# Evaluation of Penetrating Corrosion Inhibitor System

J. W. Bryant, Jr., R. E. Weyers, M. C. Brown, and R. M. Weyers

Sixteen reinforced slabs were cast with admixed chloride contents of 0.0, 0.35, 0.71, 1.4, 2.8, and 5.7 kg chloride per cubic meter of concrete. The slabs contained five isolated steel reinforcing bars with a 50-mm cover depth and were $1181 \times 1067 \times 216$ mm. The slabs were stored at an outdoor exposure site in Blacksburg, Virginia, for 7 years before being treated with an alcohol-amine corrosion inhibitor. Treatments were three applications at a rate of 2.46 $L/m^2$ over the entire surface area or over a center strip that was perpendicular to the bar direction. The concrete mixture had a water-to-cement ratio of 0.45 and a 28-day compressive strength of 34.5 MPa. Corrosion assessment measurements before treatment included acid- and water-soluble chloride contents and corrosion potentials and rates. Corrosion potentials and rates were monitored for 1 year after treatment, and about 9 months after treatment the depth of inhibitor penetration was measured qualitatively (color indicator test) and quantitatively (parts per million). Results indicated that the inhibitor penetrated to the bar depth, but there was no significant difference in the corrosion potentials and rates between the treated and the untreated slabs or areas.

The process of chloride ion– and carbonation-induced corrosion of steel-reinforced concrete structures is well known. Methods to delay the process or extend the service life may be placed into two categories: those that delay corrosion deterioration of newly constructed structures and those that extend the service life of actively corroding structures. The design engineer may choose from numerous techniques for new structures, but there are a limited number of methods for existing structures undergoing corrosion deterioration. Methods applied to existing structures may be polymer impregnation, cathodic protection, electrochemical chloride removal, or realkalization and penetrating corrosion inhibitors.

Penetrating corrosion inhibitors may be separated into two categories, according to their penetrating mechanisms: immediate capillary absorption during application and subsequent gaseous diffusion through the empty, connective concrete capillaries; and capillary absorption at application and subsequent ionic diffusion through the saturated, connective concrete capillary system. Both systems may be referred to as posttreatment methods, with the formal corrosion inhibitors called migrating corrosion inhibitors.

Initial research was conducted on both posttreatment methods under SHRP C-103 (1). The corrosion inhibitor used for penetration by ionic diffusion was calcium nitrite, and the corrosion inhibitor used for penetration by gaseous diffusion belonged to the class of alcohol-amine compounds. Both corrosion inhibitors showed promise as posttreatment products (2). Corrosion-abatement performance assessments for the calcium nitrite field implementation trials conducted under SHRP C-103 are presented elsewhere (3). This paper presents the results of an alcohol-amine penetrating corrosion inhibitor. The research was performed subsequent to the

Charles E. Via Department of Civil and Environmental Engineering, 200 Patton Hall, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0105.

SHRP C-103 research but used specimens cast during that program to determine the time to cracking following the initiation of chloride ion–induced corrosion of reinforcing steel.

## RESEARCH PROGRAM

### Specimens

Sixteen reinforced concrete slabs were cast in July 1990. The slabs contained five isolated steel reinforcing bars (see Figure 1). The slabs contained admixed chloride as sodium chloride, which ranged from 0.0 to 5.7 kg Cl⁻ per cubic meter of concrete (kg/m³). The concrete was a typical bridge deck mixture with a water-to-cement ratio (w/c) of 0.45 and a 28-day compressive strength of 34.5 MPa. The slump range was 75 to 100 mm, and the air content range was 5.5 to 6.5 percent. The slabs, 1181 × 1067 × 215 mm, had a 50-mm concrete cover over the reinforcing steel.

### Treatment

The slabs, which were stored outdoors in Blacksburg, Virginia, were about 7 years old when treated. The slabs, partially and fully treated, received three applications of an alcohol-amine penetrating corrosion inhibitor (APCI) at an application rate of 2.46 L/m². Table 1 presents the admixed acid- and water-soluble chloride contents and the treatment matrix. The APIC was applied to a 600-mm-wide center strip across the entire width of the slab and perpendicular to the five reinforcing steel bars. The APIC was applied to the entire surface of the fully treated slabs. The applications were in September 1998 following a relatively dry summer and at least 2 weeks after the last measurable rainfall.

### Corrosion Assessment

Corrosion mitigation assessment testing consisted of ambient temperature, temperature at the bar depth, corrosion potentials, copper-copper sulfate halfcell (CSE), and corrosion current density, unguarded linear polarization device (3LP). The corrosion potential and corrosion current density readings were corrected to 20°C. In addition, the depth of the penetration of the APCI was measured by the APCI manufacturer both qualitatively (color test) and quantitatively as a function of depth from a 100-mm-diameter core from each admixed chloride series. The cores were drilled with a water-cooled diamond set drill bit.

For the full-treatment slabs, corrosion potentials and rates were measured at the center of each of the five steel reinforcing bars. For the partial-treatment slabs, the corrosion potentials and rates were measured along the centerline of the treatment strip and within both untreated zones at the interface line between the treated and untreated zones on each of the five steel reinforcing bars.

A set of corrosion assessment measurements were taken before treatment and then generally once a month after treatment for 1 year. The manufacturer's APIC measurements were conducted about 9 months after treatment and before the last two measurement periods. Measurements were made on each of the five bars at the same location throughout the 1-year assessment period. Results are presented as the average of the five measurements and the 95 percent confidence limits.

### RESULTS

Figure 2 presents the ambient and concrete temperature at the reinforcing steel bar depth at each measurement period. As shown, the temperatures during the test period
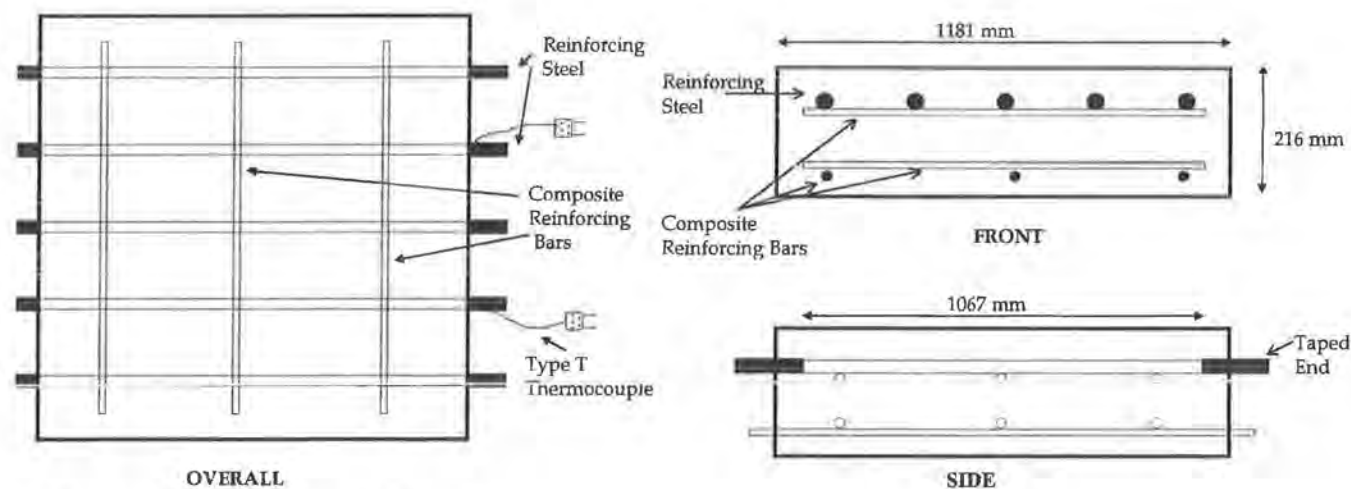


FIGURE 1   Reinforced concrete slab design.

TABLE 1  Posttreatment Test Matrix

|  | Admixed Chloride, kg/m³ | | | | | |
|---|---|---|---|---|---|---|
|  | 0.0 | 0.35 | 0.71 | 1.4 | 2.8 | 5.7 |
| Measured Cl | | | | | | |
| Acid Soluble | 0.00 | 0.20 | 0.54 | 1.4 | 2.7 | 5.5 |
| Water Soluble | 0.00 | 0.19 | 0.50 | 1.3 | 2.5 | 5.1 |
| Treatment | | | | | | |
| None | 1 | 1 | 1 | 1 | 1 | 1 |
| Partial | 0 | 1 | 1 | 1 | 1 | 0 |
| Full | 1 | 1 | 1 | 1 | 1 | 1 |

were somewhat variable and the concrete temperature generally was less than the ambient temperature. The concrete temperatures varied from a high of about 28°C during the summer months to a low of about 7°C during the winter months.

Figures 3 and 4, 5 and 6, 7 and 8, and 9 and 10 present the corrosion potential and rates for the fully treated and untreated slabs for the 0.00, 2.88, and 5.76 kg/m³ series, respectively. Admixed series 0.36, 0.72, and 1.44 kg/m³ are not presented because these relatively low admixed chloride content series are very similar to the control series of 0.00 kg/m³.

## Control Zero Admixed Chloride, Full Treatment

As shown in Figure 3, the corrosion potentials for the control zero admixed chloride full-treatment test were

generally positive throughout the test period for both the treated and the untreated zero admixed chloride slabs. Also, there is no significant difference between the treated and the untreated slabs. Thus, the APCI appears to have no influence on the corrosion potential measurements, and these slabs show a very low probability of active corrosion.

The corrosion rates were the same for both slabs before treatment. After treatment, the corrosion rates for the treated slab were significantly greater for all measurement periods except the last, about 1 year after treatment. However, in the author's experience, the corrosion rate values presented in Figure 4 would be indicative of very little active corrosion. Also, it must be pointed out that the formation of the passive layer on steel in concrete is a continuous but diminishing process with embedment time.
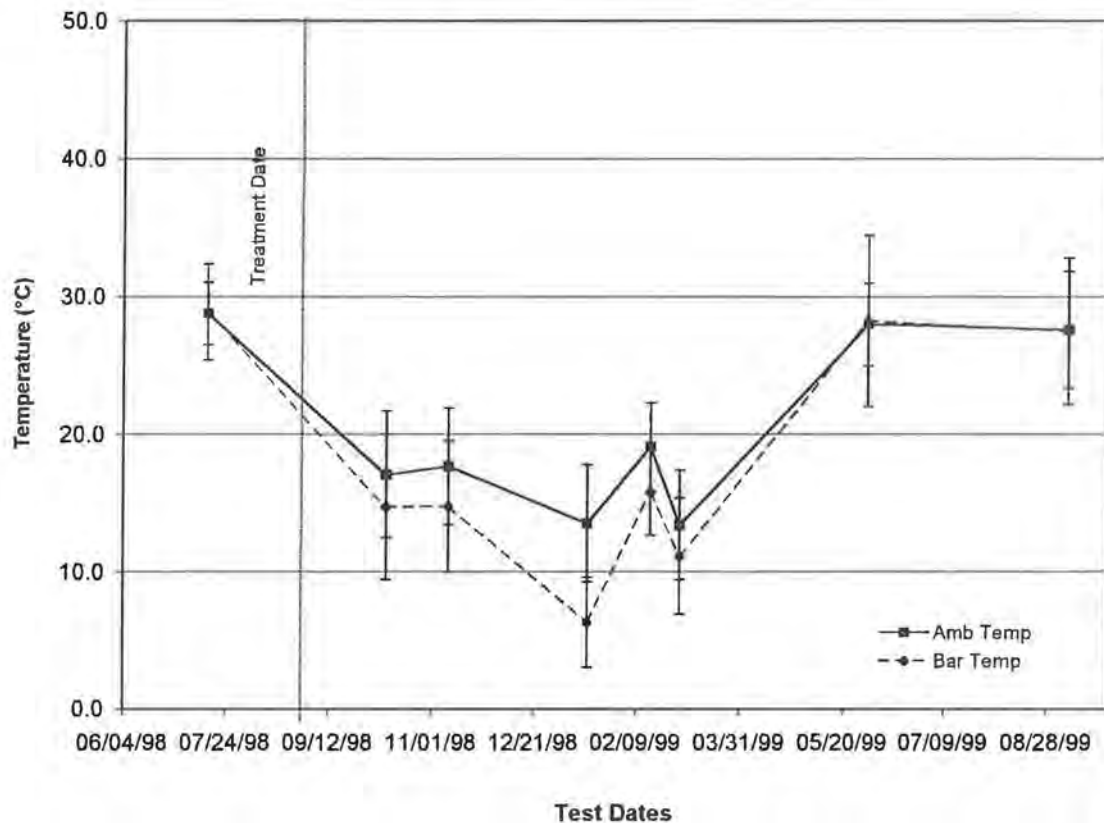


FIGURE 2  Average and 95 percent confidence limits of ambient and concrete temperature at bar depth.
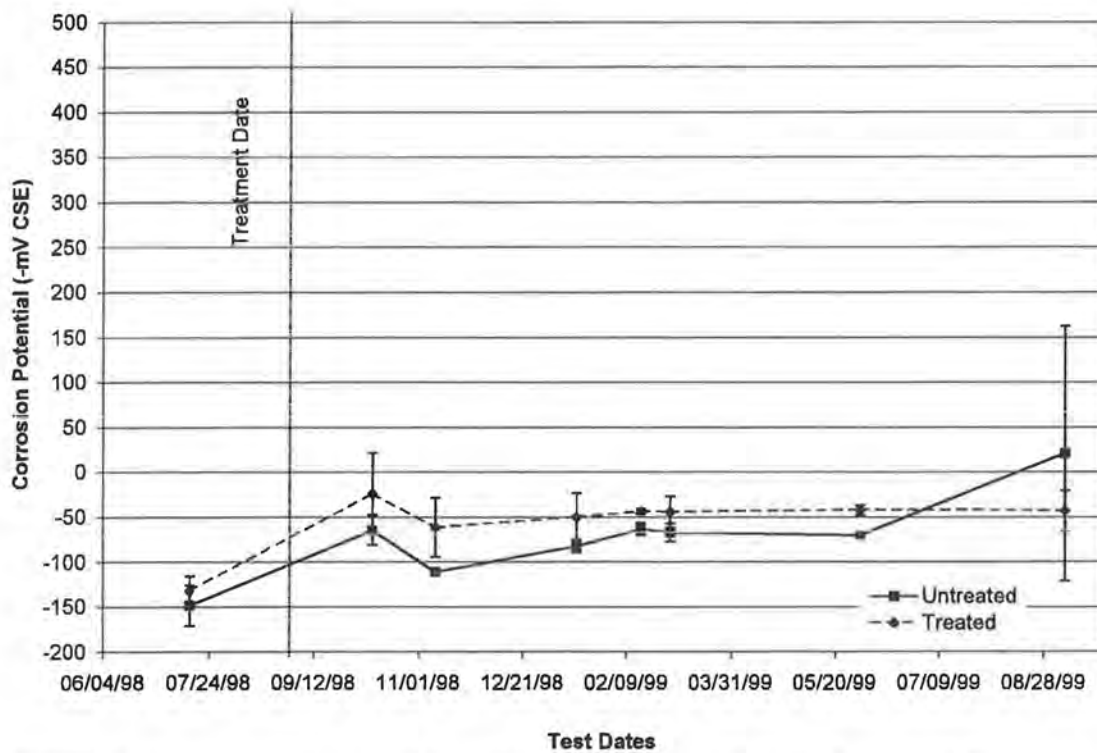
FIGURE 3    Average corrosion potentials and 95 percent confidence limits for the control full treatment series of zero admixed chlorides.
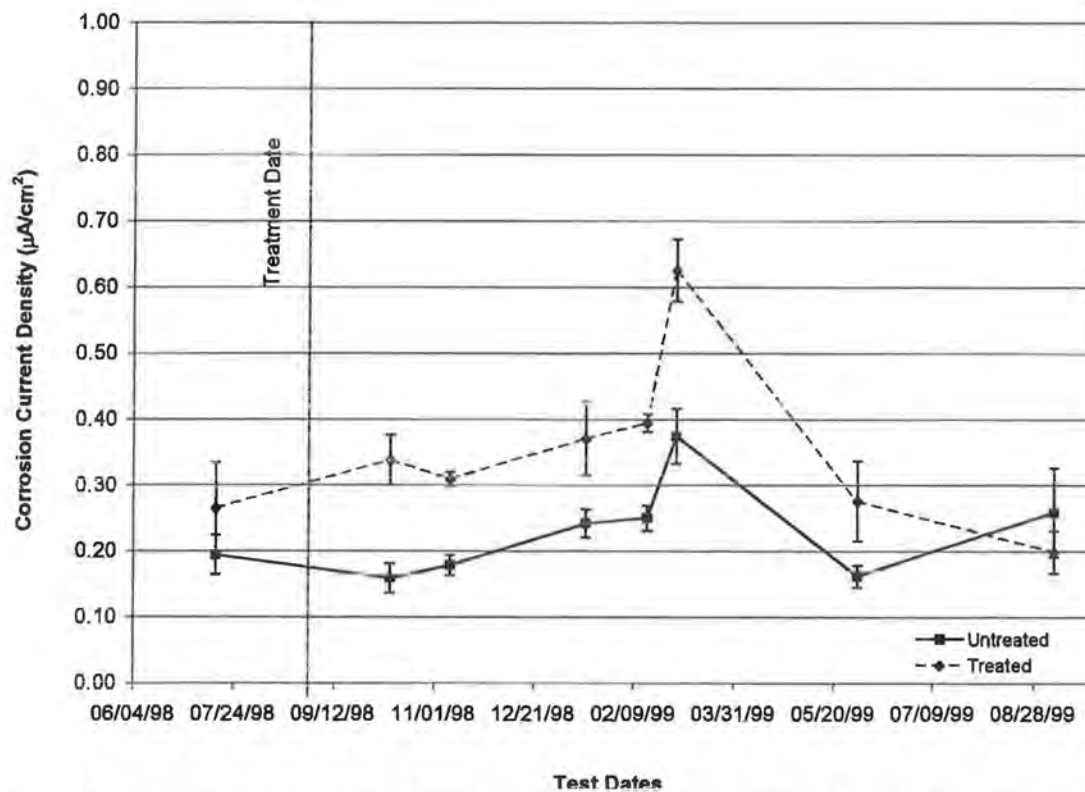


FIGURE 4    Average 3LP corrosion current density and 95 percent confidence limits for the control full treatment series of zero admixed chlorides.
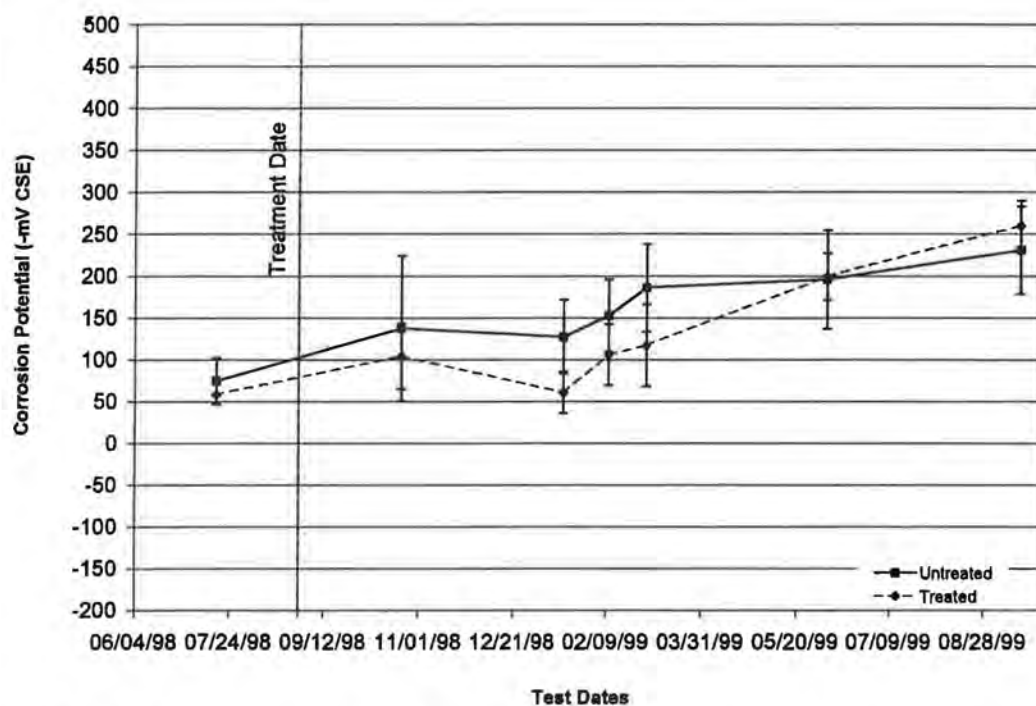
FIGURE 5    Average corrosion potentials and 95 percent confidence limits for the 2.88 kg chloride admixed full treatment series.
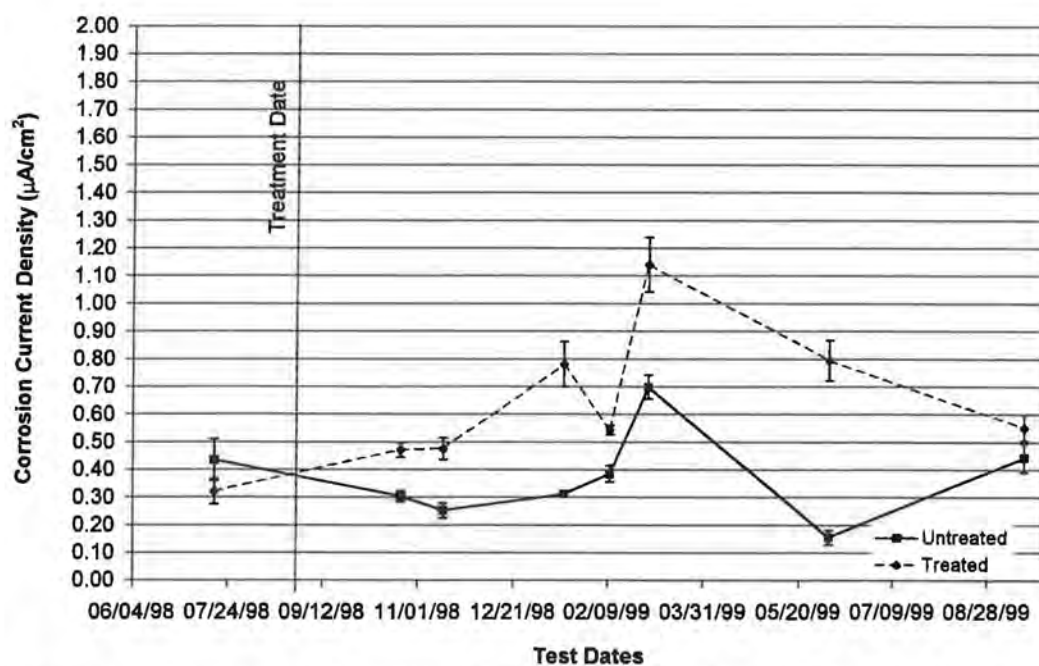


FIGURE 6    Average corrosion current density and 95 percent confidence limits for the 2.88 kg chloride admixed full treatment series.
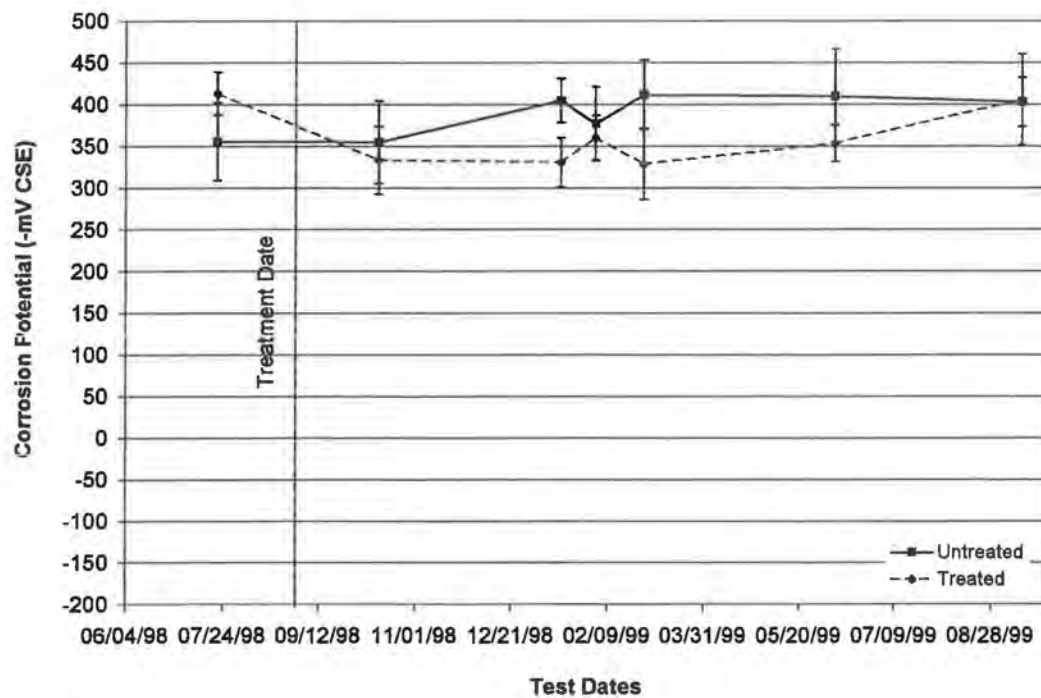
FIGURE 7 Average corrosion potentials and 95 percent confidence limits for the 5.76 kg chloride admixed full treatment series.
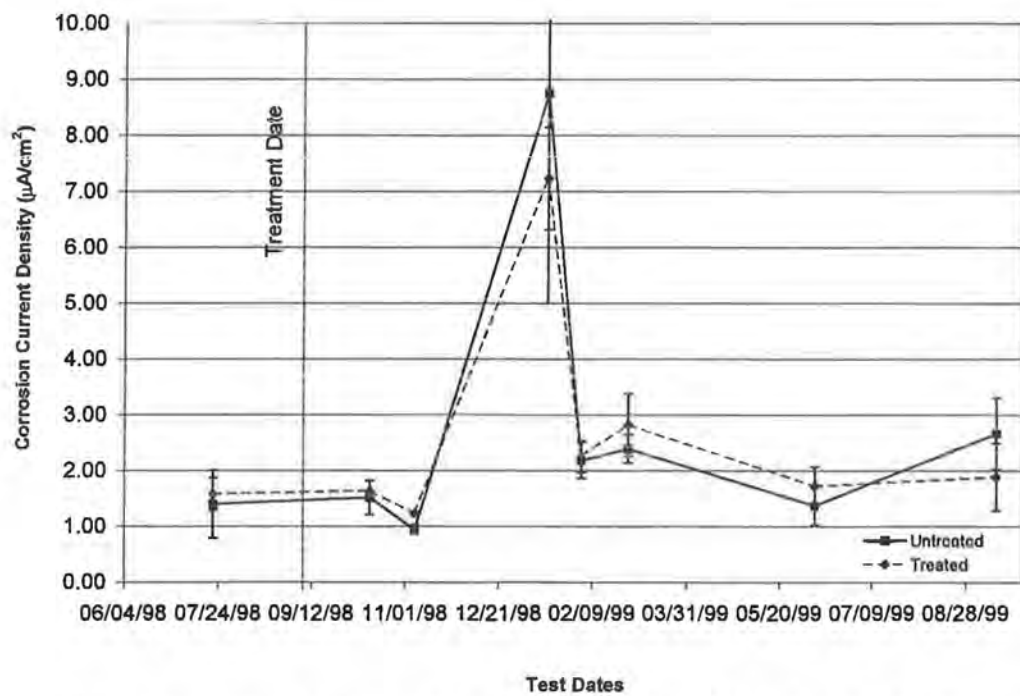


FIGURE 8 Average corrosion current density and 95 percent confidence limits for the 5.76 kg chloride admixed full treatment series.
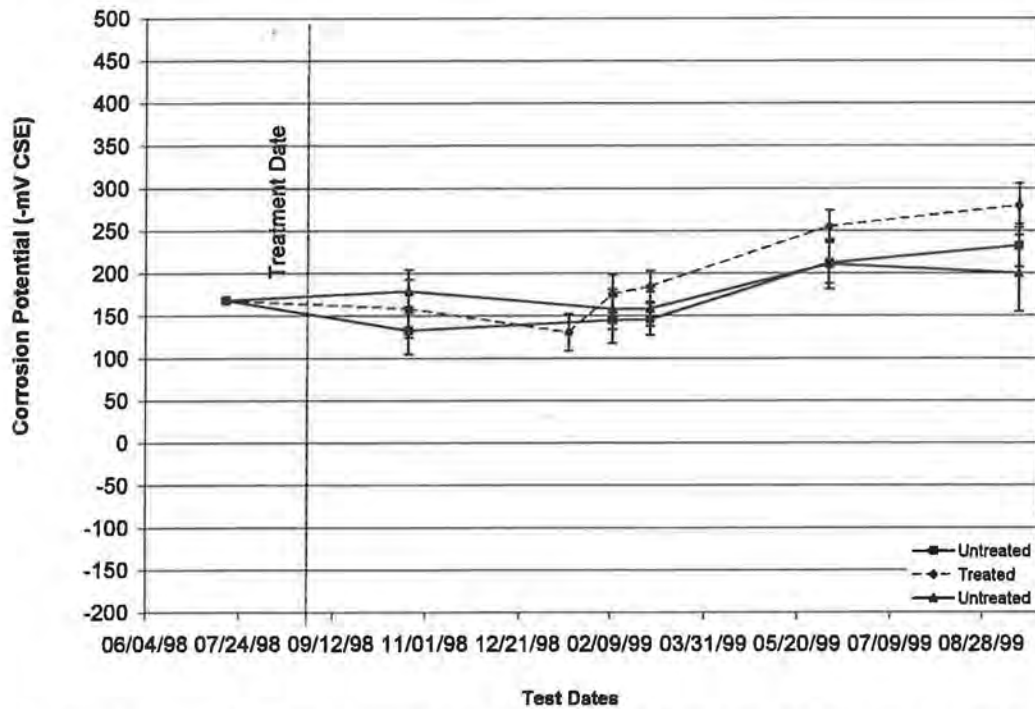
FIGURE 9   Average corrosion potentials and 95 percent confidence limits for the 2.88 kg chloride admixed partial treatment series.
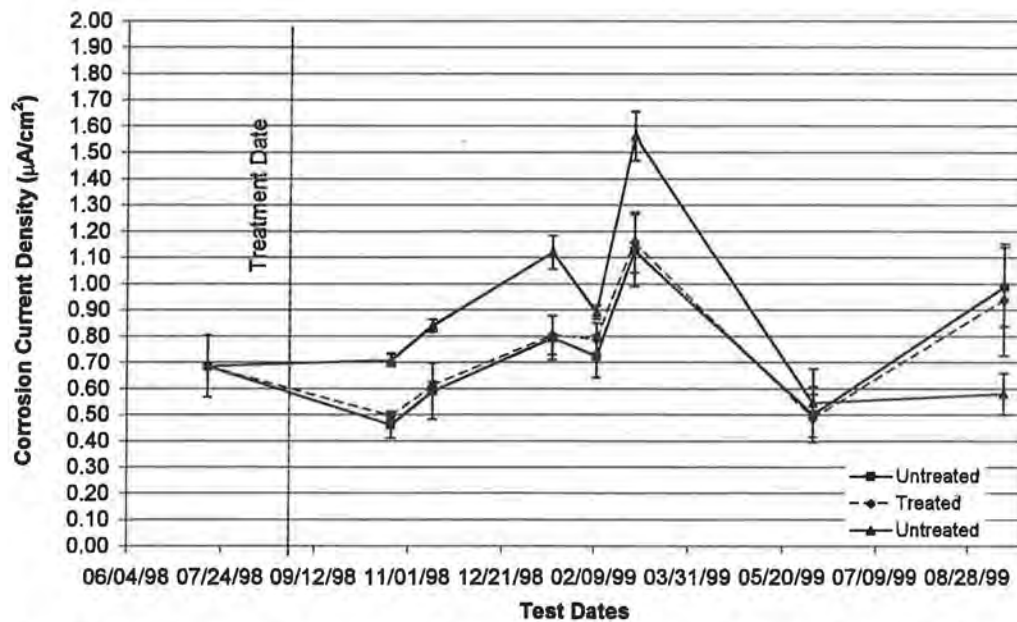


FIGURE 10   Average corrosion current density and 95 percent confidence limits for the 2.88 kg chloride admixed partial treatment series.

## 2.88 kg Series, Full Treatment

As shown in Figure 5, the corrosion potentials for the full-treatment 2.88 kg series were the same before treatment and throughout the 1-year assessment period. In general, the treated slab potentials were less negative than those for the untreated slab. The potentials become more negative throughout the test period, averaging about −60 mV CSE before treatment and about −200 mV CSE after 1 year. Accepted interpretation of these low negative values is that there is a less than 90 percent probability of active corrosion.

The corrosion rates for the 2.88 kg/m³ series were the same before treatment; see Figure 6. After treatment, the corrosion rates were significantly higher for all measurement periods except at the 1-year period. The corrosion rates for this series are greater and are indicative of active corrosion conditions although the corrosion potentials are relatively low negative values.

## 5.76 kg Series, Full Treatment

The corrosion potentials before full treatment for the 5.76 kg series and throughout the assessment period of 1 year after treatment were generally more negative than the 90 percent probability of active corrosion value of −350 mV CSE; see Figure 7. There was no significant difference between the treated and the untreated slab potentials before and after treatment.

As shown in Figure 8, the corrosion rates were more active and ranged between 1 and 3 μA/cm² throughout the test period, except for large spiked measurement of about 8 μA/cm² at about 6 months after treatment. The corrosion rate values indicate moderate active corrosion condition, 1 to 3 μA/cm², and highly active corrosion at 8 μA/cm². There is no significant difference between the corrosion rate before or after treatment.

## 2.88 kg Series, Partial Treatment

The measurements for the partial-treatment slabs with 2.88 kg chloride were taken at the center of the treatment strip and along both interface lines between treated and

untreated zones. Figures 9 and 10 present the corrosion potentials and rates for these conditions. As shown, the results are very similar to those for the fully treated series (see Figures 5 and 6). Thus, there appears to be no significant difference between the untreated and the treated sections and no reduction in corrosion activity.

## DISCUSSION OF RESULTS

For these APCIs to extend the service life of structures undergoing active chloride induced corrosion, they must

- Penetrate the cover concrete to depth of the reinforcing steel;
- Penetrate accumulated corrosion products in pitting cells to the depth where oxidation of the iron is occurring, or retard or stop the cathode reaction; and
- Inhibit active chloride induced corrosion cells in the presence of relatively high chloride concentrations.

To determine if the APCI penetrated the cover concrete, the manufacturer's representative conducted a qualitative color test and quantitatively determine the presence of the APCI in the cover concrete. The representative was first given a blind test with cores taken from treated and untreated slabs. The results of this blind test demonstrated that the color test could differentiate between the treated and untreated slabs. Subsequent tests were conducted on four cores, one each from the 0.36, 1.44, 2.88, and 5.76 kg/m³ series. Table 2 presents the results of the color and measured APCI concentrations.

As shown in Table 2, the color test showed a presence of the APCI in the concrete at all five depths for the four cores except for the 51- to 63-mm depth of the 2.88 kg admixed chloride series core. The concentration of the APCI deceased rapidly from the 13-mm depth to the 13- to 25-mm depth and continued to decrease with depth. At the depth of the reinforcing steel, the concentration of the APCI was less than 13 parts per million for three of the cores and was not detected in one of the cores. Thus it appears that the APCI did penetrate the concrete to the depth of the reinforcing steel. Also, there appears to be some relationship between color intensity and concentration. Per the manufacturer's representative, if the color test

TABLE 2  APCI Color Test and Concentration

| Depth mm | 0.35 | | 1.4 | | 2.8 | | 5.7 | | | |
| | Color Intensity | Concen. ppm | Color Intensity | Concen. ppm | Color Intensity | Concen. ppm | Color Intensity | Concen. ppm | Color Intensity | PPM |
|---|---|---|---|---|---|---|---|---|---|---|
| 0-13 | S | 1813 | VS | 650 | S | 1743 | VS | 1743 | VS | 650, 1097 |
| 13-25 | M | 338 | S | 113 | S | 391 | S | 391 | S | 1813, 113, 44, 312, 1743, 391 |
| 25-38 | M | 208 | S | 44 | M | 149 | M | 149 | M | 338, 208, <13, 95, 149 |
| 38-51 | W | 70 | M | <13 | VW | 34 | W | 34 | W | 70, <13, 51, 26 |
| 51-63 | VW | <13 | W | <13 | ND | <13 | W | <13 | VW | <13, 34 |

Note: VS: Very Strong; S: Strong; M: Moderate; W: Weak; VW: Very Weak; ND: Not Detected

detects the presence of the APCI at a very weak level, the concentration is sufficient to be an effective corrosion inhibitor. Also, it has been reported that this APCI should have penetrated to a depth of 80 mm in 28 days at the lowest penetration rate and that the APCI is effective for chloride contents up to 2 percent by weight of cement (4). For this case, the highest chloride content of 5.7 kg/m$^3$ was less than 2 percent by weight of cement (377 kg/m$^3$) or 7.5 kg/m$^3$ concrete. Thus, the APCI should have demonstrated a reduction in active corrosion of the test period for the reported test conditions. However, the APCI did not show any reduction in active corrosion of these test conditions over the 1-year test period.

Questions remain. Was the APCI chemically adsorbed on the steel surface? What concentration on the steel surface is needed to reduce or stop corrosion? Also, at what APCI/chloride ratio is the inhibitor effective? It should be pointed out that the APCI concentrations were measured in the concrete. Thus, is the APCI primarily absorbed on hardened cement surfaces rather than the corroding steel surface, and does the color test measure the active corrosion inhibitor or some other chemical compound in the inhibitor?

## CONCLUSIONS

Two conclusions may be gleaned from the results of this study. APCI penetrated the cover depth and the concentration decreased rapidly with depth. For the conditions of 50 mm of 0.45 w/c cover concrete, acid-soluble chloride contents of 0.20 to 5.5 kg/m$^3$ concrete, or water-soluble chloride contents of 0.19 to 5.1 kg/m$^3$ concrete, the APCI was not an effective posttreatment method.

## ACKNOWLEDGMENTS

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