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A TIME-RELEASE TECHNIQUE FOR CORROSION PREVENTION

C.M. Dry[1] and M.J.T. Corsaw
School of Architecture, University of Illinois at Urbana-Champaign,
Champaign, IL 61820 USA

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ABSTRACT

Researchers at the University of Illinois have developed an anti-corrosion system that is activated automatically where and when it is needed. Porous fibers are filled with calcium nitrite and coated with a salt-sensitive substance to control the response. The release of the corrosion inhibitor chemical is at the portion of the reinforcing bar in danger of corrosion when conditions would allow corrosion to initiate. In a series of tests with concrete samples containing either no protection or the conventional freely mixed calcium nitrite, this system performed well in that it delayed the onset of corrosion by at least three weeks in the laboratory specimens and reduced the amount of total corrosion by more than half. © *1998 Elsevier Science Ltd*

Introduction

Corrosion of embedded steel is one of the most significant concerns in the concrete industry today. Repair to corrosion-deteriorated structures costs the United States $325 million to $1 billion annually in the replacement of roadways, bridges, parking garages, and coastal buildings (1). The corrosion of steel reinforcing is usually caused by chloride ions that penetrate the concrete. Chloride sources include deicing salts and marine waters. The deterioration of concrete is a result of the expanding volume inside the concrete due to the corrosion products. Resultant tensile forces cause cracking and spalling, which increase the access of oxygen, water, and chloride to the bar, accelerating the process of corrosion.

In concrete, rebar is protected against corrosion by the high pH of the pore solution, however, the situation changes if chloride ions are present. The ions initiate the corrosive attack at defects in the passivating layer and react with iron to initiate corrosion. A series of reactions then occurs, resulting in autocatalytic damage. The volume of corrosion products formed exerts tensile forces on the concrete, causing cracking (2). Once the cracking is visibly noticeable, the structure usually requires significant and costly repair.

Methods to protect concrete reinforcing steel against corrosion include the use of sealers, such as silanes or siloxanes, and additives, such as microsilica and calcium nitrite. Sealers are sometimes unsuccessful because of their inability to protect the concrete if cracking occurs after treatment. Also, some commercially available sealers may actually increase the amount

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[1] To whom correspondence should be addressed.

of water absorption after application, providing easier penetration of chloride ions (3). In some structures containing microsilica, full-depth cracking has occurred due to high autogenous and drying shrinkage (4). Concretes containing calcium nitrite have generally performed extraordinarily well; however, it may affect the set time of the concrete.

Goals

Researchers at the University of Illinois School of Architecture have investigated a novel way of protecting steel reinforcement against corrosion. The method uses the corrosion-inhibiting properties of calcium nitrite, but it is not used as an admixture, eliminating the effects on set times (5). The goals of the project were to reduce the early initiation of corrosion and the cumulative amount of corrosion damage after initiation by providing corrosion prevention when and where the need occurred.

The system involves the use of coated hollow polypropylene fibers to dispense the calcium nitrite. The fibers are placed adjacent to the steel reinforcing in the concrete specimen. The calcium nitrite is contained within the fibers, but because they are porous, the fibers must be treated with a coating to maintain the containment. The coating controls the time-release of the calcium nitrite, ideally by responding to the environment of the pore solution. Polyol, one of the two coatings used by the researchers, breaks down in the presence of chloride ions. In this environment, corrosion would be possible because the protective passivating layer of steel is endangered by the presence of these same chloride ions. Therefore, at the time corrosion initiation could begin, the polyol coating dissolves, releasing the calcium nitrite. The second coating, paraffin wax, was applied to another set of fibers to simulate a mechanical release response. In this case, the rebar was heated to melt the wax, releasing the calcium nitrite. This system used an exterior source to trigger a response.

Both methods of response were investigated in the study. The specimens were compared to specimens without any corrosion-inhibitor and specimens with freely mixed calcium nitrite (the traditional method). The results of this study are presented herein and extrapolated to real life applications.

Testing

Tests were based on the ASTM "Standard Test Method for Determining the Effects of Chemical Admixtures on the Corrosion of Embedded Steel Reinforcement in Concrete Exposed to Chloride Environments" Designation G 109-92 (6). Four types of specimens were tested with two samples in each group. These types were: controls with no corrosion inhibitors, specimens with calcium nitrite freely mixed throughout the concrete as an additive, and two groups containing the time-release methods of protection. The systems were compared on the basis of the time to initiation of corrosion and the amount of corrosion occurring over time. In addition to using the total corrosion calculations discussed in ASTM, the data were evaluated according to two methods of corrosion classification criteria, one as described by Rodriguez, Ortega, and Garcia and the other by Broomfield (9,10). The samples were also opened for visual inspection to corroborate the electrochemical measurements.

The methods outlined in ASTM G 109-92 may be used when "determining the effects of chemical admixtures on the corrosion of metals in concrete." It can also be used to "evaluate materials intended to inhibit chloride-induced corrosion of steel in concrete" (7). ASTM

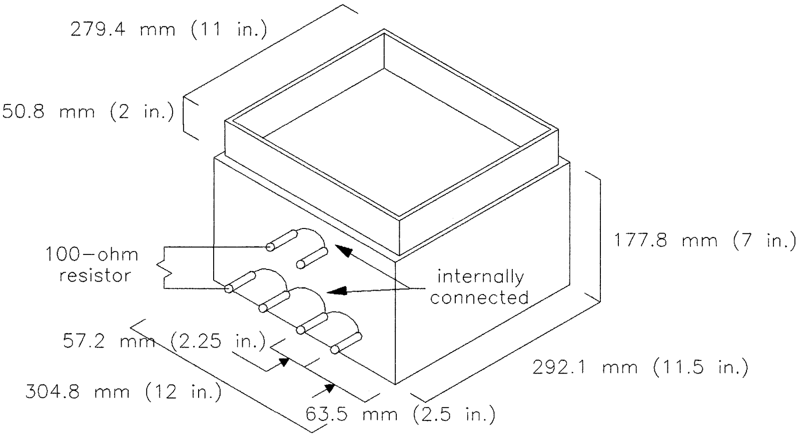

FIG. 1
Diagram of Sample Set-up

specified sample sizes and some of the measurement procedures were altered according to the needs of this specific project. The exact procedure was as follows.

The samples measured 177.8 mm (7 in.) tall by 304.8 mm (12 in.) wide and 292.1 mm (11.5 in.) deep. They contained six reinforcing bars of ASTM A36 steel with 38 mm (1½ in.) of cover, positioned and connected as shown in Figure 1. Each reinforcing bar was 381 mm (15 in.) long with 38.1 mm (1.5 in.) of each end coated using a waterproof paint. The internal connections were protected with silicon caulk. The mix for each group is shown in Table 1. The samples were manually vibrated and cured in a water bath for 28 days.

The controls and the freely mixed calcium nitrite groups were made according to the ASTM standard. For the two fiber groups, all six rebars were wound as shown in Figure 2

TABLE 1
Mixes for sample groups.

Group	Controls	Freely mixed $Ca(NO_2)_2$	Fibers coated w/wax	Fibers coated w/polyol
type 1 Portland cement	273.12 kg	273.12 kg	273.12 kg	273.12 kg
chloride-free aggregate, max. size 0.75 in. dia.	820.12 kg	820.12 kg	820.12 kg	820.12 kg
chloride-free sand	546.24 kg	546.24 kg	546.24 kg	546.24 kg
air-entraining liquid	4.33 mL	4.33 mL	4.33 mL	4.33 mL
water (0.5 W/C ratio)	136.28 kg	136.28 kg	136.28 kg	136.28 kg
$Ca(NO_2)_2$	—	4.26 mL/kg	fiber contained	fiber contained
Kurland ASTM A36 steel	6 bars	6 bars	6 bars	6 bars
polypropylene fibers	—	—	approx. 13 fibers per bar, 400 micron inside dia., 40% porosity	approx. 13 fibers per bar, 400 micron inside dia., 40% porosity

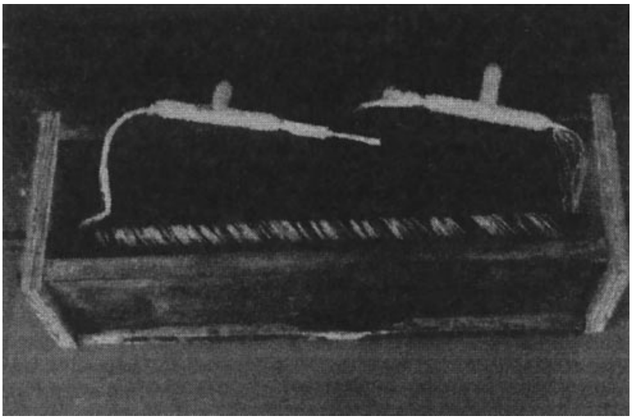

FIG. 2
Fiber-wound rebar.

with approximately 13 fibers that had already been coated in either wax or polyol. These fibers were hollow, porous polypropylene fibers with a 400-micron inside diameter and 40% porosity. They were filled by placing the fibers and a solution of calcium nitrite into a vacuum flask and using vacuum saturation techniques to draw the calcium nitrate into the fibers. After treatment, the fibers were weighed to confirm the uptake of the calcium nitrite solution. The soaked fibers were then coated in a molten bath with either wax or polyol.

One week after being removed from the water bath, the top two rebars of each sample were heated with a heating element, wattage 900-1600 w, for 30 min. (This melted the wax coating in two of the samples. The other samples were heated for consistency.) A plexiglass dam was built on each sample and sealed with silicone caulk to allow salt water to be ponded as shown in Figure 1. The samples were ponded 1 week with a salt water solution that was 1.321% sodium chloride (0.226 M) and then allowed to dry 1 week with readings taken every week. The environment of the samples was kept constant at 32°C throughout both ponding and dry cycles using a thermostat and heat lamps.

The voltage drop across a 100-ohm resistor, which was connected externally between the anode and cathode, was measured weekly. The results are shown in Table 2.

For further comparison, the ASTM G-109-92 equations for total corrosion were applied: "calculate the current flowing, I_j, from the measured voltage across the 100-ohm resistor, V_j, measured in volts as: $I_j = V_j/100$."

$$I_j = \frac{1.88 \text{ mV}}{100} \times \frac{\text{V}}{1000 \text{ mV}} = 0.0000188 \text{ amps}$$

Next, the total integrated current is calculated from:

$$\text{“}TC_j = TC_{j-1} + [(t_j - t_{j-1}) * (i_j + i_{j-1})/2]$$

where: TC = total corrosion (coulombs), t_j = time (seconds) at which measurement of the macrocell current is carried out, and i_j = macrocell current (amps) at time, t_j" (8). $TC_1 = TC_0 + [(1 - 0) * 604800 * (0.0000188 + 0)/2] = 0 + [1 * 604800 * 0.0000094] = 5.69$ C. The results of these calculations are shown in Figure 3.

TABLE 2
Voltage drop across 100-ohm resistor (mV).

Week	Control 8	Control 9	Freely mixed $Ca(NO_2)_2$ 10	Freely mixed $Ca(NO_2)_2$ 11	Fibers w/ $Ca(NO_2)_2$ coated in wax 12	Fibers w/ $Ca(NO_2)_2$ coated in wax 13	Fibers w/ $Ca(NO_2)_2$ coated in polyol 14	Fibers w/ $Ca(NO_2)_2$ coated in polyol 15
1	1.88	2.82	0.18	0.53	0.00	0.00	0.00	0.10
2	2.44	3.05	0.20	2.20	0.00	0.00	0.00	0.20
3	2.48	3.72	0.70	2.60	0.00	0.00	0.00	0.30
4	2.56	3.84	0.80	2.80	0.00	0.00	0.10	0.40
5	2.84	3.55	0.80	2.80	0.20	0.00	0.20	0.70
6	1.46	2.93	0.50	2.40	0.80	0.20	0.30	1.00
7	1.44	2.16	0.40	1.80	0.80	0.40	0.40	1.20
8	1.48	2.22	0.25	2.25	0.80	0.40	0.40	1.20
9	1.60	2.00	0.30	2.28	0.90	0.40	0.40	1.30
12	1.31	2.29	0.30	2.30	0.80	0.40	0.40	1.40
13	1.21	1.98	0.50	2.50	1.40	0.20	0.20	0.90
14	0.84	1.46	0.20	0.90		0.20	0.00	0.20
16	1.30	2.30	0.50	2.50	0.40	0.00	0.50	1.50

Results

From the voltage drop data, some observations can be made. Increases in voltage indicate that corrosion has initiated. In both the controls and the samples with freely mixed calcium nitrite, these increases occurred within the first week. In three of the fiber samples, corrosion did not initiate until at least the fourth week. These calculations make it evident that the groups with the calcium nitrite in polypropylene fibers for time release had a significantly lower total corrosion than the controls or samples with freely mixed calcium nitrite. Figure 3 shows that the group with freely mixed calcium nitrite had varied results with one experiencing as much corrosion as the unprotected samples and the other as little as the experimental systems. The total corrosion in the group with wax coating had one quarter the corrosion of the freely mixed calcium nitrite and one sixth the corrosion of the control. The group with polyol coating on the fibers had less than half the corrosion the group with freely mixed calcium nitrite had and nearly one quarter that of the control.

Two other corrosion classification criteria were used to evaluate the data. The first as outlined by Rodriguez, Ortega, and Garcia (9) classified the samples into conditions of corrosion: 0.97 to 1.83 mA/m^2 passive, 1.83 to 4.95 mA/m^2 low, 4.95 to 9.9 mA/m^2 moderate, and greater than 9.9 mA/m^2 high. The second was discussed by Broomfield (10) using categories set up according to expected time of initiation: less than 1.83 mA/m^2 no corrosion expected, 1.83 to 10.12 mA/m^2 corrosion in 10 to 15 years, 10.12 to 101.18 mA/m^2 corrosion in 2 to 10 years, and greater than 101.18 mA/m^2 corrosion expected in 2 years or less. The condition of corrosion rating and expected time until the initiation of corrosion also supported the conclusion that time release method delayed the onset and severity of corrosion, as shown in Figure 4. Both the control group and the group with freely mixed calcium

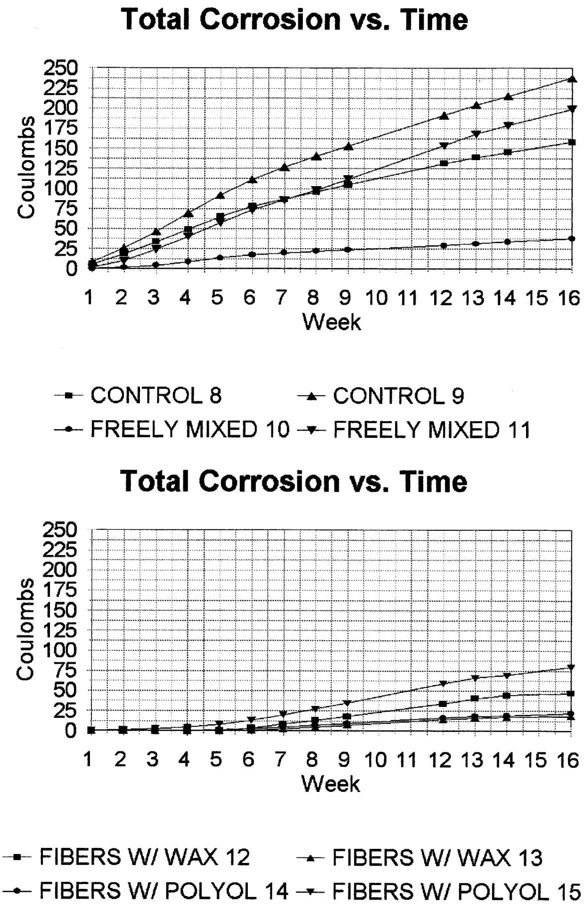

FIG. 3
Total Corrosion vs. Time.

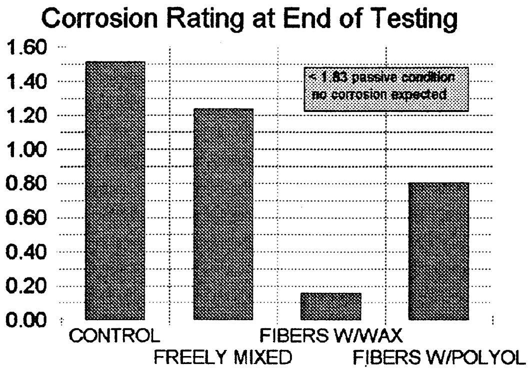

FIG. 4
Corrosion Testing at End of Testing.

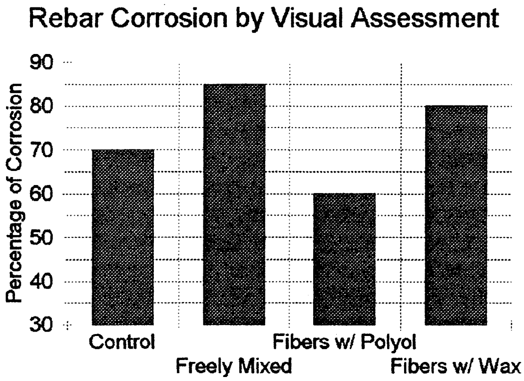

FIG. 5
Rebar Corrosion by Visual Assessment.

nitrite had much higher ratings than the other groups. In comparison, both groups of fiber samples had almost less than half the rating the control and freely mixed groups.

Visual inspection was the third method used to compare the performance of the various systems. The samples were broken open at the conclusion of the study. Two separate parties evaluated the surface area of the reinforcing bars affected by the corrosion and collaborated to reach the given percentages. As shown in Figure 5, the controls were 70% corroded and the freely mixed calcium nitrite samples were 90% corroded. The samples with calcium nitrite in polyol coated polypropylene fibers were 60% corroded and the wax coated appeared to be 85% corroded. The visual inspection corroborates the numerical findings of corrosion severity only for the polyol coated fibers.

Conclusion

The samples in which the time-release method of the calcium nitrite was employed have a later onset of corrosion that is also at a lesser intensity than the other samples. Applying these techniques would result in less corrosion in the field, lengthening the life of the steel reinforcing and thus, the structure. All methods of comparison, total corrosion, corrosion classification criteria, and visual inspection, supported this conclusion of improved performance of time release methods over current techniques. We hypothesize that the corrosion inhibitors were able to perform noticeably better because they were activated when and where they were needed at the onset of corrosion. Longer term research should be conducted on these methods to see if additional results are consistent with our findings.

Acknowlegment

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