

Effectiveness of corrosion inhibiting admixture combinations in structural concrete

Scott A. Civjan ^{a,*}, James M. LaFave ^b, Joanna Trybulski ^c, Daniel Lovett ^c,
Jose Lima ^d, Donald W. Pfeifer ^e

^a Department of Civil and Environmental Engineering, University of Massachusetts at Amherst, 235 Marston Hall, 130 Natural Resources Rd., Amherst, MA 01003, USA

^b Department of Civil and Environmental Engineering, University of Illinois, 3108 Newmark Lab, 205 N. Mathews Ave., Urbana, IL 61801, USA

^c Department of Civil and Environmental Engineering, University of Massachusetts at Amherst, 130 Natural Resources Rd., Amherst, MA 01003, USA

^d Research and Technology Development Section, Rhode Island Department of Transportation, Two Capitol Hill, Room 103, Providence, RI 02903, USA

^e Wiss, Janney, Elstner Associates, Inc., 330 Pfingsten Rd., Northbrook, IL 60062, USA

Received 22 March 2004; accepted 12 July 2004

Abstract

A long-term corrosion study was conducted to determine the effectiveness of calcium nitrite, silica fume, fly ash, ground granulated blast furnace slag, and DSS in reducing corrosion of reinforcing steel in concrete. Mixture proportions included single, double, and triple combinations of these admixtures. Non-cracked and pre-cracked slab specimens were evaluated by visual inspections, macrocell readings, half-cell potentials, and autopsies. Triple combinations of calcium nitrite, silica fume, and either fly ash or ground granulated blast furnace slag, as well as a double combination of calcium nitrite and ground granulated blast furnace slag, performed very well and are recommended in concrete mixtures exposed to severe corrosive environments. DSS outperformed the other admixtures for corrosion prevention in this study; however, it resulted in somewhat lower compressive strengths and had not been fully tested for effects on other concrete properties.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Admixture; Concrete; Corrosion; Durability; Pozzolan

1. Introduction

Corrosion of steel reinforcement in structural concrete exposed to the environment is a severe problem, especially in geographic regions where deicing salts are often used. It is common for highway departments to specify mineral and chemical admixtures in their concrete mixture proportions to minimize corrosion of rein-

forcement, thereby extending the life of a structure. Corrosion inhibiting admixtures generally work by one of two methods, namely by reducing the permeability of a concrete mixture or by interfering with the corrosion process at the reinforcement location. A variety of chemical and mineral admixtures are used in practice to reduce corrosion activity, including calcium nitrite (CN), silica fume (SF), fly ash (FA), and ground granulated blast furnace slag (BFS); other admixtures are available, but these four are the most commonly used. Newer “experimental” admixtures have also been developed, an example of which is an admixture containing disodium tetrapropenyl succinate (DSS). DSS is an

* Corresponding author. Tel.: +1 413 545 2521; fax: +1 413 577 4940.

E-mail address: civjan@ecs.umass.edu (S.A. Civjan).

experimental admixture that has only been used in limited research studies and field tests to date [1,2]. These five admixtures (CN, SF, FA, BFS, and DSS) are the focus of this study.

General literature reviews of concrete corrosion inhibiting admixture test reports have been presented by LaFave et al. [3] and Civjan et al. [4]. Therein it was reported that CN, SF, FA, and BFS have all proven effective for reducing corrosion of concrete reinforcing steel in a variety of experimental tests. However, these tests were typically conducted on concrete mixtures containing individual admixtures (often at relatively high dosages), with comparisons made to a control (no admixtures) and/or to another concrete mixture containing a different single admixture. There is very limited information regarding the corrosion inhibiting effectiveness of combinations of these admixtures. Only a few studies have been published using admixture combinations, and these were typically performed with combinations of at most two admixtures [4].

Results of the literature review showed favorable corrosion inhibiting properties for all five admixtures used in the current study. SF has also been shown to potentially lead to concrete cracking if not consolidated and cured under more rigorous standards than typical mixture designs, resulting in increased corrosion activity. Possible undesirable aspects of the other four admixtures include reduced long-term strength gain with CN, a decrease in chloride threshold with FA, delayed setting time with BFS, and a decrease in compressive strength with DSS [4].

A survey was conducted of the departments of transportation and highway departments in the six New England states to determine their use of chemical corrosion inhibitors and mineral durability enhancing admixtures in structural concrete [4]. All of these states except Vermont have used CN as a corrosion inhibitor, and all have also used mixture proportions containing SF, FA, and/or BFS. A majority of the New England states have used combinations consisting of one chemical and one mineral admixture, with even some limited use of CN in combination with multiple mineral admixtures reported. Connecticut and Rhode Island also reported recent use of amines and esters as an inhibitor. In recent years, most New England states have typically used epoxy coated reinforcing steel in conjunction with the corrosion inhibiting admixtures.

Typical New England highway department concrete mixture proportions employ a combination of two admixtures, with some including an additional mineral admixture. It is of interest to determine the effectiveness of these combinations and whether each additional admixture improves performance, or if there is possibly a single or double combination that is more effective. This study was undertaken to address these questions.

2. Testing program

An accelerated corrosion study was undertaken to evaluate the effectiveness of the following admixtures in structural concrete: CN, SF, FA, BFS, and DSS. The test regimen was a modification of ASTM G 109–99 [5], based on an approach used effectively on previous FHWA research projects [6]. Fourteen concrete mixtures were tested, as outlined in Table 1. Admixtures were applied at the following dosages: CN at 14.8 l/m³ (3 gal/yd³), SF at 6% cement replacement (by weight), FA at 15% cement replacement (by weight), BFS at 25% cement replacement (by weight), and DSS added at 1/2% cement content (by weight). Mixtures included a control (M1), single admixtures (M2 through M6), and double combinations (M7 through M10) or triple combinations (M11 and M12) of admixtures. Each double or triple combination included a chemical admixture (CN) in addition to one or two mineral admixtures (SF, FA, and/or BFS), except for M10 (CN/DSS). Two mixtures (M13 and M14) replicated admixture combinations (those of M7 and M11, respectively), but with a higher water-to-cementitious material (w/cm) ratio. Specimens were cast in replicates of three, with two non-cracked (“A” and “B”) and one pre-cracked (“C”), for each mixture. Cracks in the pre-cracked specimens extended to the level of reinforcement and simulated cracks parallel to and directly over the length of reinforcing steel embedded in concrete. This models the possibility of narrow cracks in a bridge deck that could allow direct access of chlorides to the reinforcing steel.

2.1. Test specimens

The type of test specimen used was chosen to approximate the situation of a concrete bridge deck with two layers of reinforcing steel. Slab specimen dimensions were 180 mm × 305 mm × 305 mm (7 in. × 12 in. × 12 in.), as indicated in Fig. 1. Each specimen had top and bottom 16 mm (5/8 in.) diameter (#5) “black” (uncoated) reinforcing steel bars with 25 mm (1 in.) clear cover. The clear cover used in the test specimens was somewhat less than would be expected in typical bridge construction, in order to accelerate the testing. Cracks in the pre-cracked specimens were formed using stainless steel metal shims (0.30 mm (0.012 in.) thick), cast into the concrete surface at the time of concrete placement and removed after the initial set of the concrete. During subsequent testing, the top surface of each specimen was exposed to chlorides, while the sides were sealed and the bottom surface was open to the air.

In Table 1, the total cementitious and pozzolanic material is reported as part of the cementitious materials (cm) in calculating the w/cm ratio, including portland cement, SF, FA, and BFS. A concrete w/cm ratio of

Table 1
Test specimens

Mix	Mix components	Specimen	Notes
M1	Control; w/cm = 0.40	M1A	M1A replaced
		M1A-R	
		M1B	Pre-cracked
		M1C	
M2	14.8 liter/m ³ CN; w/cm = 0.40	M2A	Pre-cracked
		M2B	
		M2C	
M3	6% SF; w/cm = 0.40	M3A	M3B replaced Pre-cracked
		M3B	
		M3B-R	
		M3C	
M4	15% FA; w/cm = 0.40	M4A	M4B replaced Pre-cracked
		M4B	
		M4B-R	
		M4C	
M5	25% BFS; w/cm = 0.40	M5A	Pre-cracked
		M5B	
		M5C	
M6	1/2 % DSS; w/cm = 0.40	M6A	Pre-cracked
		M6B	
		M6C	
M7	14.8 liter/m ³ CN + 6 % SF; w/cm = 0.40	M7A	Pre-cracked
		M7B	
		M7C	
M8	14.8 liter/m ³ CN + 15% FA; w/cm = 0.40	M8A	Pre-cracked
		M8B	
		M8C	
M9	14.8 liter/m ³ CN + 25% BFS; w/cm = 0.40	M9A	Pre-cracked
		M9B	
		M9C	
M10	14.8 liter/m ³ CN + 1/2 % DSS; w/cm = 0.40	M10A	Pre-cracked
		M10B	
		M10C	
M11	14.8 liter/m ³ CN + 6% SF + 15% FA; w/cm = 0.40	M11A	Pre-cracked
		M11B	
		M11C	
M12	14.8 liter/m ³ CN + 6% SF + 25% BFS; w/cm = 0.40	M12A	Pre-cracked
		M12B	
		M12C	
M13	14.8 liter/m ³ CN + 6% SF; w/cm = 0.47	M13A	Pre-cracked
		M13B	
		M13C	
M14	14.8 liter/m ³ CN + 6% SF + 15% FA; w/cm = 0.47	M14A	Pre-cracked
		M14B	
		M14C	

Note. All w/cm ratios are based on total cementitious material.

0.40 was used for 12 of the 14 mixtures to represent typical concrete per New England state highway department specifications. Two of the mixtures (M13 and M14) had a w/cm ratio of 0.47. This higher w/cm ratio is still within the expected range for normal AASHTO Class A (AE) 0.45 w/cm ready-mixed concrete specified

for bridge construction. While the lower w/cm ratio is more representative of actual concrete bridge mixture proportions, the resulting reduced permeability of the concrete could have required an extended time frame for obtaining significant results. The higher w/cm ratio of 0.47, therefore, allowed for additional acceleration

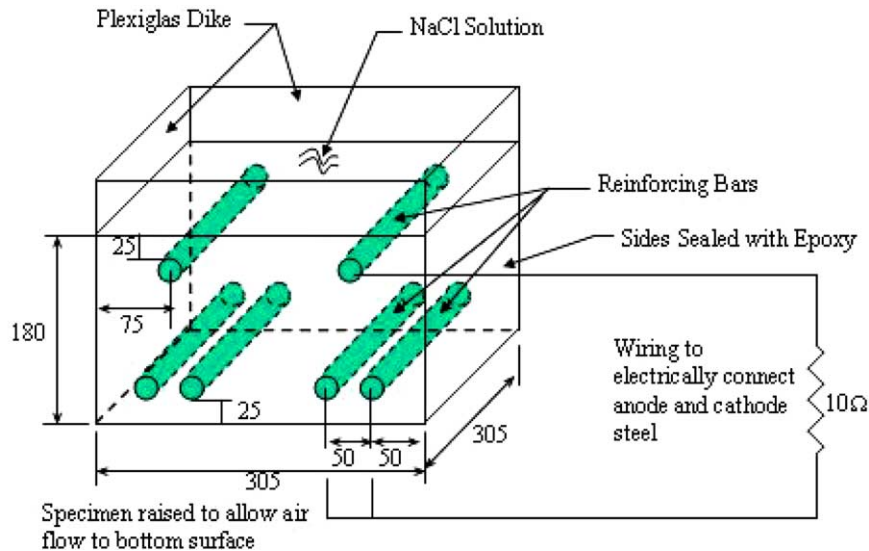


Fig. 1. Geometry of test specimens.

of testing, similar to in many other studies. However, those two mixtures may not completely accurately model admixture behavior in a more typical low w/cm mixture concrete. All of the concrete mixture proportions are specified in Table 2.

Coarse aggregate was 19 mm (3/4 in.) maximum size crushed stone conforming to AASHTO M 80-87 [7]. Fine aggregate conformed to AASHTO M 6-03 [8]. Both of the aggregates used are approved by the Massachusetts Highway Department, with aggregates from these sources currently used for highway projects in western Massachusetts. The bulk specific gravity was 2.9 and 2.7 for the coarse and fine aggregates, respectively, while the absorption capacity was 1.20% and 1.35% for the coarse and fine aggregates, respectively (ASTM C 127-01 [9], ASTM C 128-01 [10]). The coarse and fine aggregates were tested for acid soluble chloride content using ASTM C 1152-03 [11]; both aggregates contained less than 0.008% acid-soluble chloride.

Portland Type I/II cement (ASTM C 150-02 [12]) was used in all concrete mixtures. The SF conformed to ASTM C 1240-03 [13]. The Class F FA conformed to ASTM C 618-03 [14], and the ground granulated BFS conformed to ASTM C 595-03 [15]. The CN was used as a 33% solution in water and conformed to ASTM C 494-99 [16]. The DSS material was an experimental admixture provided as a 20% solution in water. The air-entraining admixture conformed to ASTM C 260-01 [17], while the superplasticizer was a Type F high-range water reducer conforming to ASTM C 494-99 [16].

The ASTM A 615 Grade 60 steel reinforcing bars were cut to length, drilled, and tapped to receive a 1/4 × 20 bolt for holding a lead wire in contact with the end of the bars. The reinforcing bars were wire-brushed to remove mill scale and any corrosion products

and were then placed in an oven at 115 °C (240 °F) to remove any moisture and minimize corrosion. The bars were kept in the oven until shortly before concrete placement.

Concrete was mixed and placed in accordance with ASTM C 192-02 [18]. The specimens were cured under wet burlap and polyethylene film for a period of approximately four days; this curing represents realistic construction field conditions. Compressive strengths were determined based on concrete cylinder tests at 28 days; these results are presented in Table 2, along with the air content (per AASHTO T 199-00 [19]) and slump values determined at the time of casting.

After a minimum of eight weeks at ambient laboratory conditions, the sides of the specimens were sealed with two coats of epoxy to prevent any chlorides from reaching the reinforcing steel from the specimen sides. A plexiglas dike around the top edges contained the chloride solution during periods of ponding. The specimens were placed on a plinth of wood that allowed free circulation of air to the underside of the specimens. Top and bottom reinforcing steel layers were electrically connected with a 10-Ω resistor between one of the top reinforcing bars and the corresponding two bottom bars (Fig. 1). A 10-Ω resistor was recommended by McDonald et al. [6], who showed shorter stabilization times using this arrangement.

Delays in the manufacture and delivery of DSS caused testing of mixtures M6 and M10 to begin one complete ponding cycle (24 weeks, as described in more detail below) after the others. At that time, three other non-cracked specimens (M1A, M3B, and M4B) were replaced due to early cracking. The replacement specimens are designated with an “R” after the mixture designation. The macrocell and half-cell readings, described in more detail below, correlating to the replaced specimens

2.3. Corrosion activity monitoring

Four evaluation methods were used to record the amount of corrosion activity in the specimens: visual inspections, half-cell potential readings, macrocell corrosion readings, and destructive evaluations (“autopsies”). The first of these simply involved periodically examining the specimens for any changes in appearance, including rust or precipitate on the surface, and measuring the width of any cracks that developed.

Copper–copper sulfate half-cell potential readings were used to evaluate corrosion activity, per ASTM C 876-91 [20]. A lead wire from a high-impedance voltmeter was connected to one of the top reinforcing bars in a test specimen, while the other terminal of the voltmeter was connected to the half-cell, which was placed on the top concrete surface of the specimen above the reinforcement, using a properly prepared electrical junction device. The magnitude of the electrical half-cell potential is considered to be an indicator of whether or not there is active reinforcing steel corrosion; potentials more negative than a critical value indicate a high probability of corrosion. ASTM C 876-91 specifies that potentials greater (more positive) than -0.20 V or less (more negative) than -0.35 V indicate 90% probabilities of no corrosion activity or of corrosion activity, respectively. Others have found that potentials more negative than about -0.24 V almost always signify active corrosion in laboratory testing [6,21]. Therefore, for the current study, potentials of -0.24 and -0.35 V were both used as reference points. Half-cell readings were taken at the conclusion of ponding during the wet/dry cycles (once per week) and from one to three times during the continuous (12-week) ponding periods.

Macrocell corrosion current was obtained by measuring the voltage across a resistor between each set of one top and two bottom reinforcing bars. This is a measure of the mass of reinforcing steel consumed by the corrosion process (or extent of corrosion). The top steel (exposed to chloride-rich concrete) acted as the anode, and the bottom steel (in low-chloride concrete) acted as the cathode. Macrocell readings measure the activity level of electron flow from the anodic to the cathodic steel through the concrete. Macrocell corrosion readings were taken every weekday during the wet/dry cycles, and every other weekday (Monday, Wednesday, and Friday) during the continuous 12-week ponding periods.

The macrocell readings were converted into iron loss data. The conversion was made by dividing the voltage from each reading by the value of the resistor ($10\ \Omega$) and then multiplying this result by the average number of hours at that reading, providing cumulative corrosion current. The corrosion current was then used to calculate the percentage of iron lost from each reinforcing bar, using the following expression [6,22]:

Metal loss in grams/amp-hour

$$\begin{aligned}
 &= \text{atomic weight} / [(\text{Faraday's constant}) \\
 &\quad * (\text{electron charge change})] \\
 &= \frac{(55.8\ \text{g/mol})(3600\ \text{s/h})}{96489(\text{amp s})/\text{mol}(2\ \text{electrons})} \\
 &= 1.04\ \text{g/amp-hour}.
 \end{aligned} \tag{1}$$

Finally, two specimens from each mixture, the pre-cracked specimen and one of the non-cracked specimens (one non-cracked specimen only for mixtures M6 and M10), were destructively evaluated for visual assessment of rusting on the surface of the reinforcing bars at the conclusion of testing. Chloride contents of the autopsied non-cracked specimen from each mixture were also determined. Holes were drilled to a 38 mm (1 1/2 in.) depth in the concrete, and the displaced material corresponding to three different depths was recovered. Analysis was done in conformance with AASHTO T 260-97 [23], reporting water-soluble chloride.

3. Test results

The performance of the reinforced concrete slab test specimens was evaluated through visual inspections, half-cell data, macrocell data, autopsies, and chloride ingress testing. Presented data includes 108 weeks of testing on 40 test specimens (representing all fourteen concrete mixtures). Two non-cracked DSS specimens were autopsied (M6A and M10A) after 84 weeks of testing. Companion DSS specimens (M6B and M10B) include the full 108 weeks of data.

In addition to the corrosion properties studied, it was noted that a lower compressive strength (by about 25% in comparison with the control) was obtained from mixture M10 (CN/DSS); the mixture with only DSS (M6) also had a moderately lower compressive strength (Table 2). Concrete strength reduction has previously been identified as a possible concern with DSS materials [24]. For many corrosive environments, such as a typical deck slab, concrete strength is not critical. In addition, attained concrete strengths of DSS concretes can be high with proper attention to mix proportions. An increase in compressive strength (by about 15% in comparison with the control) was noted for mixtures that included BFS (M5, M9, and M12), as well as in mixtures with multiple mineral admixtures (M11 and M12).

3.1. Visual inspections

Crack measurements were obtained using a manual crack gage. When observed, crack widths usually stabilized at approximately 0.2 mm (0.01 in.), with the exception of the SF specimens where the cracks continued to widen throughout testing.

Mixtures for which the non-cracked specimens did not show any visible cracking at the conclusion of testing were CN (M2), DSS (M6), CN/FA (M8), CN/BFS (M9), and CN/DSS (M10). Other mixtures for which one of the two non-cracked specimens showed no visible cracking included BFS (M5), CN/SF/FA (M11), CN/SF/BFS (M12), CN/SF with the higher w/cm ratio (M13), CN/SF/FA with the higher w/cm ratio (M14), and the re-cast FA specimen (M4B-R).

Most pre-cracked specimens had crack extensions at the tips of the pre-formed cracks by the end of the first full 24-week cycle of ponding. Exceptions to this were specimens with DSS (M6C and M10C), which did not exhibit any crack extensions, and specimens with combinations of CN/SF/FA (M11C) and of CN/SF with the higher w/cm ratio (M13C), which took in excess of one year of testing to produce any crack extensions.

Time to cracking was generally not a good indicator of corrosion activity, compared to the half-cell and macrocell criteria described later. While time to cracking did provide information regarding the elapsed time until there was direct access to the reinforcing steel by chlorides, the cracks themselves were often more of a symptom of corrosion than a cause and thus were not an effective measure for evaluating the initiation of corrosion.

3.2. Half-cell potential data

Half-cell potential data for one of the sampling locations on non-cracked control specimen M1A-R is shown in Fig. 3(a). A noticeable increase in half-cell potential typically corresponded directly to a significant increase in macrocell corrosion readings (reported below). The time it took for the potentials to reach -0.24 and -0.35 V was noted; the first visible “jump” in potential readings was usually enough to exceed the -0.24 V value (but not necessarily -0.35 V). Macrocell corrosion data (reported in detail in the next section) indicated that initial macrocell corrosion activity usually occurred somewhere between the time it took the half-cell readings to reach -0.24 and -0.35 V. Furthermore, half-cell potentials of -0.35 V were never reached in some specimens where there was nonetheless clear evidence of corrosion as determined by autopsies.

Half-cell potentials of non-cracked specimens for the control and pozzolanic single admixtures (M1, M3, M4 and M5) exceeded -0.24 V within the first few weeks (less than 30 days) of testing, with the exception of M4-R. Non-cracked DSS (M6) and CN/DSS (M10) mixtures did not exceed -0.24 V throughout the testing program. The non-cracked CN (M2) mixture had only one of four locations reach -0.24 V (a few weeks prior to the completion of testing). In general, potentials of -0.24 V were attained much later in the testing cycle for non-cracked double and triple admixture combina-

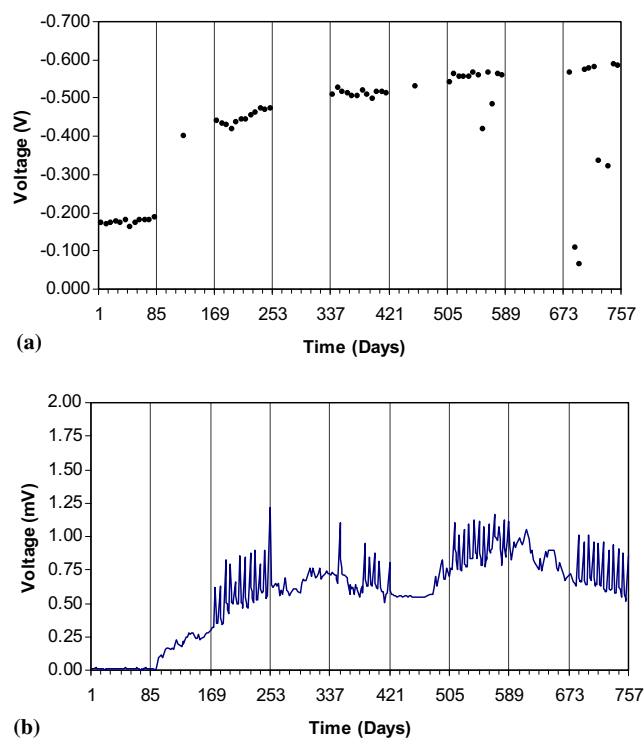


Fig. 3. Sample data for specimen M1A-R. (a) Half-cell data, (b) macrocell data.

tions, if at all. All pre-cracked specimens had half-cell potentials in excess of -0.35 V within the first wet/dry cycle (one week) of testing, except for those from the two mixtures with DSS (M6C and M10C) that took from one to six months to reach such high potentials.

3.3. Macrocell corrosion data

The raw macrocell corrosion data (voltage) was graphed versus time; a plot for non-cracked control specimen M1A-R can be seen in Fig. 3(b). In general, pre-cracked specimens showed significantly higher corrosion activity than their non-cracked counterparts. An exception to this was the original non-cracked SF specimens (M3A and M3B), where shrinkage cracking occurred early in the specimens and subsequent corrosion activity was actually higher than in the pre-cracked counterpart. On the other hand, the CN/SF combination (M7) had initial corrosion activity much higher in the pre-cracked specimen, but with time this decreased while the non-cracked specimens had increased corrosion activity. Eventually all three M7 specimens reached similar macrocell voltage values.

Two features in the macrocell plots were particularly significant (Fig. 3(b)). These were the time it took for initial corrosion activity to occur and then the time for the corrosion readings to elevate significantly. “Initial corrosion activity” was defined as a macrocell reading of 0.1 mV (at approximately 14 weeks (100 days) in

Fig. 3(b)), while an “elevated corrosion reading” was defined as a macrocell reading of at least 0.5 mV (at approximately 25 weeks (175 days) in Fig. 3(b)). The values of the macrocell corrosion readings for these two points were chosen in part based on judgment after an evaluation of the data for all of the test specimens.

Many of the non-cracked control and single admixture specimens showed initial corrosion activity almost immediately. However, non-cracked specimens from CN (M2) and DSS (M6) mixtures never reached macrocell corrosion levels corresponding to initial corrosion

activity, nor did the re-cast FA specimen (M4B-R). The time to elevated corrosion readings was typically also almost immediate for those non-cracked control and single admixture specimens showing early initial corrosion activity. (The only exception was one reinforcing steel reading location in one BFS specimen (M5B) that showed early initial corrosion activity but never exhibited an elevated corrosion reading.) Of the non-cracked specimens with double admixture combinations, only the CN/SF mixture (M7) showed consistently elevated macrocell corrosion readings. For specimens including pre-cracks, all mixtures except those with

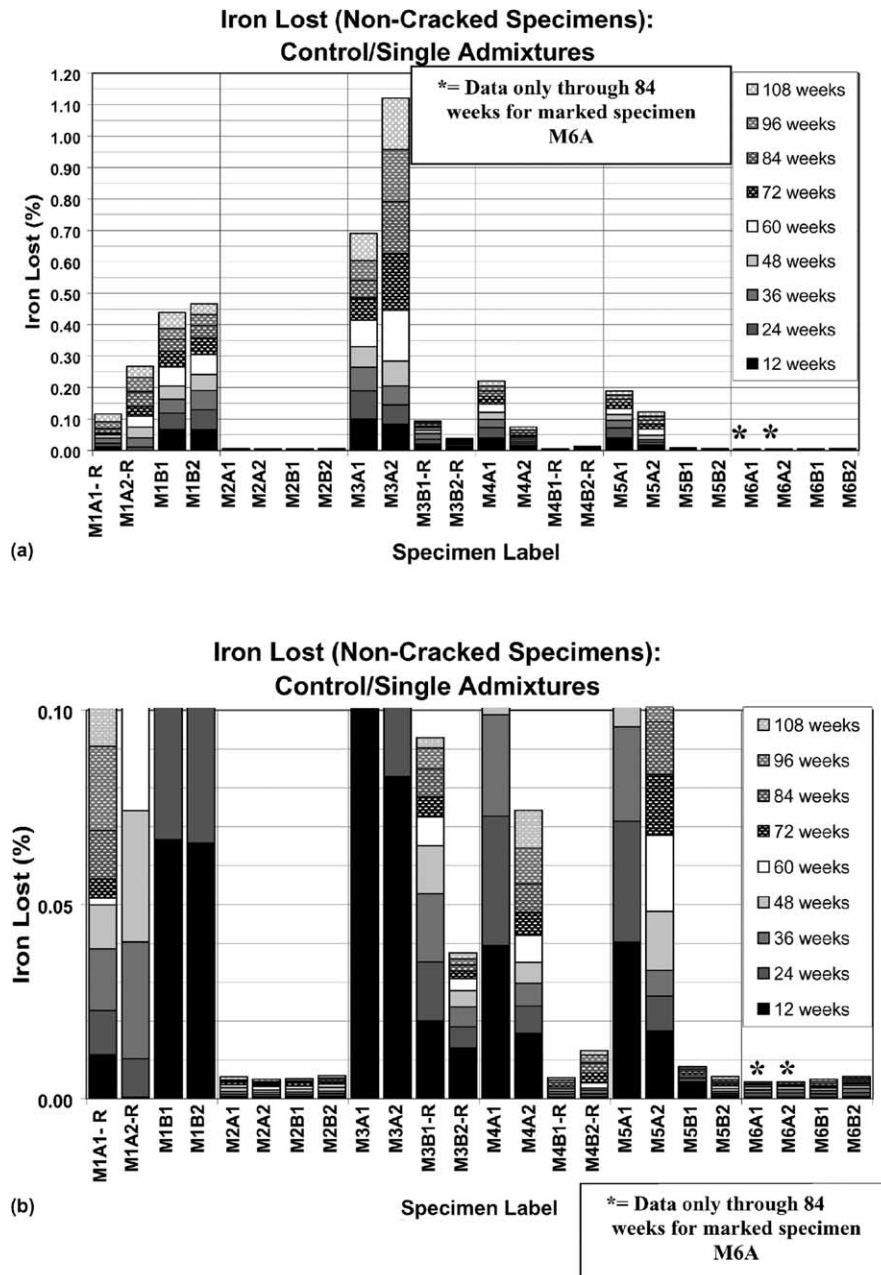


Fig. 4. Iron lost data—control and single admixtures. (a) Full scale, (b) detailed scale.

DSS (specimens M6C and M10C) showed almost immediate elevated macrocell corrosion readings.

In general, the time it took to reach initial macrocell activity in single admixture specimens corresponded to the -0.35 V half-cell criterion, while the -0.24 V criterion correlated well to initial macrocell activity in the better performing combinations. Times to elevated macrocell readings (at least 0.5 mV) were generally indicated by the time to reach the -0.35 V half-cell criterion. However, elevated macrocell readings and -0.35 V half-cell potentials were not attained in some specimens that corroded, as determined by the autopsies (M8A2, M9B1, and M11A2). For these specimens, initial macrocell activity and the -0.24 V half-cell criterion indicated corrosion activity. Therefore, for determining the time

to initiation of corrosion, initial macrocell activity and a half-cell criterion of -0.24 V appear to be adequate, although visual inspection for a sudden increase in half-cell readings appears to be a better criterion for half-cell significance.

3.4. Cumulative corrosion current data

As a measure of overall corrosion activity, cumulative macrocell current provided much more insight into specimen performance than absolute instantaneous current. This data provided information on the total corrosion over time. In addition to providing a comparison of admixture effectiveness for preventing corrosion from initiating, cumulative corrosion current data also

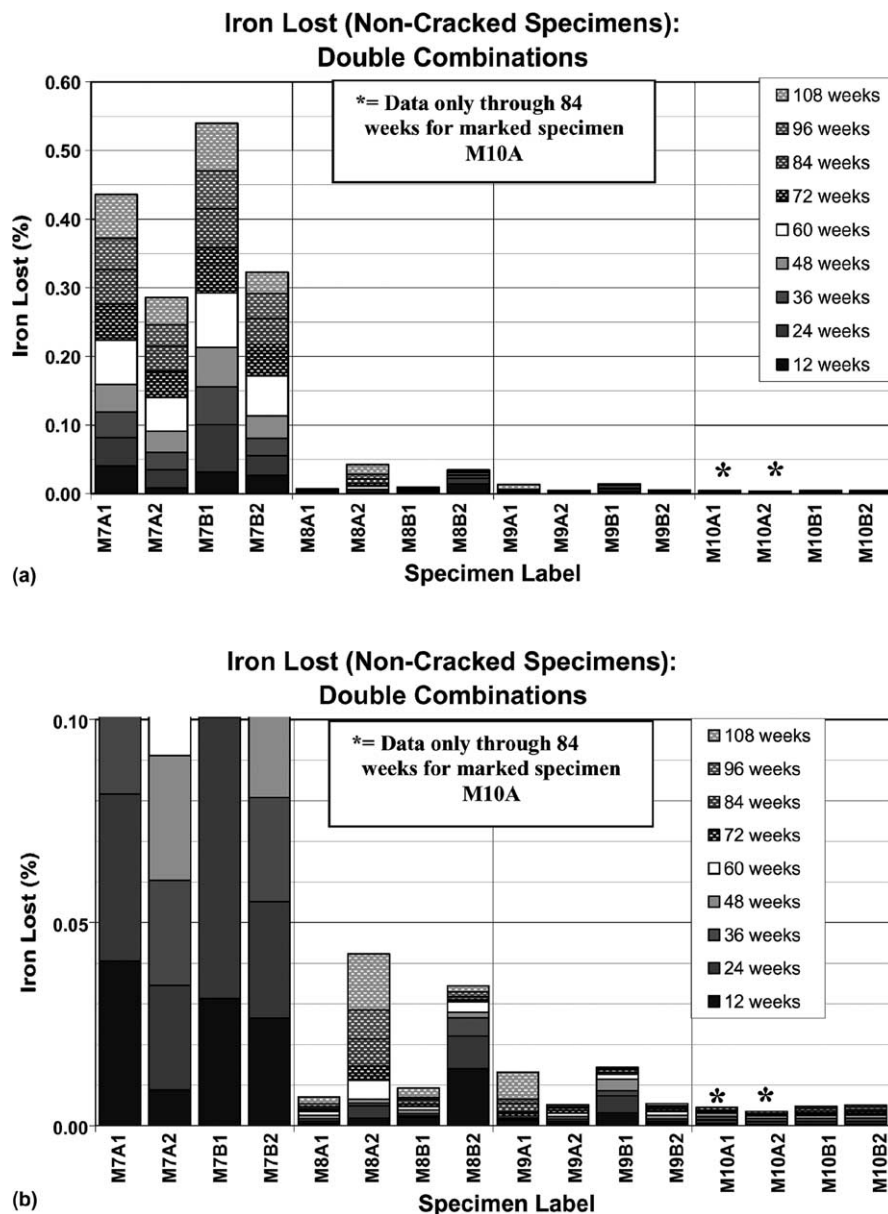


Fig. 5. Iron lost data—double admixtures. (a) Full scale, (b) detailed scale.

indicated the effectiveness in limiting corrosion activity once corrosion had initiated. Macrocell data was converted into approximate iron lost data based on the relationship presented earlier in Equation (1). In general, the cumulative corrosion current data confirmed the overall trends observed with respect to half-cell potential and macrocell corrosion criteria for identifying corrosion initiation. For non-cracked specimens (Figs. 4–6), minimal cumulative iron lost was consistently found in mixtures with CN (M2), DSS (M6), CN/BFS (M9), CN/DSS (M10), and CN/SF/FA (M11), while very low values occurred for mixtures with CN/FA (M8) and CN/SF/BFS (M12).

When pre-cracking was introduced (Fig. 7), the DSS and CN/DSS specimens (M6C and M10C) showed sig-

nificantly less cumulative corrosion than the control. Among other pre-cracked single admixture specimens, the FA (M4C) (and one reading location of the BFS (M5C)) specimens also had reduced iron losses of only about one-fourth to one-half of the control, while CN alone (M2C) showed little improvement over the control. The combinations of CN/FA (M8C) and CN/BFS (M9C) provided cumulative corrosion reductions on the order of those for just FA (M4C), a marked improvement over CN alone (M2C), indicating the benefit of FA or BFS in mitigating corrosion in cracked specimens.

Benefits of FA and BFS were also seen when comparing non-cracked SF (M3) and CN/SF (M7) specimens (which developed micro-cracking) to non-cracked

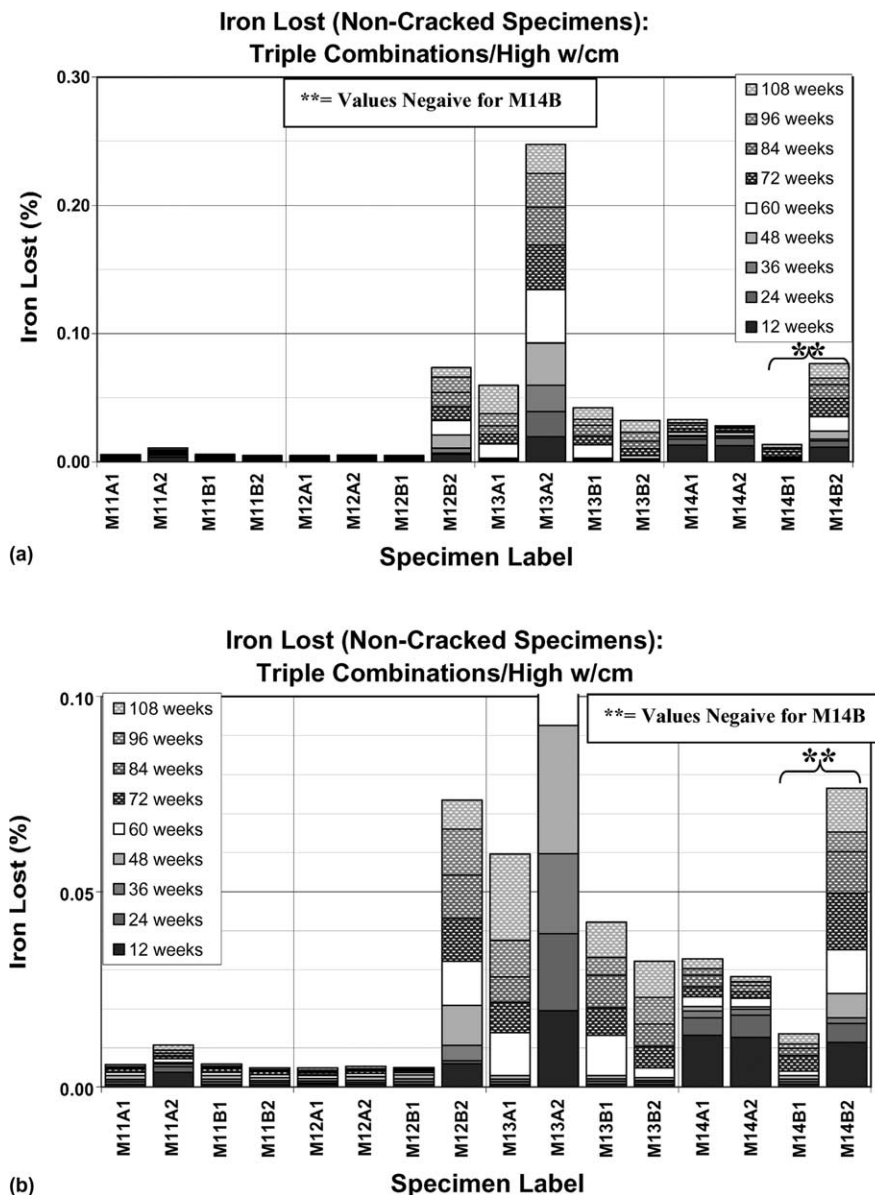


Fig. 6. Iron lost data—triple admixtures and high w/m. (a) Full scale, (b) detailed scale.

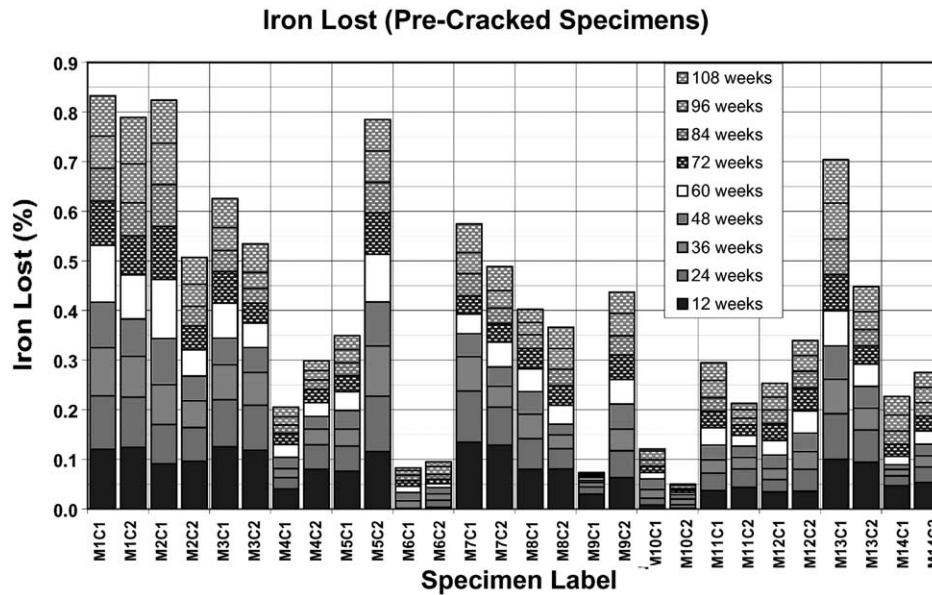


Fig. 7. Iron lost data—pre-cracked specimens.

CN/SF/FA (M11) and CN/SF/BFS (M12) specimens. The addition of FA or BFS to a SF mixture (M11 and M12) appeared to minimize micro-cracking of the incompletely cured concrete, as well as to reduce corrosion rates in cracked sections. Pre-cracked and non-cracked specimens for the triple combination mixtures of CN/SF/FA (M11) and CN/SF/BFS (M12) performed well; however, neither of these improved significantly on the double admixture specimens with CN/BFS (M9).

When the higher w/cm ratio of 0.47 was used, the CN/SF combination (M13) provided improved corrosion resistance in non-cracked specimens vs. the low w/cm CN/SF (M7) non-cracked specimens, most likely due to reduced micro-cracking. The CN/SF/FA triple combination, however, was more effective in non-cracked specimens at the lower w/cm ratio of 0.40 (M11) than at an elevated w/cm ratio of 0.47 (M14). In pre-cracked specimens, double combinations (M13C vs. M7C) and triple combinations (M14C vs. M11C) performed similarly at both w/cm ratios.

3.5. Performance ratings

A direct evaluation of the relative cumulative corrosion performance is presented in Tables 3 and 4 for non-cracked and pre-cracked specimens, respectively. In these tables, the iron lost data from Figs. 4–7 has been used to determine the relative performance of each mixture compared to that of the control at each half-cycle (every 12 weeks) of testing. Averages of all available data (4 readings for specimens A and B, 2 readings for specimens C) were used. (The final 24 weeks of data for non-cracked M6 and M10 specimens had only 2 readings to average because one of the non-cracked

specimens from each of these mixtures had already been autopsied.) Due to the very different behavior between specimen M3A and re-cast specimen M3B-R, Table 3 lists both the average M3 data and the data for only M3B-R.

For each 12-week cumulative corrosion period, all specimens were rated in relation to the respective control mixture as follows:

- Excellent behavior (“A”) indicates cumulative iron loss less than 1/20th of the control.
- Very Good behavior (“B”) indicates cumulative iron loss 1/20th to 1/10th of the control.
- Good behavior (“C”) indicates cumulative iron loss 1/10th to 1/3rd of the control.
- Fair behavior (“D”) indicates cumulative iron loss 1/3rd to 1/2 of the control.
- Marginal behavior (“E”) indicates cumulative iron loss 1/2 to 9/10ths of the control.
- Poor behavior (“F”) indicates cumulative iron loss exceeding 9/10ths of the control.

Non-cracked specimens are rated with respect to the non-cracked controls (M1AB) in Table 3. It can be seen that “Excellent” behavior was observed in the non-cracked specimens for mixtures with CN (M2), DSS (M6), CN/BFS (M9), CN/DSS (M10), and CN/SF/FA (M11). “Good” to “Very Good” performance was seen in the non-cracked specimens for mixtures with CN/FA (M8) and CN/SF/BFS (M12), as well as for the higher w/cm mixtures with CN/SF (M13) and CN/SF/FA (M14). “Poor” behavior was only seen in non-cracked specimens for mixtures with SF (M3) and CN/SF (M7), most likely due to micro-cracking. Some non-cracked

Table 3
Rating^a of non-cracked specimens

Mix	Time									Notes
	12 weeks	24 weeks	36 weeks	48 weeks	60 weeks	72 weeks	84 weeks	96 weeks	108 weeks	
M1AB	NA	NA	NA	NA	NA	NA	NA	NA	NA	
M2AB	A	A	A	A	A	A	A	A	A	
M3AB	F	F	F	F	F	F	F	F	F	»Control
M3B-R only	D	D	D	C	C	C	C	C	C	Improving
M4AB	D	D	C	C	C	C	C	C	C	Improving
M5AB	D	D	C	C	C	C	C	C	C	Improving
M6AB	A	A	A	A	A	A	A	A	A	
M7AB	E	F	F	F	F	F	F	F	F	>Control
M8AB	C	C	B	B	B	B	B	B	B	Improving
M9AB	A	A	A	A	A	A	A	A	A	
M10AB	A	A	A	A	A	A	A	A	A	
M11AB	A	A	A	A	A	A	A	A	A	
M12AB	B	A	A	A	B	B	B	B	B	
M13AB	C	C	C	C	C	C	C	C	C	
M14AB	C	C	C	C	C	C	C	C	C	

A: Excellent <0.05.

B: Very Good 0.05–0.10.

C: Good 0.11–0.33.

D: Fair 0.34–0.50.

E: Marginal 0.51–0.90.

F: Poor >0.91.

^a Rating corresponds to the ratio of cumulative iron loss of the specimens relative to the control specimens (M1AB).

specimens with SF (M3B-R), FA (M4), BFS (M5), and CN/FA (M8) did improve substantially relative to the control over time.

Pre-cracked specimens are compared to the pre-cracked control (M1C) in Table 4. At best, pre-cracked specimens performed in the “Good” to “Very Good” range (for DSS (M6C) and CN/DSS (M10C) mixtures). Borderline “Good” to “Fair” performance was observed in specimens from mixtures with FA (M4C), CN/BFS (M9C), CN/SF/FA (M11C), CN/SF/BFS (M12C), and CN/SF/FA at the higher w/cm ratio (M14C). Corrosion rates in pre-cracked specimens with SF (M3C), FA (M4C), CN/SF (M7C), and CN/FA (M8C) did slow significantly with time, in comparison with the control.

DSS clearly outperformed all other admixtures and admixture combinations when concrete cracking was present, providing significant corrosion resistance even when chlorides had direct access to the reinforcing steel. For cracked specimens, triple combinations of CN/SF/BFS or CN/SF/FA (M11C, M12C, and M14C), a CN/BFS double combination (M9C), and FA alone (M4C) also provided significant improvements over the other single or double combinations of traditional admixtures studied.

A summary ranking of all non-cracked and pre-cracked specimens based on iron lost is given in Table 5. A relative magnifier of iron loss referenced to the non-cracked specimens of the best performing mixture, CN/DSS (M10), is listed. The relative results in this table agree with the results from the other evaluation methods

reported. Note that cracking was typically observed in initially non-cracked specimens with greater than about 0.1% iron loss (and often well before this level of corrosion).

3.6. Autopsies

Autopsy results for 26 specimens are shown in Table 6. For each mixture, the pre-cracked specimen and one of the non-cracked specimens were autopsied at 108 weeks. Mixtures M6 and M10 had just one non-cracked specimen autopsied at that same calendar time, corresponding to 84 weeks of testing for those specimens. All bottom reinforcing steel was removed and had no corrosion product, with the exception of specimens M14B and M14C, which had a small amount of visible corrosion. Corroded surface area for those bottom reinforcing bars and for the top reinforcing bars in all specimens is reported in the table; note that this is surface area only and is not a representation of the volume of corroded material.

Overall, none of the pre-cracked specimens showed significantly less corroded surface area than the control specimens (note that specimens with DSS, M6C and M10C, were not autopsied). However, in non-cracked specimens, mixtures with CN (M2), DSS (M6), or combinations of the two (M10) showed no corrosion product. The triple combination of CN/SF/BFS (M12) also showed no corrosion product in the non-cracked specimen autopsied (although it is noted that specimen M12B had higher iron losses reported but was not

Table 4
Rating^a of pre-cracked specimens

Mix	Time									Notes
	12 weeks	24 weeks	36 weeks	48 weeks	60 weeks	72 weeks	84 weeks	96 weeks	108 weeks	
M1C	NA	NA	NA	NA	NA	NA	NA	NA	NA	
M2C	E	E	E	E	E	E	E	E	E	
M3C	F	F	E	E	E	E	E	E	E	Improving
M4C	D	D	D	D	D	D	C	C	C	Improving
M5C	E	E	E	E	E	E	E	E	E	Improving slightly
M6C	A	A	B	B	B	B	C	C	C	
M7C	F	F	E	E	E	E	E	E	E	Improving
M8C	E	E	E	E	D	D	D	D	D	Improving
M9C	D	D	D	D	C	C	C	C	C	Improving slightly
M10C	A	B	B	C	C	C	C	C	C	
M11C	C	D	C	C	C	C	C	C	C	
M12C	C	C	C	C	C	D	D	D	D	
M13C	E	E	E	E	E	E	E	E	E	
M14C	D	C	C	C	C	C	C	C	C	Improving

A: Excellent < 0.05.

B: Very Good 0.05–0.10.

C: Good 0.11–0.33.

D: Fair 0.34–0.50.

E: Marginal 0.51–0.90.

F: Poor > 0.91.

^a Rating corresponds to the ratio of cumulative iron loss of the specimens relative to the control specimens (M1C).

Table 5
Ranking of all mixture designs

Mix	Average cumulative iron loss (%) through 108 weeks	Magnifier over M10AB	Notes
M10AB	4.93E–03	1×	No cracking
M6AB	5.39E–03	1×	No cracking
M2AB	5.45E–03	1×	No cracking
M11AB	6.80E–03	1×	Cracking in one specimen only
M9AB	9.54E–03	2×	No cracking
M12AB	2.22E–02	4×	Cracking in one specimen only
M8AB	2.33E–02	5×	No cracking
M14AB	3.78E–02	8×	Cracking in one specimen only
M3B-R only	6.52E–02	13×	Specimen with no initial cracking
M4AB	7.82E–02	16×	Cracking in one specimen only
M5AB	8.13E–02	16×	Cracking in one specimen only
M10C	8.54E–02	17×	No additional cracking
M6C	8.88E–02	18×	No additional cracking
M13AB	9.54E–02	19×	Cracking in one specimen only
M14C	2.51E–01	51×	
M4C	2.52E–01	51×	
M11C	2.54E–01	51×	
M9C	2.55E–01	52×	
M12C	2.96E–01	60×	
M1AB	3.22E–01	65×	Control
M8C	3.84E–01	78×	
M7AB	3.96E–01	80×	
M3AB	4.86E–01	98×	Premature cracking in A
M7C	5.31E–01	108×	
M5C	5.67E–01	115×	
M13C	5.76E–01	117×	
M3C	5.80E–01	118×	
M2C	6.65E–01	135×	
M1C	8.11E–01	164×	Control

Table 6
Percent area corroded—autopsied specimens

Specimen	Area corrosion (%)	Specimen	Corroded area (%)
M1B1	17	M1C1	28
M1B2	16	M1C2	47
M2A1	0	M2C1	23
M2A2	0	M2C2	23
M3A1	58	M3C1	62
M3A2	65	M3C2	44
M4A1	16	M4C1	34
M4A2	15	M4C2	30
M5A1	7	M5C1	27
M5A2	7	M5C2	53
M6A1	0	M6C1	NA
M6A2	0	M6C2	NA
M7A1	70	M7C1	60
M7A2	46	M7C2	25
M8A1	0	M8C1	35
M8A2	7	M8C2	52
M9B1	8	M9C1	9
M9B2	0	M9C2	41
M10A1	1	M10C1	NA
M10A2	0	M10C2	NA
M11A1	0	M11C1	67
M11A2	6	M11C2	21
M12A1	0	M12C1	40
M12A2	0	M12C2	19
M13A1	27	M13C1	48
M13A2	14	M13C2	33
M14B1	1	M14C1	69
M14B2	3	M14C2	64
M14B1 bottom	5	M14C1 bottom	2
M14B2 bottom	4	M14C2 bottom	1

autopsied). Reduced corrosion product was also found in non-cracked specimens from mixtures with BFS (M5), CN/FA (M8), CN/BFS (M9), and CN/SF/FA (M11 and M14). Mixture designs with SF alone (M3) or CN/SF (M7) showed significantly more surface corrosion than the control.

3.7. Chloride ingress data

Data from chloride ingress analyses, obtained from autopsied non-cracked specimens, is presented in Table 7. Results show that the control developed significant ingress of chloride ions through the aggressive cyclic ponding. Chloride concentrations at the level of the reinforcing steel were on the order of surface chloride concentrations in the control (M1), as well as in mixtures with SF (M3), CN/SF (M7), and CN/SF at the higher w/cm ratio (M13). Roughly half of the surface chloride concentration was found at the level of the reinforcement in mixtures containing CN (M2), FA (M4), BFS (M5), CN/BFS (M9), CN/SF/FA (M11), and CN/SF/BFS (M12). Significantly less chloride was found at the level of the reinforcement (as a percentage of the surface concentration) in mixtures with DSS (M6) and CN/DSS (M10).

Table 7
Water soluble percent chloride by weight of concrete

Specimen	Depth		
	0–13 mm	13–25 mm	25–38 mm
M1B	0.53	0.49	0.46
M2A	0.49	0.28	0.25
M3A	0.42	0.39	0.37
M4A	0.46	0.42	0.26
M5A	0.46	0.38	0.17
M6A ^a	0.23	0.06	0.05
M7A	0.79	0.71	0.64
M8A	0.65	0.54	0.36
M9B	0.48	0.29	0.11
M10A ^a	0.22	0.13	0.04
M11A	0.30	0.25	0.13
M12A	0.51	0.30	0.13
M13A	0.54	0.50	0.43
M14B	0.79	0.68	0.45

^a Note. Data is from autopsied specimens, after 108 weeks of testing for all but M6A and M10A, which were after 84 weeks of testing.

4. Summary and conclusions

A long term corrosion study was conducted to determine the effectiveness of several admixtures (CN, SF, FA, BFS, and DSS), used in single, double, and triple combinations, for reducing corrosion of reinforcing steel in structural concrete. A total of fourteen concrete mixtures were evaluated. Accelerated testing on slab specimens (in triplicate for each concrete mixture) was performed under an aggressive test regimen consisting of salt water ponding and drying of specimens. Visual inspections, macrocell corrosion readings, half-cell potentials, and chloride ingress data were used for purposes of assessing the absolute and relative performance of the various specimens. Cumulative macrocell corrosion current data was the most informative of the test methods used; however, all criteria indicated similar trends in the results.

CN as a single admixture provided excellent protection against corrosion in non-cracked concrete but was not particularly effective in the presence of cracking, where chlorides could directly access the reinforcing steel anode. In this case the chloride threshold level was quickly exceeded. For such cracked conditions, DSS alone or in combination with CN showed the least cumulative corrosion current, far surpassing the performance of the other admixtures and admixture combinations studied. DSS appeared to have mechanisms of protection quite different from those in the other admixtures included in this study, both greatly reducing concrete's permeability and precluding corrosion even in specimens with cracks extending to the level of the reinforcing steel. It is not clear whether this was due to hydrophobic properties preventing transport through the crack and/or due to partial inhibition of the corrosion

process even at extremely high chloride levels. The negative impact of DSS on concrete compressive strength, as well as unknown effects on other concrete properties and possible interactions with other admixtures, remain as issues that may need to be resolved prior to widespread acceptance.

Mixtures with only SF, as well as with SF in combination with CN, showed a greater tendency for micro-cracking than other mixtures when cured as in this study. When early micro-cracking was prevented, performance of SF mixtures was similar to that of mixtures with the other pozzolanic admixtures (FA and BFS). The potential for early micro-cracking in SF concrete appeared to be minimized when FA or BFS was also included in the mixture proportions.

All of the admixtures and admixture combinations studied have merit. For optimal protection against corrosion in structural concrete, a triple combination of CN, SF, and FA (or a double combination of CN and BFS), all at moderate dosages, is recommended. A triple combination of CN, SF, and BFS would also be effective, although the addition of SF may add cost without much improvement in minimizing corrosion. All of the recommended mixtures also resulted in higher compressive strengths than in the control concrete, indicating an overall improvement in material performance and quality. With further verification of its effects on concrete material properties (and possible chemical interactions), DSS could also be an extremely effective admixture for preventing corrosion of steel reinforcement in concrete transportation structures, with a modest decrease in compressive strength.

Acknowledgments

Funding for this research was provided by the New England Transportation Consortium (NETC). Valuable laboratory assistance was provided by Jason Pisano and Alexander Bonnar. This paper, prepared in cooperation with the NETC, does not constitute a standard, specification, or regulation. The contents of this paper reflect the views of the authors, who are responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the views of the NETC or the Federal Highway Administration.

References

- [1] Allyn M, Frantz GC. Corrosion tests with concrete containing salts of an alkenyl succinic acid. *ACI Mater J* 2001;98(3):224–32.
- [2] Sime JM. Connecticut Department of Transportation, Newington, CT. Personal Communication. July 17; 2002.
- [3] LaFave JM, Pfeifer DW, Sund DJ, Lovett D, Civjan SA. On the use of mineral and chemical durability enhancing admixtures in structural concrete. *Concrete Int* 2002;24(8):71–8.
- [4] Civjan SA, LaFave JM, Lovett D, Sund DJ, Trybulski J. Performance evaluation and economic analysis of combinations of durability enhancing admixtures (mineral and chemical) in structural concrete for the Northeast USA. Summary Final Report prepared for the New England Transportation Consortium (NETC); 2002.
- [5] ASTM G 109-99. Standard test method for determining the effects of chemical admixtures on the corrosion of embedded steel reinforcement in concrete exposed to chloride environments. Annual book of ASTM standards, V. 3.02. American Society for Testing and Materials, Philadelphia, PA; 2003.
- [6] McDonald DB, Pfeifer DW, Sherman MR. Corrosion evaluation of epoxy-coated, metallic-clad, and solid metallic reinforcing bars in concrete (FHWA-RD-98-153). Federal Highway Administration, Washington, DC; December 1998.
- [7] AASHTO M 80-87. Coarse aggregate for portland cement concrete. Standard specifications for transportation materials and methods of sampling and testing, V. 1A, American Association of State Highway and Transportation Officials, Washington, DC; 2003.
- [8] AASHTO M 6-03. Fine aggregate for portland cement concrete. Standard specifications for transportation materials and methods of sampling and testing, V. 1A, American Association of State Highway and Transportation Officials, Washington, DC; 2003.
- [9] ASTM C 127-01. Standard test method for density, relative density (specific gravity), and absorption of coarse aggregate. Annual book of ASTM standards, V. 4.02, American Society for Testing and Materials, Philadelphia, PA; 2003.
- [10] ASTM C 128-01. Standard test method for density, relative density (specific gravity), and absorption of fine aggregate. Annual book of ASTM standards, V. 4.02, American Society for Testing and Materials, Philadelphia, PA; 2003.
- [11] ASTM C 1152-03. Standard test method for acid-soluble chloride in mortar and concrete. Annual book of ASTM standards, V. 4.02, American Society for Testing and Materials, Philadelphia, PA; 2003.
- [12] ASTM C 150-02. Standard specification for portland cement. Annual book of ASTM standards, V. 4.01, American Society for Testing and Materials, Philadelphia, PA; 2003.
- [13] ASTM C 1240-03. Standard specification for use of silica fume as a mineral admixture in hydraulic-cement concrete, mortar, and grout. Annual book of ASTM standards, V. 4.02, American Society for Testing and Materials, Philadelphia, PA; 2003.
- [14] ASTM C 618-03. Standard specification for coal fly ash and raw or calcined natural pozzolan for use as a mineral admixture in concrete. Annual book of ASTM standards, V. 4.02, American Society for Testing and Materials, Philadelphia, PA; 2003.
- [15] ASTM C 595-03. Standard specification for blended hydraulic cements. Annual book of ASTM standards, V. 4.01, American Society for Testing and Materials, Philadelphia, PA; 2003.
- [16] ASTM C 494-99. Standard specification for chemical admixtures for concrete. Annual book of ASTM standards, V. 4.02, American Society for Testing and Materials, Philadelphia, PA; 2003.
- [17] ASTM C 260-01. Standard specification for air-entraining admixtures for concrete. Annual book of ASTM standards, V. 4.02, American Society for Testing and Materials, Philadelphia, PA; 2003.
- [18] ASTM C 192-02. Standard practice for making and curing concrete specimens in the laboratory. Annual book of ASTM standards, V. 4.02, American Society for Testing and Materials, Philadelphia, PA; 2003.
- [19] AASHTO T 199-00. Air content of freshly mixed concrete by the chace indicator. Standard specifications for transportation materials and methods of sampling and testing, V. 2A, American Association of State Highway and Transportation Officials, Washington, DC; 2003.

- [20] ASTM C 876-91. Standard test method for half-cell potentials of uncoated reinforcing steel in concrete. Annual book of ASTM standards, V. 3.02, American Society for Testing and Materials, Philadelphia, PA; 2003.
- [21] Perenchio WF. Corrosion of reinforcing steel. In: Klieger P, Lamond JF, editors. Significance of tests and properties of concrete and concrete-making materials. Philadelphia, PA: American Society for Testing and Materials; 1994. [Chapter 17].
- [22] Virmani YP, Clear KC, Pasko Jr TJ. Time to corrosion of reinforcing steel in concrete slabs. Calcium nitrite admixture or epoxy coated reinforcing bars as corrosion protection systems (FHWA/RD-83/012), vol. 5. Washington, DC: Federal Highway Administration; 1983.
- [23] AASHTO T 260-97. Sampling and testing for chloride ion in concrete and concrete raw materials. Standard specifications for transportation materials and methods of sampling and testing, V. 2B, American Association of State Highway and Transportation Officials, Washington, DC; 2003.
- [24] Allyn M, Frantz GC. Strength and durability of concrete containing salts of alkenyl-succinic acid. *ACI Mater J* 2001;98(1):52–8.