomel electrode for 10 to 30 min before each impedance experiment. Impedance data were collected from 65 kHz to 0.01 Hz using a 10-mV RMS sine wave excitation superimposed on the dc open circuit potential. Data were acquired using a Solartron 1286 Electrochemical Interface and a Solartron 1255 Frequency Response Analyzer, both under software control.

Impedance measurements were made after 6 and 8 days of exposure to the inhibitor/SPS solutions. A stable  $R_p$  value was obtained for all inhibitors by Day 8 as noted by duplication of the Day 6 values. This condition represents the environment of new rebar in fresh concrete before the intrusion of chlorides. Once stability was achieved, the solutions were doped with sodium chloride, and changes in  $R_p$  were monitored as a function of time. In Phase 1, the sodium chloride was added in one dose to achieve a concentration of 3.5 weight percent (0.6M), which is similar to that of seawater.

In Phase 2, the chloride was added in four equal increments over a period of 12 to 14 days to achieve a final concentration of 3.5 weight percent. The incremental additions were believed to more closely resemble the conditions encountered by embedded rebar, as chloride diffuses to the rebar level over time, and also allowed for a more sensitive delineation of inhibitor performance. After 8 days in the inhibitor/SPS solutions, the rebar was challenged with chloride added in four equal amounts at Days 8, 12, 16, and 22 (Days 0, 4, 8, and 14 if the time of introduction is taken as Day 0). The open circuit potential and polarization resistance were recorded throughout the exposure.

Rebar samples were cleaned ultrasonically in hexane before exposure to the test solutions.

## Electrochemical Cell Design

The design of the electrochemical cell used in both phases is shown in Figures 1 and 2. The main body of the cell was a 1-liter polymethylpentene beaker. This material was selected because it is transparent and resistant to alkaline attack. Corrosion tests using highly alkaline solutions in glass cells could be suspect because of the alkaline solubility of glass and the known inhibitive characteristics of silicate.

Based on experiences in Phase 1, the following modifications were made to the cell for Phase 2:

*Sample holder.* In Phase 1, a section of No. 5 rebar 28 mm long was sandwiched between two polymer cylinders: a short end-cap on the bottom and a longer top segment. Insula-

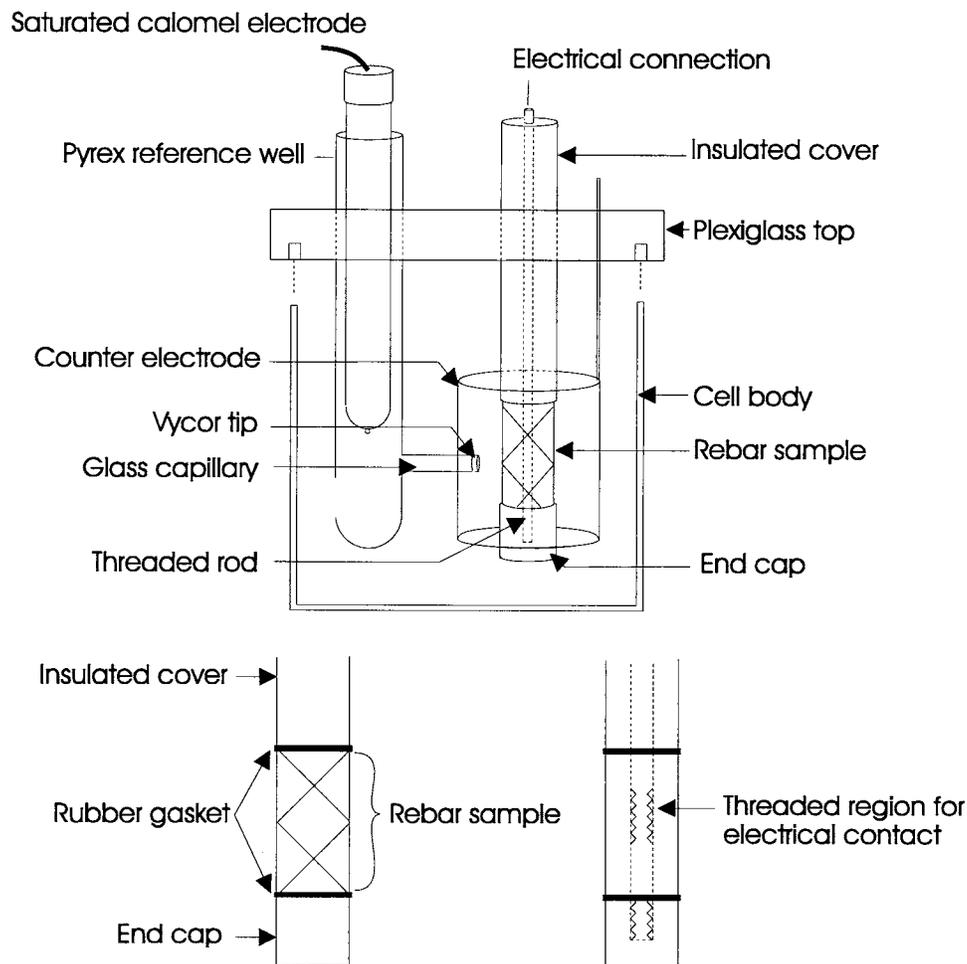
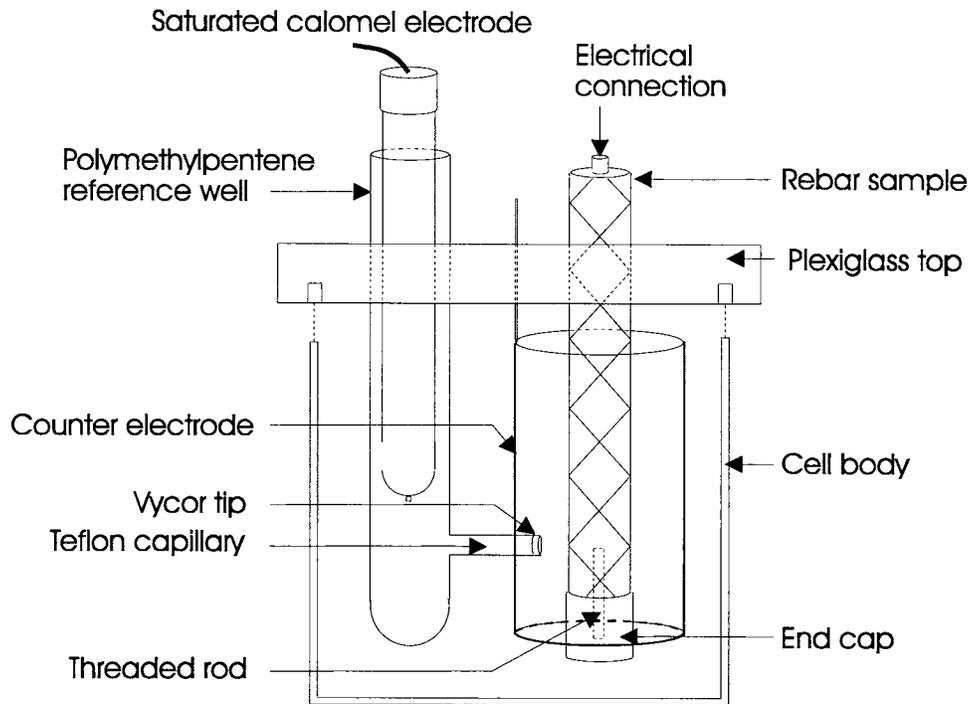


Figure 1. Electrochemical Cell and Rebar Sample Holder Used in Phase 1



**Figure 2. Electrochemical Cell and Method of Rebar Sample Presentation in Phase 2**

ting the cut ends of the rebar from testing is essential because of the difference in electrochemical activity between the mill scale on the rebar surface and air-formed oxide on the cut ends. The bottom end-cap was made of polyvinyl-chloride because of its ability to maintain shape under stress, and the larger top segment was made of Teflon because it is chemically inert. In testing corrosion inhibitors, particularly in low concentrations, all sources of chemical contamination must be eliminated from the cell materials. Rubber gaskets were used at both ends of the rebar between the steel and the polymer cylinders to prevent crevice corrosion attack at these interfaces. Prevention of crevice attack in long-term exposures is essential in the analysis of the inhibitor performance. Electrical connection to the rebar was made by a central threaded steel rod that extended up through the top insulating polymer cylinder.

At the end of Phase 1, crevice corrosion was observed between the gasket material and the rebar. To eliminate this problem, the sample holder was modified as shown in Figure 2. The probability of crevice attack was minimized by reducing the amount of crevice area presented to solution. This was accomplished using a longer (11.5 cm) rebar sample that could extend out of the cell and required sealing of just the bottom end. Although this eliminated the top crevice of the previous design, it also introduced a gas/electrolyte/rebar triple point at the meniscus where the SPS wet the top of the rebar. Electrical connection to the rebar was made with a metal screw threaded into the top of the rebar.

Crevice corrosion was prevented at the bottom crevice by applying a chromate conversion coating to the bare end that was then top coated with epoxy. The chromate conversion coating is a benchmark surface pretreatment used by the industry to protect steel from corrosion. The top coat prevented any residual chromate species in the conversion coating from entering the test solution. As a final precaution, a rubber gasket was also used in some samples.

*Counter electrode.* A platinum clad niobium mesh was used as a counter electrode. This mesh was formed into a cylinder 3.5 cm in diameter and 5 cm in length placed concentric to the rebar to provide uniform current distribution. Electrical connection to the counter electrode was established with two platinum-coated titanium wires (1.6 mm diameter).

*Reference well.* A Pyrex reference well with a glass Luggin-Haber capillary was used in Phase 1 because a polymethylpentene well had not been located at that time. A Vycor glass frit was attached to the end of the capillary using heat shrinkable tubing. The glass frit prevented contamination of the reference electrode by the test solution while maintaining ionic continuity.

The investigators became concerned that the high pH of the SPS (pH 12.5) would attack the glass reference well and release silica that could itself inhibit corrosion. To minimize the amount of glass exposed to the test solution, the reference well was fabricated from polymethylpentene in Phase 2, and the capillary was made from small diameter Teflon tubing. The tubing was inserted into an undersized hole in the reference well and sealed at the well junction using a Teflon adherent cement.

## **Test Solutions**

There is continual debate over the efficacy of using SPS for the screening of electrochemical phenomena associated with embedded rebar. Compounding this controversy is the question concerning the appropriate SPS chemistry. Because of the time needed to develop rebar corrosion in actual concrete specimens, there is a definite advantage in using SPS when screening a large number of potential inhibitors. However, the results obtained in SPS may not represent the results obtained in concrete because of the many differences in diffusion and chemical binding characteristics of the concrete. Thus, promising candidates identified in SPS must also be tested in long-term concrete exposures.

### *Phase 1*

Saturated calcium hydroxide solution (pH 12.3) was used as the SPS. Inhibitors were added to yield a concentration of 10 mM, which is an extremely low concentration of inhibitor, particularly if challenged with the high chloride concentrations encountered in service. However, this concentration was chosen so that the truly superior performers could be identified, since the best commercial inhibitors (e.g., chromates) can provide excellent protection even at this concentration.

One difficulty in testing some of the commercial inhibitors is that the concentration of the active ingredient(s) is unknown. This makes direct comparisons between the inhibitor efficiencies of commercial and candidate materials very difficult if not impossible for those situations. Inhibitor concentration in any application is an extremely important variable that should be investigated in a full-matrix investigation of potential inhibitors. Such an investigation would include a detailed examination of the effects of inhibitor concentration, inhibitor-to-chloride ratio, temperature, etc.

### *Phase 2*

In this round of experiments, the performance of the inhibitors was tested in an alternate SPS chemistry<sup>30</sup> that had an increased alkali content and a higher pH (pH 13.5). This chemistry is argued to more closely resemble the pore solutions recovered from concretes. Initial tests revealed that the extremely alkaline conditions of this SPS dissolved the Vycor frits used to separate the reference electrode from the test solution. Other cell components were stable. Rather than search for an alternate separator material for this SPS, experiments were resumed in the former SPS, i.e., saturated calcium hydroxide.

Test inhibitors (including CI-1 and CI-3) were added to saturated calcium hydroxide to achieve a final inhibitor concentration of 50 mM. Estimates were made for the appropriate concentration of CI-2 (12.57 ml of CI-2 in 800 ml of SPS), but the exact concentration of active ingredients was not known.

### **Visual Examination**

As a final method of evaluation, the rebar was removed from the cells, rinsed with tap water, and allowed to air dry so that a visual ranking of corrosion could be made.

## **RESULTS AND DISCUSSION**

### **Electrochemical Data**

As discussed previously, the results of the inhibitor testing in Phase 1 were compromised by the crevice attack, and a new sample presentation scheme was developed in Phase 2. Another modification was the addition of sodium chloride in small incremental steps, which more closely resembles the chloride buildup in the field and also allows more sensitivity in inhibitor performance delineation.

The objective of this study was to compare the corrosion inhibition efficiency of a series of candidate and commercial inhibitors on an equivalent molar basis. Candidate inhibitors were

added to saturated calcium hydroxide to a concentration of 50 mM except for one of the commercial inhibitors, CI-2. The concentration of the active ingredients in “as-received” CI-2 could not be determined within the time and budget of this project. Therefore, it is possible and likely that CI-2 was added in a greater concentration than the other compounds. This possibility must be factored into the evaluation and ranking of CI-2.

### Open Circuit Potential

The open circuit potential is the mixed potential established by the total anodic and cathodic processes on the electrode surface. Although this potential value cannot provide information on reaction rates, it can indicate the relative corrosion protection (or susceptibility) of a sample. More noble (positive) potential values are indicative of corrosion protection and more active (negative) values are indicative of corrosion.

Table 1 lists the inhibitors in decreasing order based on the open circuit potential measured after 1 day and 22 days of exposure to chloride ions. Between these two measurements, the chloride ion concentration was increased through small incremental additions, as discussed previously.

**Table 1. Open Circuit Potentials of Rebar in 50 mM Solutions of Inhibitor and Saturated Calcium Hydroxide at Day 1 and Day 22 of Chloride Exposure**

Rank	Day 1 Inhibitor	Day 1 $E_{oc}$ V <sub>SCE</sub>		Day 22 Inhibitor	Day 22 $E_{oc}$ V <sub>SCE</sub>
1	Ba metaborate	-0.353		Ba metaborate	-0.523
2	CI-2	-0.391		Sr chromate	-0.611
3	Control	-0.421		CI-1	-0.611
4	CI-1	-0.429		CI-2	-0.621
5	disod.β-glyceroPA	-0.437		disod.β-glyceroPA	-0.671
6	Sr chromate	-0.453		Control	-0.694
7	Na phos., dibasic	-0.472		Na phos., monobas.	-0.703
8	Na metavanadate	-0.484		Na phos., dibasic	-0.704
9	CI-3	-0.489		Na metavanadate	-0.719
10	Na phos., monobasic	-0.545		CI-3	-0.817

Of the two time periods shown, the most important data in terms of inhibitor performance are those for the longer term data at Day 22. Since the typical chloride-to-inhibitor ratio recommended for field application is 1:1, the ratio for the final days of exposure (0.3 M/0.050 M) represents extremely harsh conditions. Therefore, any sign of improved performance in these conditions is considered significant.

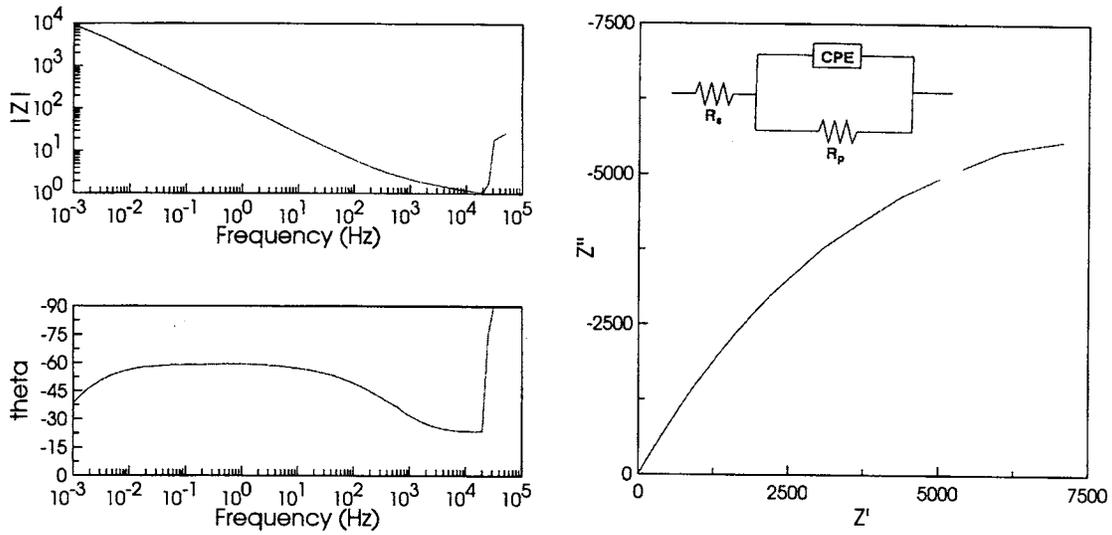
Several observations were significant. Although strontium chromate is considered the benchmark inhibitive pigment in organic coatings, barium metaborate had a significantly more noble  $E_{oc}$ . Two of the commercial inhibitors had values very similar to those for strontium chromate, whereas the values for the remainder of the inhibitors decreased significantly below that for chromate. The third commercial inhibitor, CI-3, had the most active  $E_{oc}$ . Even though  $E_{oc}$  does not provide corrosion rate information, it does provide some insight into the thermodynamic driving force for corrosion and can be factored into the ranking process. A more thorough ranking protocol should examine the  $E_{oc}$  (and other electrochemical parameters) over a range of inhibitor concentrations.

## Polarization Resistance

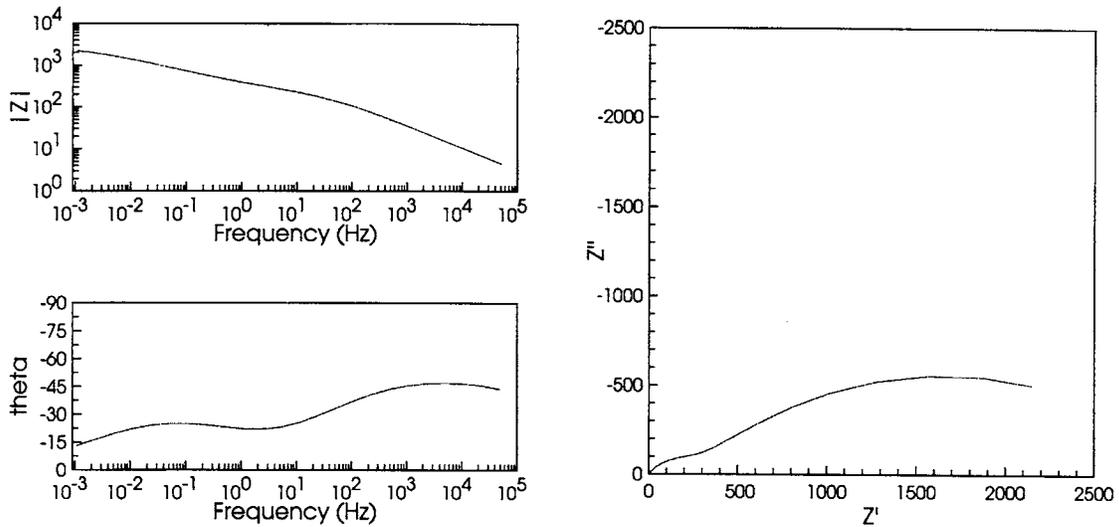
The polarization resistance can be used to calculate the corrosion current ( $i_{corr}$ ) through the Stern-Geary equation if the anodic and cathodic Tafel slopes are known, and if the corrosion is uniform over the sample surface. Since the observed rebar corrosion was not uniform in these inhibitor environments, the polarization resistance was retrieved from the impedance data and used directly to compare inhibitor performance. In general, a higher polarization resistance results in better inhibitor performance.

Typical impedance data in the complex plane and Bode format are shown in Figures 3 and 4 for rebar exposed to SPS/inhibitor and for rebar exposed to SPS/inhibitor/chloride. The equivalent circuits used to determine  $R_p$  are also shown. Except for CI-2 and strontium chromate, all impedance data could be analyzed for  $R_p$  using the single-time constant equivalent circuit shown in Figure 3. A constant phase element was used rather than a pure resistor because of the distributed nature inherent in the impedance response of thermal oxides on steel as well as steel in chloride containing electrolytes. Two broad relaxations were observed for CI-2 and strontium chromate. The high-frequency relaxation was proposed to arise from a barrier layer, whereas the low-frequency relaxation process was ascribed to the double-layer capacitance and faradaic processes occurring in the breaches of the barrier layer. A detailed verification of this second model in future research is warranted.

The very slow corrosion rates (high  $R_p$ ) and large double-layer capacitances associated with the steel interface in the inhibited SPS gave rise to a very large interfacial time constant, which moved the low-frequency intercept of the real axis ( $R_p$ ) to extremely low frequencies. Thus, the acquisition of  $R_p$  values in the pre-chloride exposures relied heavily on the use of a complex nonlinear least square fit to the circuit model. The interfacial time constant decreased significantly upon the addition of chloride, so that  $R_p$  could be acquired more readily.



**Figure 3. Typical Bode (left) and Nyquist (right) Plots for Single-Time Constant Impedance Response.** Data are for steel in SPS with no chloride.  $R_s$  = solution resistance,  $CPE$  = constant phase element,  $R_p$  = polarization resistance.



**Figure 4. Typical Bode (left) and Nyquist (right) Plots for Two-Time Constant Response.** Data are for steel in SPS/CI-2/chloride at Day 13 of chloride exposure.  $R_s$  = solution resistance,  $CPE$  = constant phase element,  $R_{po}$  = pore resistance,  $R_c$  = charge transfer resistance.

The  $R_p$  values were determined for approximately 1 week before the addition of chlorides to ensure that the interface was stable. The  $R_p$  values for the various inhibitors just before the chloride additions are shown in Table 2. They ranged from  $10^3$  to almost  $10^6$  ohms, with CI-2, disodium  $\beta$ -glycerophosphate, and dibasic sodium phosphate having much higher values than the other compounds.

**Table 2. Polarization Resistance Before Chloride Addition**

Inhibitor	$R_p$ (ohms)
CI-2	$7.42 \times 10^5$
Disodium $\beta$ -glycerophosphate	$6.82 \times 10^5$
Sodium phosphate (dibasic)	$2.47 \times 10^5$
Sodium phosphate (monobasic)	$1.28 \times 10^5$
Sodium metavanadate	$6.01 \times 10^4$
CI-1	$3.90 \times 10^4$
Barium metaborate	$3.04 \times 10^4$
Control	$2.09 \times 10^4$
Strontium chromate	$1.96 \times 10^4$
CI-3	$5.41 \times 10^3$

Figures 5 and 6 show  $R_p$  as a function of time following chloride addition for the candidate inhibitors. The data are presented in two graphs for clarity. The times of chloride addition are marked by the vertical lines having filled triangles. One of the most obvious results is the very large  $R_p$  values for CI-2. As previously stated, these data cannot be compared to the other inhibitor data because of the unknown, and most likely significantly higher, inhibitor concentration. The  $R_p$  values for all other candidate and commercial inhibitors fell within a more compact range.

Three types of  $R_p$  vs. time trends were observed over the 22- to 27-day exposure and were designated as Type 1, Type 2, and Type 3 behavior. Type 1 behavior was characterized by a drop in  $R_p$  after chloride addition followed by some degree of recovery before the next chloride addition. This type of behavior was seen in CI-2, barium metaborate, CI-1, and sodium metavanadate. Type 2 behavior was characterized by  $R_p$  values that decreased continuously upon chloride exposure over the entire exposure period. Inhibitors with Type 2 behavior were disodium  $\beta$ -glycerophosphate and sodium phosphate (dibasic). Type 3 behavior consisted of a slow decrease in  $R_p$  followed by a gradual recovery that was not associated with chloride additions. Strontium chromate exhibited Type 3 behavior.

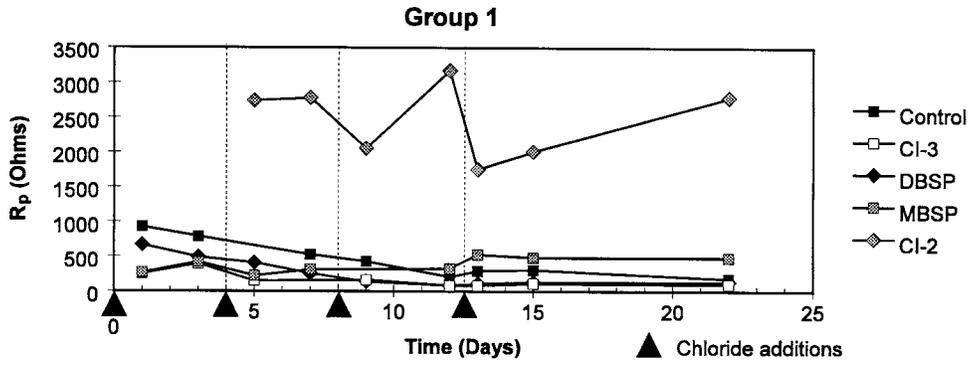


Figure 5a.  $R_p$  Versus Time for Four Inhibitors and Control in Phase 2

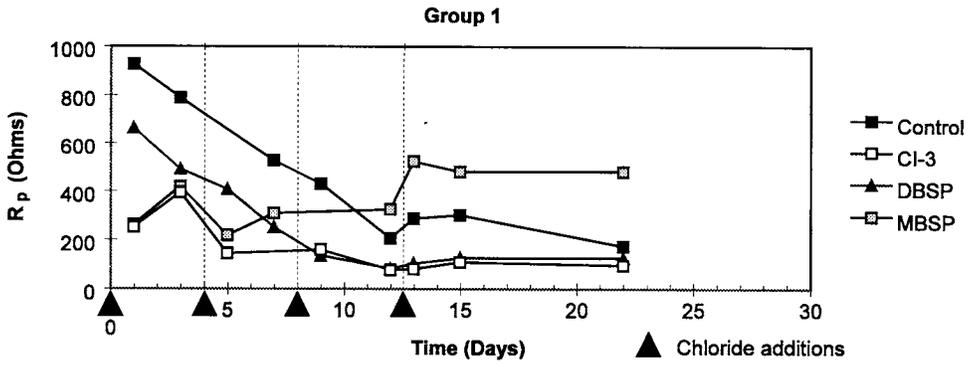


Figure 5b. Same as Figure 5a But with Different Vertical Scale

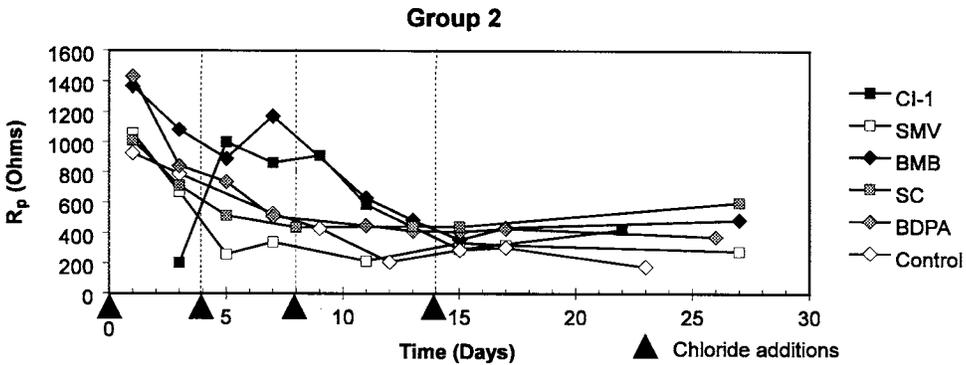


Figure 6.  $R_p$  Versus Time for Remaining Inhibitors in Phase 2

These trends point to the importance of recording performance data over a significant time period. The length of the period is difficult to define, as even 27 days may not be enough time to document the long-term behavior of certain inhibitor types. For example, interphasial inhibitors rely on the production of a barrier layer composed of inhibitor and corrosion product and, therefore, may not obtain complete protection until after some period of low  $R_p$  behavior. This could explain the Type 1 and Type 3 behavior. Thus, another important factor that must be considered in inhibitor evaluation is time.

The inhibitors are ranked in Table 3 according to their final  $R_p$  value at Day 27 and the “type” or trend in  $R_p$  in the period following the last exposure period. The designators “+” and “-” indicate that the  $R_p$  is either increasing or decreasing respectively, and a “0” designator indicates that  $R_p$  is maintaining a constant value. Thus, if two inhibitors had the same or similar  $R_p$  values, but one was a + type and the other a 0 or - type, the + type would be a higher rank. Just as  $E_{oc}$  alone should not be used to evaluate a corrosion inhibitor, neither should the absolute value of  $R_p$  alone. An ideal evaluation of  $R_p$  data should include a quantitative assessment of the area of corrosion, since the current density will determine the rate of localized corrosion phenomena. The area and type of corrosion in the various inhibitors were ranked qualitatively (to be discussed). Accurate quantification of corrosion area could be accomplished in future studies but is non-trivial because of the irregular surface height of a cylindrical ribbed rebar.

As Table 3 shows, barium metaborate and strontium chromate were the best performers (neglecting CI-2), similar to the open circuit data. Interestingly, sodium phosphate-monobasic had a higher  $R_p$  than CI-1 even though it had the lower  $E_{oc}$  at this time ( $-0.703 V_{SCE}$ ). As stated

**Table 3. Ranking of Inhibitors Based on Absolute Value and Trend of  $R_p$  at Day 27 of Chloride Exposure**

Rank	Inhibitor	$R_p$ (ohms)	Trend Type
1	CI-2	2781	+
2	Strontium chromate	600	+
3	Barium metaborate	485	+
4	Sodium phosphate, monobasic	482	0
5	CI-1	422	+
6	Disodium $\beta$ -glycerophosphate	373	-
7	Sodium metavanadate	278	-
8	Control	175	-
9	Sodium phosphate, dibasic	127	0
10	CI-3	96	-

previously, the profile of  $R_p$  vs. time is an important issue in the final evaluation of an inhibitor. A closer examination of the time profile (Figure 5B) for sodium phosphate-monobasic revealed a very low value in the initial days of chloride exposure, so that the increase in  $R_p$  may be a result of a thickening corrosion product layer. This could have both good and bad implications depending on whether the layer thickness reaches a protective, steady-state value or whether it continues to increase and introduce tensile stresses in the concrete.

Only CI-2, sodium metavanadate, barium metaborate, strontium chromate, and disodium  $\beta$ -glycerophosphate had consistently higher  $R_p$  values over most of the time than the control cell. Thus, several of the “inhibitors” might be regarded as “dangerous” inhibitors in that they increase the corrosion rate if used at a concentration below some critical chloride-to-inhibitor ratio. This is typical of anodic inhibitors such as calcium nitrite.

When earlier time periods were examined when the  $[\text{Cl}^-]:[\text{inhibitor}]$  ratio was lower, several inhibitors stood out as excellent performers: barium metaborate, disodium  $\beta$ -glycerophosphate, and CI-1. It is suggested in future comparisons using these electrochemical methods that the chloride be added at a slower rate, with longer times between additions. This will help refine the ability to delineate between close inhibitors and perhaps identify the critical chloride-to-inhibitor ratio.

### Visual Inspections

Upon removal, localized “waterline” attack at the solution/rebar meniscus was very noticeable on several of the samples. This phenomenon was most likely due to the loss of inhibitor in the carbonated region of the surface solution, particularly at the solution/sample meniscus. This meniscus region also had increased oxygen availability because of the narrow diffusion boundary provided by the thin electrolyte layer in this region. Although the presence of this phenomenon was initially regarded as a detracting feature of this method for sample presentation, it may have some testing advantage, since the inhibitor performance under a worst case scenario (high chloride, high  $\text{O}_2$ , low pH) can be documented. These crevicing conditions are frequently encountered in the rebar macrocell test (ASTM G109) and confound the interpretation of results. Therefore, the visual performance ranking was separated into two categories: (1) the general surface, discounting waterline corrosion, and (2) waterline corrosion. These rankings are shown in Table 4. The individual evaluations of the samples along with photographs are provided in the Appendix.

Table 4 shows the excellent performance of disodium  $\beta$ -glycerophosphate and barium metaborate in the bulk solution and disodium  $\beta$ -glycerophosphate at the electrolyte meniscus. These inhibitors performed better than two of the three commercial inhibitors and might be as good as or better than the third commercial inhibitor (CI-2) if tested at similar concentrations.

**Table 4. Ranking of Corrosion Based on Visual Observations at End of 27-Day Exposure**

Rank	General Surface	Waterline Attack
1	CI-2	CI-2
2	Strontium chromate	Disodium $\beta$ -glycerophosphate
3	Disodium $\beta$ -glycerophosphate	Control
4	Barium metaborate	CI-3
5	Control	Sodium phosphate, monobasic
6	Sodium metavanadate	Sodium metavanadate
7	CI-1	Strontium chromate
8	CI-3	Barium metaborate
9	Sodium phosphate, dibasic	Sodium phosphate, dibasic
10	Sodium phosphate, monobasic	CI-1

### Final Ranking

A final ranking of the inhibitors was established through the integration of the performance data in all of the categories examined in this study: open circuit potential, polarization resistance, visible corrosion on the general surface, and visible corrosion at the waterline. This ranking is summarized in Table 5. The numerical indices for the ranking were determined by the rank position; therefore, the lower the value, the better the corrosion resistance. A second ranking was established that excluded  $E_{oc}$  data. As discussed previously,  $E_{oc}$  is a mixed potential that indicates the relative cathode-to-anode ratio but does not provide corrosion rate information. Thus, some may argue that this value may be misleading in some cases.

All of the performance indicators were weighted equally. It is quite possible that the weighting of the indicators could or should be something other than unity weighting, but no models or alternate methods exist within the corrosion community at this time. Finally, it must be kept in mind that these rankings were based on the performance of one sample, which was necessary so that a large number of candidate compounds could be examined. Subsequent testing must include a statistical evaluation with a larger number of samples per compound.

Discounting the excellent performance of CI-2 that must be disqualified because of its unknown concentration, it is very important to note the outstanding performance of barium metaborate and disodium  $\beta$ -glycerophosphate. These two compounds performed as well as or better than strontium chromate, which is typically regarded as a benchmark for inhibitive pig-

**Table 5. Overall Ranking of Inhibitors**

Rank	Rank*	Inhibitor	$E_{oc}$	$R_p$	Vis. Gen.	Vis. Wtrln.	Total	Total*
1	1	CI-2	4	1	1	1	7	3
2	2	Sr chromate	2	2	2	7	13	11
3	3	Ba metaborate	1	3	4	8	16	15
3	2	$\beta$ -glyceroPA	5	6	3	2	16	11
4	4	Control	6	8	5	3	22	16
5	6	CI-1	3	5	7	10	25	22
6	5	Na phos-mono	7	4	10	5	26	19
7	5	Na metavan.	9	7	6	6	28	19
8	6	CI-3	10	10	8	4	32	22
9	7	Na phos-dib.	8	9	9	9	35	27

\*This ranking excludes the open circuit potential data.

ments in aerospace coatings. Strontium chromate is not a potential candidate for admixtures because of the toxicity and carcinogenicity of the  $Cr^{+6}$  ion. These two candidates also outperformed two of the three commercial inhibitors by a very wide margin.

Five of the inhibitors, including two of the commercial inhibitors, had poorer corrosion performances at the end of the exposure than the control solution (no inhibitor). This is not surprising for this type of test and should not preclude further evaluation of these compounds at higher concentrations. As discussed, anodic inhibitors are sensitive to inhibitor concentration and will actually accelerate corrosion if the inhibitor concentration falls below a critical concentration. This critical concentration will also depend on the [Cl]:[inhibitor] ratio.

## CONCLUSIONS

- Based strictly on the screening methods and corrosion performance data developed in this investigation, two compounds should be advanced to corrosion testing as inhibitive admixtures: barium metaborate and disodium  $\beta$ -glycerophosphate.
- Other obvious factors must be examined in the total qualification of an admixture, e.g., the effect of the inhibitor on concrete curing and strength properties, cost, and toxicity.

## RECOMMENDATIONS

- Barium metaborate and disodium  $\beta$ -glycerophosphate should be examined for effects on concrete cure and strength properties. A totally benign result in this regard is not necessary as other additives may be added to the concrete mix to compensate for changes produced by the inhibitor. This is the practice used with commercially available inhibitors.
- Additional SPS studies should be performed that examine the effect of inhibitor concentration and the [Cl]:[inhibitor] ratio to determine an optimum performance range.
- A suitable ionic membrane that can withstand a pH of 13.5 should be identified for studies in alkali-modified SPS.
- The performance of candidate inhibitors must be examined in concrete because of potential chemical interactions among the chloride, cement, and inhibitor.
- Additional test methods should be developed that allow for rapid screening and analysis of sample corrosion because of the need for large numbers of samples to provide statistical verification and evaluate multiple test variables (e.g., inhibitor concentration, chloride concentration, wet/dry cycling, cracking). A suitable test for this task is the “mini-bar” test method proposed by Taylor and Lane to NCHRP in Project 10-45.<sup>31</sup>

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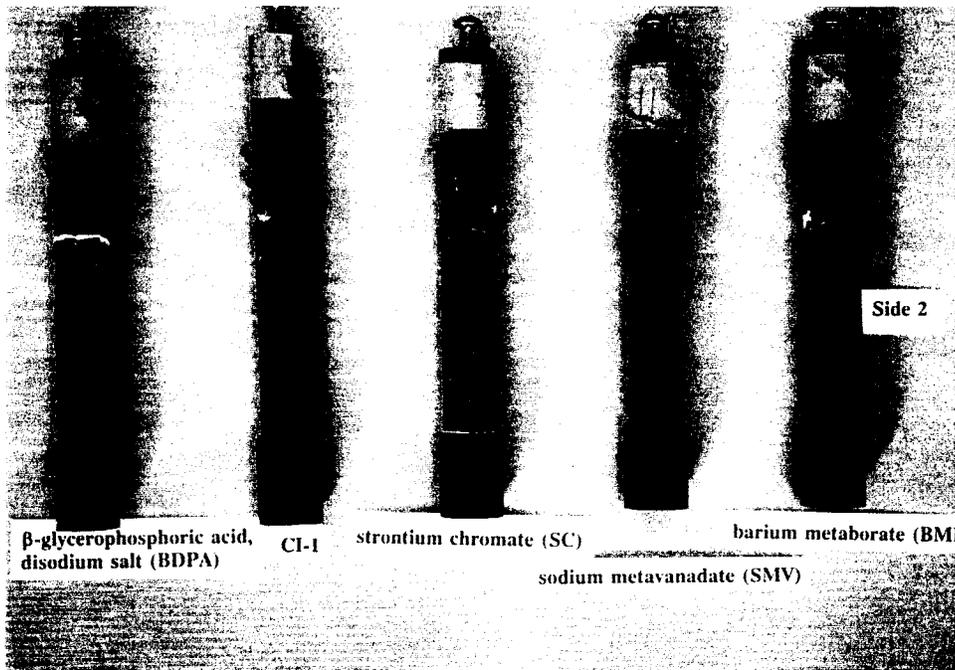
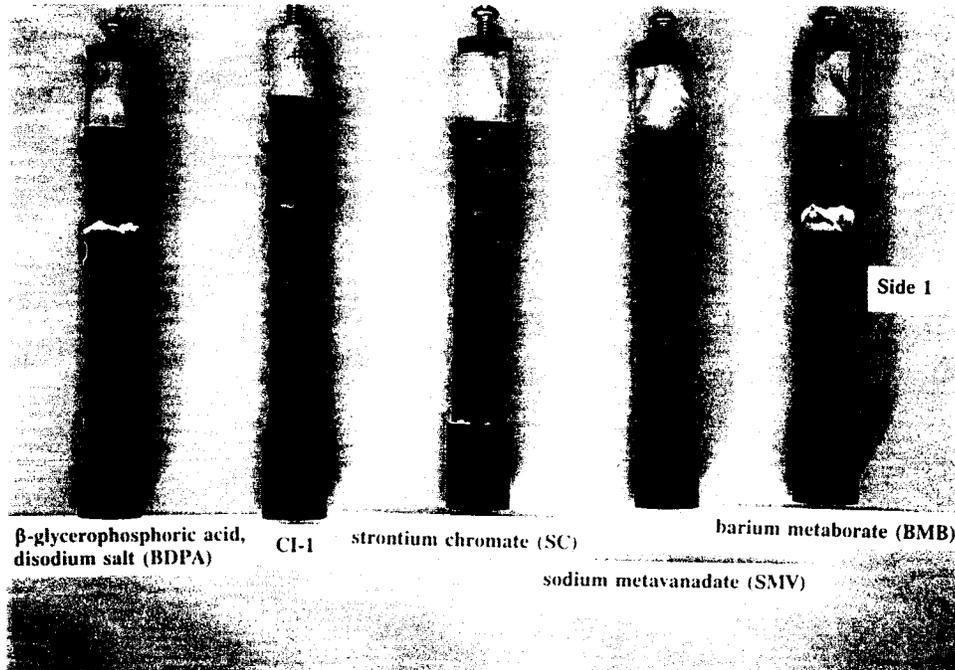
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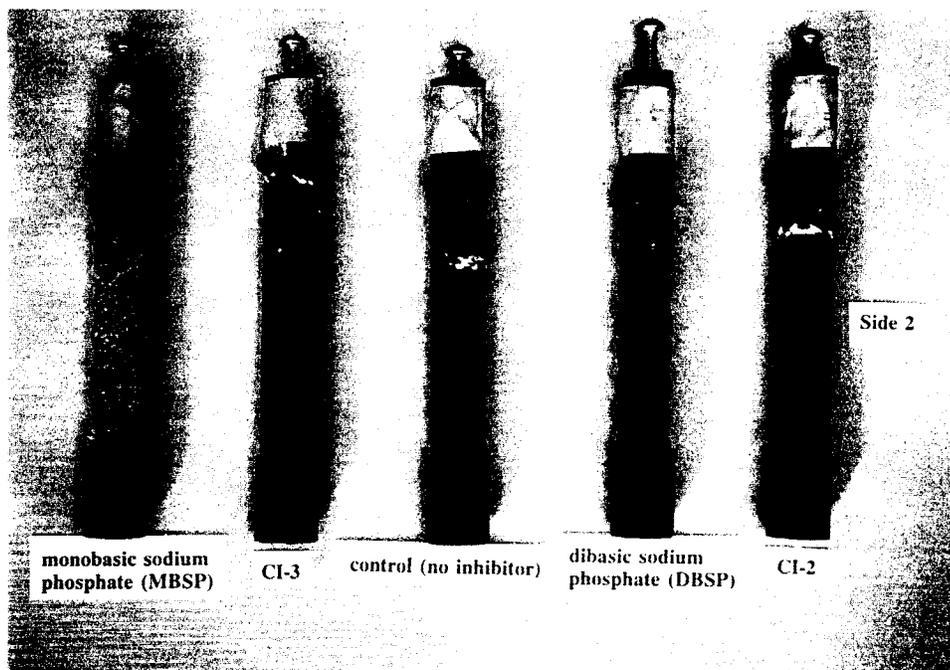
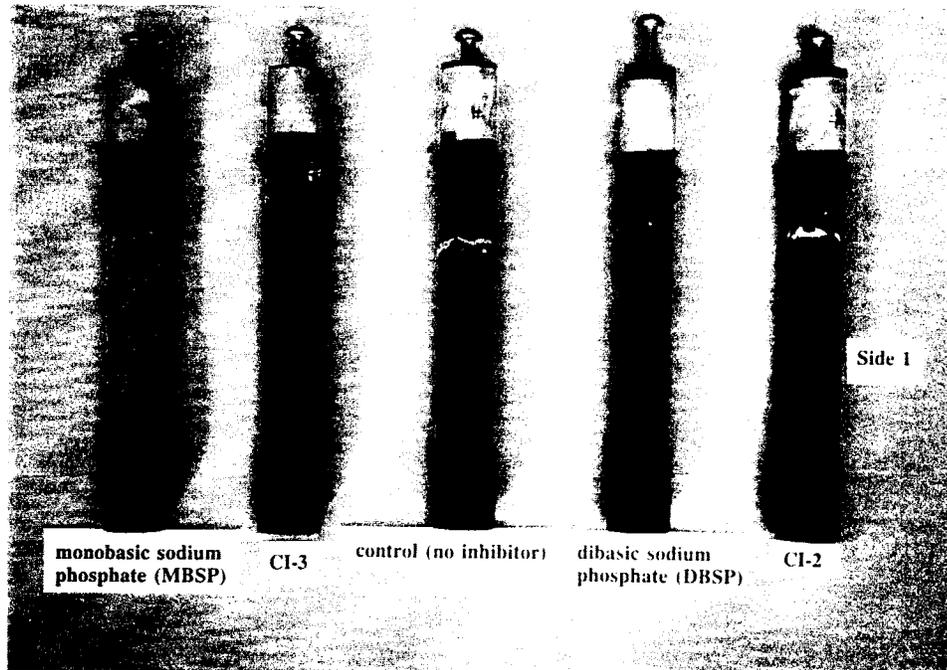
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## **APPENDIX**

### **Photographs of Rebar Samples and Notes on Sample Cells**

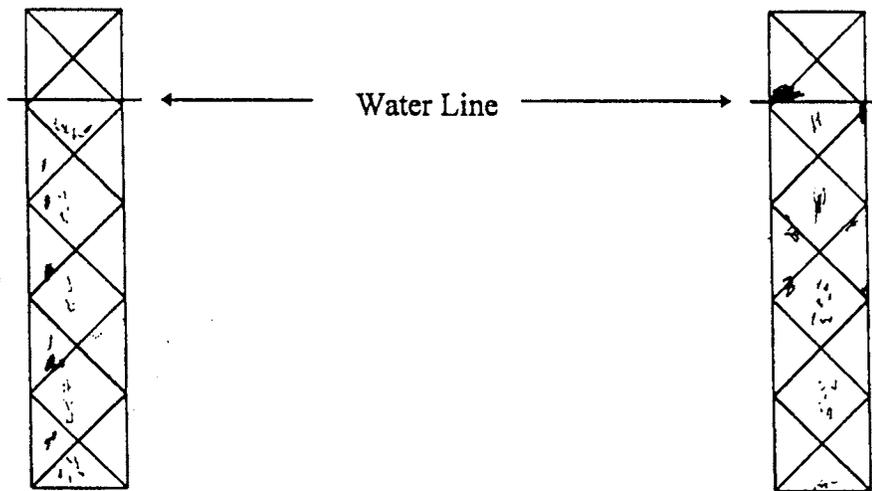


Front and Back of Rebar Samples Following Exposure to Candidata Inhibitors and Chloride Solutions



Front and Back of Rebar Samples Following Exposure to Candidata Inhibitors and Chloride Solutions

Cell # 1  
Inhibitor: Control



comments:

Moderate water line corrosion.  
Mill scale broke down, several large nodules of corrosion.

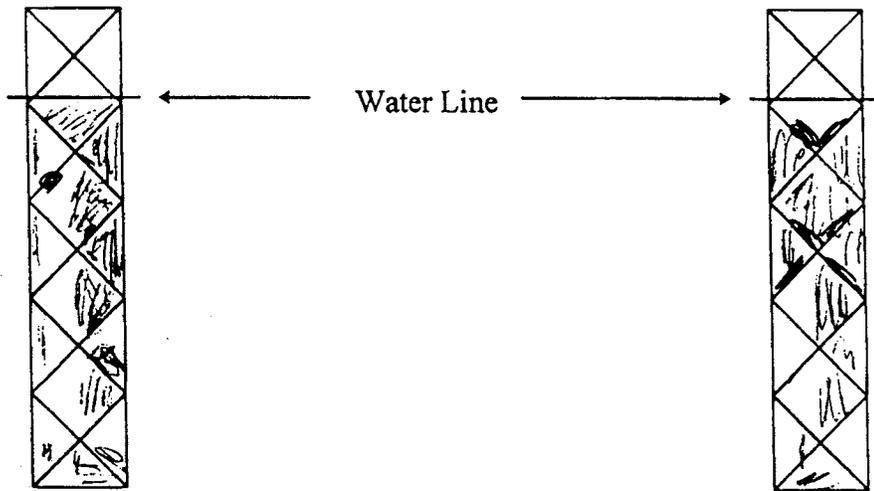
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Cell # 2

Inhibitor: CI-3



comments:

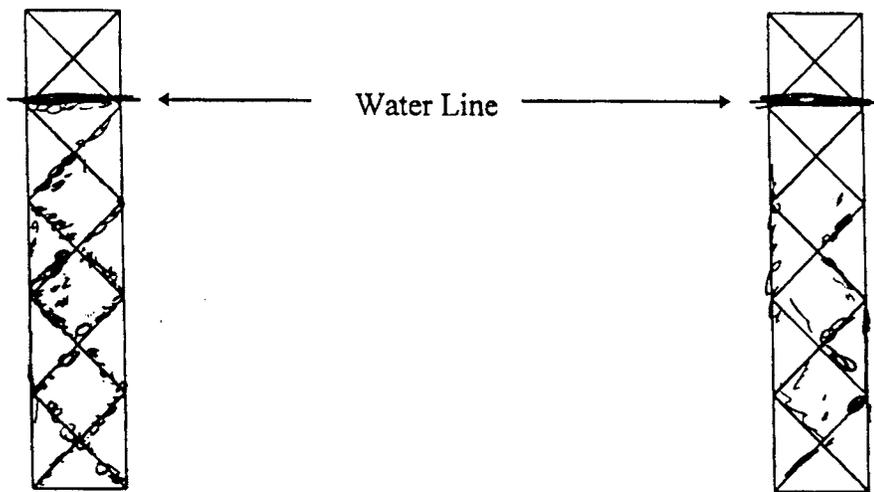
Little waterline corrosion.

Some large nodules begging to develop.

General surface corrosion over approximately 80% of area.

Cell # 3

Inhibitor: Sodium phosphate, dibasic



comments:

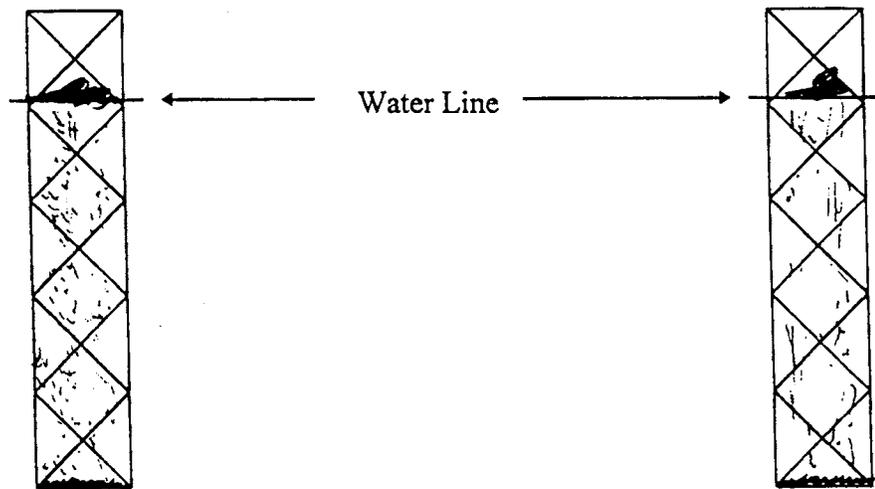
Extensive waterline corrosion.

Large nodules of corrosion formed on ribbed portion of surface.

Some attack in unribbed areas.

Cell # 5

Inhibitor: CI-1



comments:

Very heavy waterline corrosion.

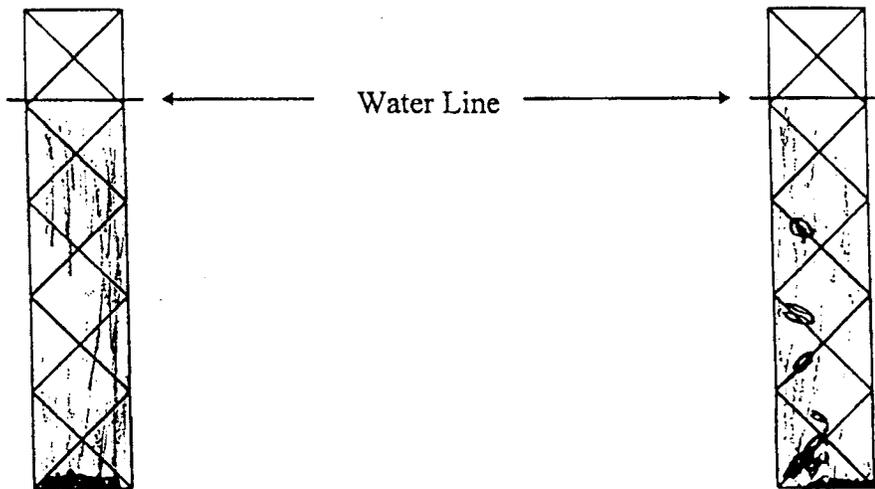
Pitting corrosion on 60-70% of surface.

Some nodules beginning to form.

Some attack at end-cap.

Cell # 6

Inhibitor: Sodium phosphate, monobasic



comments:

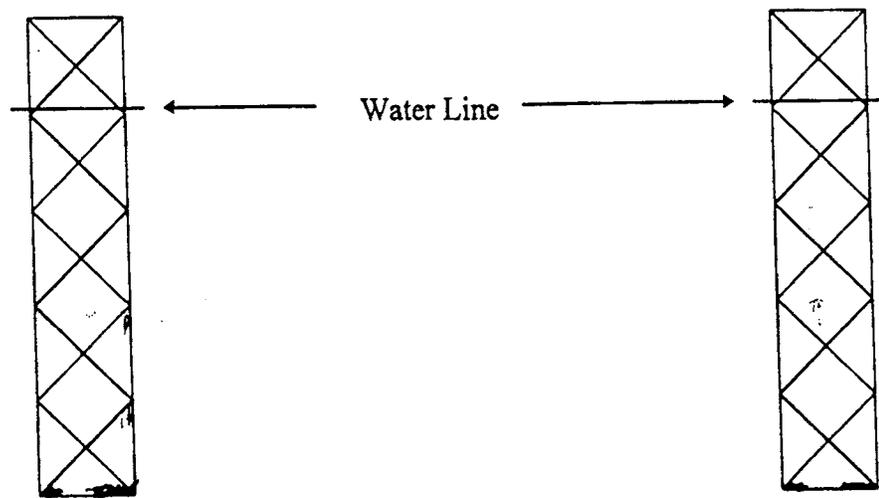
Moderate waterline corrosion.

Surface is completely corroded with corrosion product which has a yellow stain.

Large nodules present. Some corrosion at end-cap.

Cell # 7

Inhibitor: CI-2



comments:

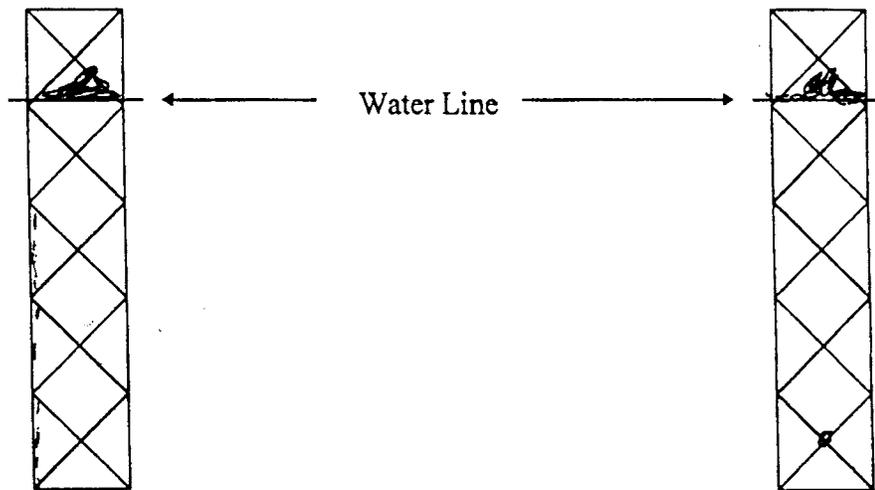
No waterline corrosion.

Some corrosion at end-cap.

Very small areas of light corrosion on surface.

Cell # 8

Inhibitor: Strontium chromate



comments:

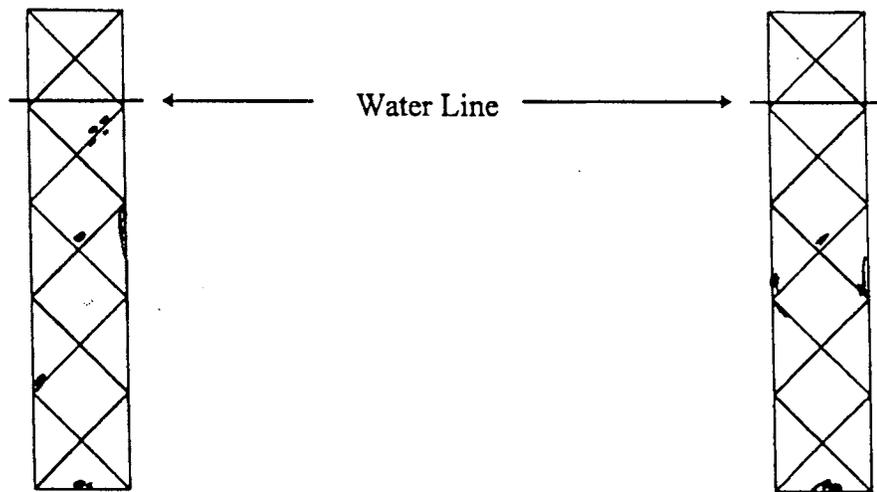
Heavy waterline corrosion.

A few small areas of light corrosion (possibly staining).

No end-cap corrosion.

Cell # 9

Inhibitor: disodium  $\beta$ -glycerophosphate



comments:

No waterline corrosion.

Concentrated corrosion in a few small areas.

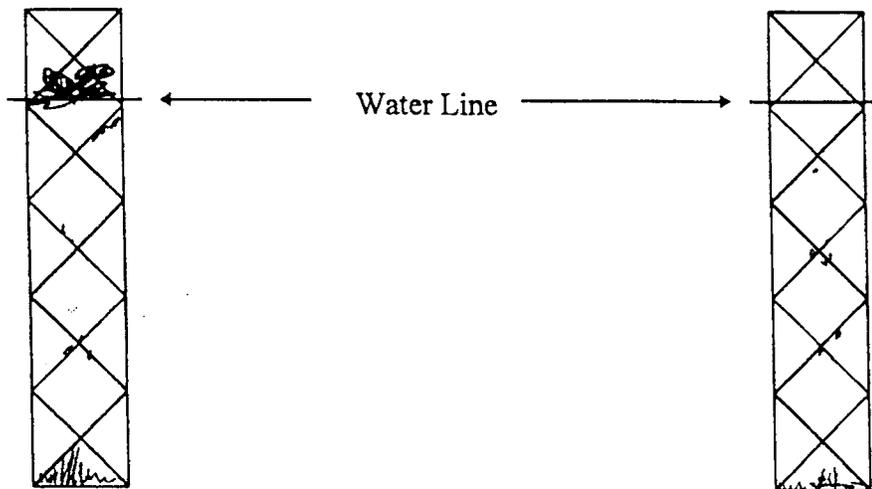
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Cell # 10

Inhibitor: Barium metaborate



comments:

Extensive waterline corrosion on one side.

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Surface corrosion present near end-cap.

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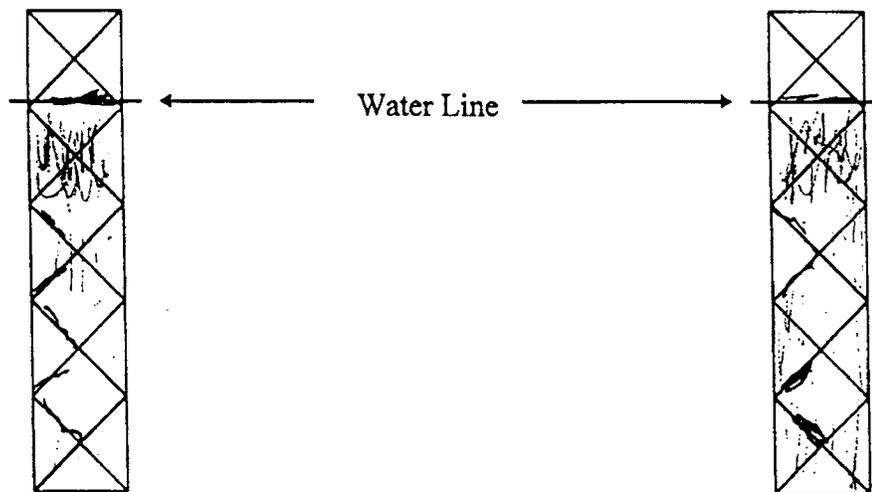
A few scattered nodules of corrosion.

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Cell # 11

Inhibitor: Sodium metavanadate



comments:

Moderate waterline corrosion.

90% surface (not necessarily from corrosion) discolored.

Some large nodules beginning to form.