Screening Test for Rebar Corrosion Inhibitors

S. Dressman, T. Osiroff, J. G. Dillard, J. O. Glanville, and R. E. Weyers

The chloride-induced corrosion of steel reinforcing bars (rebars) in concrete structures can be vitiated by the presence of chemical compounds that serve as corrosion inhibitors. A simple, quick procedure has been developed to test for the relative effectiveness of inhibitors. The test is based on the observable corrosion of multiple test specimens under specified conditions. Details of the test procedure are reported along with the results for a range of inhibitors.

This paper is one of four related reports that describe the results of basic research studies aimed at answering the question of how corrosion inhibitors can be applied to mitigate bridge component reinforcing steel corrosion if the concrete remains in place during the rehabilitation process. This paper attempts to answer the question as to what corrosion inhibitors might work and how can they be tested in the laboratory. Other papers in this series deal with the questions of the mechanism of action of the corrosion inhibitors (Dillard et al., a companion paper in this Record), the mobility of corrosion inhibitors through concrete (Dillard et al., another companion paper in this Record), and electrochemical studies of inhibition phenomena (Webster et al., a companion paper in this Record). This last paper includes a comparison of the results of corrosion screening tests, surface analytical studies, and electrochemical studies of a series of inhibitors.

According to pessimistic estimates, as a consequence of their contamination by chloride salts, as many as one-half of all highway bridges in the United States (1) are deteriorating from reinforcing bar (rebar) corrosion. A similar situation prevails in the United Kingdom (2). Rebar corrosion in bridges is an outcome of the repeated wintertime application of deicing salts such as sodium chloride and calcium chloride. Reviews of the problem are available (3,4). Chloride-induced corrosion destroys the rebar and causes formation of corrosion products. The corrosion products occupy a greater physical volume than the rebar itself and cause internal expansion that leads to cracking and spalling of the concrete cover. Once cracking and spalling have occurred, the rebar is accessible to further chloride-induced corrosion—and so conditions deteriorate rapidly.

Using corrosion-inhibiting agents is a traditional approach to preventing or slowing the corrosion of steel. Most corrosion inhibitors for steel find use in acidic or neutral conditions—where uninhibited attack may be rapid; corrosion of steel under alkaline conditions experienced by rebar in concrete is slow. However, because of the long life required of reinforced bridges and because corrosion is induced by chloride contamination, corrosion inhibitors are useful (5). At least two corrosion inhibitors are currently in use for the protection of rebar. The use of calcium nitrite as an admixture has become fairly widespread during the past decade, and concrete made with added calcium nitrite has considerable resistance to chloride-induced corrosion (6,7). A different approach to inhibition involves the use of a corrosion additive as a minor component of the road salt. For this purpose, sodium monofluorophosphate (MFP) has been used (Domtar Corp., Mississauga, Ontario).

Substances were sought that could be applied to existing, chloride-contaminated bridge components that would penetrate the concrete, and that would, on arrival at the rebar, stop or inhibit corrosion. The advantage of inhibitor substances is obvious: their use would allow the relatively inexpensive treatment of rebar corrosion in existing bridge components without the need for removal of concrete. Proving the efficacy of any proposed inhibitor is ultimately a task for field trials and practical testing. However, screening tests can be conducted under laboratory conditions to test (a) inhibitor effectiveness, and (b) inhibitor penetration through concrete. The use of a visual estimation method to judge inhibitor effectiveness is described in a later section.

Corrosion of rebar in chloride-contaminated concrete occurs where aqueous solutions within the pores of the concrete contact the rebar. The existence of such pore solutions is necessary to provide a conduit by which chloride ion may diffuse from the surface of the concrete to the rebars, several inches below the surface of the deck. In the work reported here, a synthetic pore solution (8) was used to simulate the practical situation.

In order to measure the relative effectiveness of inhibitors, a high concentration of sodium chloride was added to the simulated pore solution, and the corrosivity of the chloride-doped simulated pore solution was estimated by the amount of visual corrosion produced in multiple rebar specimens exposed under standardized conditions. The procedure used was modified from ASTM Standard G46–76, *Standard Practice for Examination and Evaluation of Pitting Corrosion*. The selection of materials to be tested was strongly guided by what was available commercially (9).

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

OBJECTIVES

The main objective in undertaking this work was to develop a rapid, inexpensive screening test to study inhibiting agents for potential corrosion of rebar in concrete. Related studies have focused on the related questions of chemical surface changes (Dillard et al., a companion paper in this Record), of the relative mobility of inhibitors through concrete paste (Dillard et al., a companion paper in this Record), and on the electrochemical potential change during the process of corrosion and its inhibition (Webster et al., a companion paper in this Record). It was envisioned that candidate inhibitors identified by means of the test would be carried foward into a program of scaled-up testing and eventually taken to full-scale field testing.

A second objective was to use the test to conduct a survey of possible materials. As part of the investigation, numerous technical representatives of companies that offer corrosion inhibitors were contacted. Thus, the selection of candidate materials was based on the industrial state of the art.

EXPERIMENTAL

Test rebar was obtained from a single heat produced by a local electric furnace from a scrap recycle source. Rebar was cleaned by rinsing with hexane (commercial solvent grade, of mixed isomers) but otherwise used in an as-received condition. Corrosion test pieces were prepared in the form of half-cylinders by longitudinally cutting approximately 1-in-long sections of rebar. Synthetic pore solution was prepared by weighing on a laboratory balance using reagent grade laboratory chemicals. The composition of the synthetic pore solution was chosen to to be sodium hydroxide (0.300 M), potassium hydroxide (0.600 M), and saturated calcium hydroxide in distilled water. Chloride-doped pore solution contained an additional 3.5 weight percent (wt.%) of sodium chloride. Before use, all solutions were air-saturated by passing air through them for $1\frac{1}{2}$ to 2 hr.

Rebar test specimens were prepared in replicate (usually 5 or 10 replicates per test) by placing approximately 10 mL of the aerated test solution in a small plastic vial and putting a single rebar test piece into the solution. The rebar test pieces were completely submerged. The vials were loosely capped and placed in a laboratory oven and maintained at 60°C. Solutions were replenished periodically and replaced every 2 weeks.

From time to time, each test specimen was carefully examined with a 5× hand magnifying lens and graded on the basis of an estimate of the percentage of the surface corroded. Corrosion was taken to be any surface modification; no attempt was made to distinguish between corrosion of varying morphology, i.e., between area or pitting corrosion. The recorded corrosion value was then taken as the ratio of the altered surface to total surface, multiplied by 100, and reported as percent corrosion. The corrosion observations were made on the original (curved) surface of the rebar (not the freshly cut surface).

For experiments to test the comparative effect of inhibitors, accurately weighed quantities of the inhibitors were added to the chloride-doped simulated pore solution. Control solutions were chloride-doped pore solution without added corrosion inhibitor. Corrosion inhibitors were obtained as reagent grade chemicals from laboratory supply houses. Commercial products were obtained as manufacturers' samples. Their manufacturer and chemical nature are summarized in the following list.

- Monsanto Chemical Co.
  - Dequest 2000, amino tris(methylene phosphonic acid), 50 percent active aqueous solution
  - Dequest 2010, hydroxy-ethylidene diphosphonic acid, 60 percent active aqueous solution
  - Dequest 2054, hexapotassium hexamethylene diamine (methylene tetraphosphonate), 35 percent active aqueous solution.
- Alox Chemical Co.
  - Alox 901
  - Alox 502A
  - Alox 2291
  - Alox 319F
  - Alox 350
  - Alox 2162
  - Aqualox 2268
- Angus Chemical Co.
  - Alkaterge T-IV, oxazoline compound
  - Amine CS-1135, oxazoladine blend
- Miranol Inc.
  - Miramine TOC, substituted imidazoline of tall oil fatty acid
  - Monocor BE, borate ester
- Mona Industries Ltd.
  - Monacor 39, imido ester carboxylic acid derivative
- Witco Corp.
  - Witcamine PA 78-B, salt of fatty imidazoline
  - Witcamine PA 60-B, slat of fatty imidazoline

In order to calculate molarities of commercial samples of proprietary composition and, hence, unknown molecular weight, a molecular weight of 250 g/mol was assumed.

RESULTS AND DISCUSSION

Preparation of Rebar Samples

Because corrosion effects are highly dependent on surface phenomena, it was recognized that considerable thought should be given to the way in which the test pieces were prepared. Various treatments with acids were investigated and x-ray photoectron spectroscopy (XPS) studies made. The surface analytical composition (obtained from surface chemical analysis with XPS) is reported in detail elsewhere (Dillard et al., a companion paper in this Record). The surface composition of the rebar is considerably different from the bulk composition, with high surface concentrations of copper and zinc reflecting the origin of the steel as recycled from shredded automobiles.

Cleaning with a hydrocarbon solvent (hexane) was the preparation method most likely to yield good results in accelerated, laboratory corrosion tests. However, cleaning with hexane does not significantly alter the surface composition. The

rebar in the aged bridge components to be protected by the method described here is likely to be virgin steel, not recycled steel. Thus, the question of surface catalytic effects on corrosion is open. The results reported are valid on the basis of the assumption that the steel used yields a fair relative assessment of the various corrosion inhibitors.

During the studies, most of the corrosion occurred on the gridiron regions of the specimens, i.e., on the raised regions of the deformations formed into the rebar to enhance bonding between the concrete and the steel. Weighing the test specimens as a method of estimating corrosion was considered, but the possible improved accuracy was judged to not outweigh the considerable extra effort involved.

Development of the Screening Test

At the beginning of this study, all of the basic test parameters were open to investigation. Preliminary experiments implied that testing would have to be conducted at the elevated temperature if results were to be achieved after a reasonably short time. The final choice of 60°C is sufficiently high for rapid testing, yet sufficiently low that the needs for solution replenishment and replacement are kept within manageable limits.

The baseline data by which the extent of corrosion in chloride-doped pore solution at 60°C was judged are presented below. Under the conditions finally selected for the screening tests, the controls suffer surface corrosion to the extent of about 1 percent a day. The results are based on 10 replicate specimens and the standard deviations of the average percent corrosion are indicated.

Time (days)	Percent Corrosion
35	26 ± 8
56	52 ± 22

Depite the fact that this test is based solely on visual estimates of the extent of corrosion, the estimated standard deviations indicate that with a sufficient number of replicate samples a good estimate of corrosion can be reliably obtained. Overall, a relative standard deviation of 20 to 40 percent for a wide range of inhibitors is found. On the basis of this criterion, the screening test may be judged to be reasonably successful.

Experiments using the known corrosion inhibitors sodium nitrite and sodium MFP were useful in choosing how long to conduct the tests, at what temperature to maintain the oven, and when to either replenish or change solutions.

During the preliminary phase of the investigation, a number of studies were made of the effect of specific inhibitor concentration on the extent of corrosion. Table 1 presents the effect of varying sodium nitrite concentration on the percent corrosion; Table 2 presents the effect of varying sodium molybdate concentration. Sodium nitrite is one of the best available inhibitors under the test conditions, and Table 1 indicates that it is effective even at concentrations as low as 0.00200 M. Conversely, sodium molybdate is one of the worst inhibitors under the test conditions. Corrosion in sodium molybdate (0.00200 M) environment is indistinguishable from that in the control solutions. However, Table 2 indicates that sodium molybdate has a modest inhibiting effect at high concentration.

On the basis of these and other concentration studies, an inhibitor concentration of 0.00200 M was used in the screening test. Other final parameters in the screening test are shown in the following list summarizing the recommended procedures.

Parameter	Specification
Test solution	sodium hydroxide (0.300 M) potassium hydroxide (0.600 M), saturated with calcium hydroxide 3.50 at.% sodium chloride, aerated for minimum of 90 min
Test specimen	Half-cylinder of rebar, 1 in. long Rebar prepared by hexane cleaning
Test conditions	60°C for 30 days with bi-weekly replacement of the test solution One rebar test specimen submerged in 10 mL of test solution in a small vial
Samples	Minimum of five replicates
Evaluation	Visual estimation per ASTM G46–76.

Selection and Performance of the Corrosion Inhibitors

The known corrosion inhibitors for rebar in steel were among those first tested. As presented in Table 3, both sodium nitrite and sodium MFP rank high on the basis of the results obtained. These results are encouraging in that they demonstrate that the rapid screening test has practical value. Although by themselves they do not validate the test, had these inhibitors performed badly the test itself would be suspect.

A number of criteria were used in selecting materials to be tested. Known inhibitors in alkaline systems, such as sodium mestasilicate, were natural candidates. The phosphonic acid

TABLE 1 CORROSION INHIBITION BY SODIUM NITRITE

Sodium nitrite concentration mol/L	Percent Corrosion	Number of replicates
0.00200	5.4 ± 2	10
0.0100	6.2 ± 2	10
0.0500	4.8 ± 2	10
0.100	3.8 ± 1	10
0.500	3.4 ± 1	10
control (at 28 days)	21%	

NOTE: Corrosion of rebar samples in chloride-doped pore solution at 60° C. Reported values are the average of 10 replicate samples at each concentration. Exposure time: 28 days.

TABLE 2   CORROSION INHIBITION BY SODIUM MOLYBDATE

Sodium molybdate concentration mol/L	Percent Corrosion	Number of replicates
0.00200	25 ± 14	10
0.0110	23 ± 9	10
0.0500	13 ± 7	10
0.100	11 ± 3	10
0.500	8 ± 2	10
control (at 33 days)	25%	

NOTE: Corrosion of rebar samples in chloride-doped pore solution at 60° C.
Reported values are the average of ten replicate samples at each concentration.
Exposure time: 33 days.

salts (Dequests) were selected because of their high solubility in alkaline systems and potential ability to form surface films. Consulting a standard listing of commercially available inhibitors (*10*) provided many sources of up-to-date information, and industry experts were asked for their recommendations whenever possible.

Eventually, a wide range of potential inhibitors were tested. Details of the chemical composition (where known) and the sources of the inhibitors are described in the experimental section. The results of these studies are presented in Table 3. Because the test is relatively inexpensive to conduct, many commercial materials could be investigated in a relatively short period of time.

The mode of action of the various inhibitors can be studied using surface sensitive analytical techniques (Dillard et al., a companion paper in this Record). These studies show that sodium tetraborate forms a surface film on the rebar. There is also evidence that borate ion is more mobile than chloride in concrete (Dillard et al., a companion paper in this Record). Further studies are planned using the screening test. In particular, pursuing the inhibiting potential of different borates would be of interest.

TABLE 3   SUMMARY RESULTS OF INHIBITOR SCREENING TESTS

Inhibitor	Exposure (days)	Percent Corrosion
Alox 901	34	4.8
Sodium nitrite	28	5.4
Sodium monofluorophosphate	28	5.4
Aqualox 2268	28	5.6
Sodium tetraborate	28	5.6
Alox 350	34	6.4
Alox 2162	34	6.4
Miramine TOC	34	6.4
Alox 600	34	6.8
Monacor 39	34	7.2
Sodium nitrate	34	8.0
Sodium silicate (1:3.22, $Na_2O:SiO_2$)	34	9.8
Sodium metasilicate	34	10.0
Sodium carbonate	34	10.0
Alox 502 A	34	10.2
Witco PA 78B	34	10.4
Alox 2291	34	10.6
Witco PA 60B	34	10.8
Sodium dihydrogen phosphate	28	12.6
Amine CS-1135	34	12.8
Alox 319F	34	12.8
Potassium dichromate	34	14.0
Dequest 2010	21	15.0
Potassium nitrate	34	15.0
Dequest 2000	28	15.0
Monacor BE	34	15.4
Calcium borate	34	19.0
Dequest 2054	21	20.8
Calcium sulfate	34	22.4
Sodium molybdate	33	25.0
Control (no inhibitor)	35	26.0

NOTE: Values reported are the averages of five replicate samples exposed to chloride-doped pore solution at 60° C for the number of days stated. The inhibitor concentration was 0.00200 M.

CONCLUSIONS

A useful, rapid screening technique has been developed to test the effectiveness of corrosion inhibitors for rebar corrosion in steel. Known corrosion inhibitors, recommended for this use, such as sodium nitrite and sodium MFP, perform well in the test. These results tend to confirm the utility and validity of the test.

Under the conditions chosen, a visually estimated corrosion of greater than 9 percent is sufficient to exclude a particular inhibitor from further testing. Highly promising corrosion inhibitors are those that exhibit less than 7 percent corrosion under the test conditions. Further studies using the test should be made.

Many organic commercial inhibitors also perform well, as do certain borate salts. Tests of the practical efficacy of borate salts in the treatment of chloride-contaminated bridge decks where the chloride-contaminated concrete remains in place are warranted because borate salts are inexpensive. Certain of the organic corrosion inhibitors may find use in treating the rebar in situations where bridge deck rehabilitation involves concrete removal and exposure of the rebar.

ACKNOWLEDGMENTS

REFERENCES

1. *Seventh Annual Report to Congress—Highway Bridge Replacement and Rehabilitation Program.* Office of Engineering, Bridge Division, FHWA, U.S. Department of Transportation, 1986, 59 pp.
2. *The Performance of Concrete Bridges—A Survey of 200 Bridges.* Her Majesty's Stationary Office, London, 1989.
3. Chloride Corrosion of Steel in Concrete. ASTM 629, (D. E. Tonini and S. W. Dean, eds.) ASTM, Philadelphia, Pa., 1977.
4. D. G. Manning and J. Ryell. *Durable Bridge Decks.* Ontario Ministry of Transportation and Communications, Toronto, April 1976.
5. N. E. Hammer. Inhibitors for use on Reinforcing Steel in Concrete. *Corrosion Inhibitors* (C. C. Nathan, ed.), 1973, pp.190–195.
6. N. S. Berke. The Effects of Calcium Nitrite and Mix Design on the Corrosion Resistance of Steel in Concrete. Paper 132, presented at the Annual Meeting of the National Association of Corrosion Engineers, San Francisco, 1987.
7. Y. P. Virmani. *Time-to-Corrosion of Reinforcing Steel in Concrete Slabs, Volume VI: Calcium Nitrite Admixture.* FWHA-RD-88-165. FHWA, U.S. Department of Transportation, 1988.
8. A. Moragues, A. Macias, and C. Andrade. Equilibria of the Chemical Composition of the Concrete Pore Solution. *Cement and Concrete Research*, Vol. 17, 1986, pp. 173–182.
9. *McCutheon's Functional Materials: Corrosion Inhibitors.* Manufacturing Confectioner Publishing, Glen Rock, N.J., 1989.