FINAL REPORT

AN EVALUATION OF NEW INHIBITORS FOR REBAR CORROSION IN CONCRETE

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LIST OF SYMBOLS

ρ	Density
A	Cross-sectional area
AMA	Aminoethylethanolamine
ATP	2-aminothiophenol or orthoaminothiophenol
BGP	Di-sodium β-glycerophosphate
Cl^-	Chloride ion
CN	Calcium nitrite
CPE	Constant phase element
DCI	Calcium nitrite commercial mix from W.R. Grace
DS	Di-n-butyl sulfoxide
EIS	Electrochemical impedance spectroscopy
L	Length
LN	Lithium nitrate
LP	Linear polarization
m	Mass
mpy	Mils (one-thousandth of an inch) per year
NA	Sodium metasilicate
NO_2	Nitrite ion
ORR	Oxygen reduction reaction
PA	Phosphonic acid (also known as aminotrimethylenephosphonic acid (AMP) and nitrilotrisphosphonic acid)
R	Resistance
RCM	Resistance change method
SEM	Scanning electron microscope
SSD	Saturated surface dry condition of aggregate
TCRUs	Temperature Corrected Resistance Ratio Units
W_{air}	Weight of mortar or concrete in air
W_{water}	Weight of mortar or concrete in water
w/c	Water to cement ratio
XPS	X-ray photoelectron spectroscopy

ABSTRACT

The corrosion of reinforcing steel in concrete is estimated to affect more than 50 percent of the 575,000 bridges in the United States. One approach to mitigating this problem is to use corrosion-inhibitive compounds admixed into the concrete paste. This study sought to examine the corrosion-inhibition performance of a series of compounds admixed into high-quality concrete and to delineate the effects of these compounds on the concrete with regard to the corrosion process.

A series of eight compounds were admixed into Type A4 concrete. The compounds tested were aminoethylethanolamine, aminothiophenol, di-sodium β-glycerophosphate, calcium nitrite, di-n-butyl sulfoxide, lithium nitrate, sodium metasilicate, and nitrilotrisphosphonic acid. Concrete blocks were cast, into which were placed 0.009-in-diameter 1040 steel wires. The corrosion rate was assessed via a resistance change measurement (RCM) of these wires over time using a temperature-corrected four-point resistance measurement. The time-to-open circuit for the wires was also monitored. RCM was compared to (1) electrochemical impedance spectroscopy results of tests conducted in a simulated pore solution, and (2) chloride permeability measurements of the concrete as per ASTM C 1202. The effect of the admixtures on the compressive strength and density of the concrete was also assessed.

RCM and time-to-open circuit results showed that four test inhibitors had equal or better corrosion prevention at 2 years of testing compared to a widely used commercial mix (DCI). These test inhibitors included di-sodium β-glycerophosphate (0.283 mol/ft^3 and 0.815 mol/ft^3), aminoethylethanolamine (0.815 mol/ft^3), lithium nitrate (0.815 mol/ft^3), and sodium metasilicate (0.815 mol/ft^3). After 100 weeks, 33 to 44 percent of the wires were active in concrete admixed with these test compounds, whereas only 25 percent of the wires were active in concrete admixed with DCI. This research has also shown that the performance of a corrosion inhibitor in high-quality concrete is a function of numerous interrelated factors that are not predicted from any single laboratory test.

These tests provide promising results for alternative inhibitive admixtures for standard Type A4 concrete. It is recommended that additional tests be conducted on concrete mixtures containing slag and fly ash using multiple concentrations of the four most promising inhibitors. Further testing may lead to the implementation of a better corrosion-inhibiting admixture, thus increasing the service life of bridges.

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INTRODUCTION

Greater than 50 percent of the 575,000 bridges in the United States are affected by rebar corrosion, and approximately 20 percent have been deemed structurally deficient.[1] The cost to repair or replace these bridges exceeds several billion dollars.[2] Concerns for cost and safety associated with this problem prompted the enactment of the Surface Transportation Efficiency Act of 1991. This act required that all infrastructure projects slated to receive federal funds be designed for a long service life. One approach for the life extension of reinforced concrete structures is through the combined use of several corrosion mitigation strategies including, but not limited to, cathodic protection, metallic coatings, epoxy coatings, alternative cementitious materials (e.g., pozzolans), and inhibitors.[2] This study examined inhibitive admixtures for concrete.

A formulation with calcium nitrite as the active ingredient is the most widely used commercial inhibitor for concrete systems in the United States. Calcium nitrite has been proven effective in preventing accelerated corrosion related to chloride contamination of concrete.[3-6] This inhibitor provides anodic inhibition by raising the valence state of iron in the oxide from +2 to +3 and thus provides a more stable passive film. Although it has not been shown in concrete, anodic inhibitors typically require a critical concentration to prevent increased localized attack over uninhibited systems. This general property of anodic inhibitors is further complicated by the fact that calcium nitrite is water soluble, thus creating a possible scenario of inhibitor leach-out over time and a reduction in concentration to below the critical value. Another problem with calcium nitrite is its toxicity.[7] These shortcomings of calcium nitrite have prompted an investigation to discover new inhibitors capable of placement in concrete with minimal effects to the structural properties of concrete and capable of protecting rebar in concrete against chloride attack.

The long times needed for testing inhibitive admixtures *in situ,* i.e., in concrete, has led to a need for a relatively rapid, quantitative, and accurate method to assess the efficacy of corrosion prevention by admixtures in high-quality concrete. One approach used by these authors is the resistance change method (RCM). The RCM has enabled rapid and unambiguous evaluation of commercial and experimental inhibitors in high-quality concrete.[8-10] This method allows determination of relative corrosion rates by measuring the change in resistance of steel wires over time in concrete that has been ponded with sodium chloride. The RCM is believed by the authors to be the appropriate tool to rapidly and confidently identify new corrosion inhibitors for concrete. However, it must be kept in mind that this is a relatively new tool and is not yet accepted as standard practice.

PURPOSE AND SCOPE

This study examined the ability of a series of chemical compounds to prevent corrosion of steel when the compound is admixed into high-quality concrete. At present, there is no universally accepted practice with regard to testing corrosion inhibitors when admixed into high-quality concrete. This study employed the RCM on steel wires having similar bulk and surface chemistry to rebar to assess the corrosion-inhibition properties in high-quality concrete. These RCM results were compared to an inhibitor screening test that uses electrochemical impedance spectroscopy (EIS) to measure the polarization resistance (R_p) of rebar in a simulated pore solution (SPS). The identification of a valid laboratory screening test that could more conveniently predict the experimental results in concrete would be a valuable research tool.

It is desirable that the addition of an inhibitive admixture does not alter the curing or mechanical properties of the hardened concrete. Thus, this study also examined the effects of the inhibitive admixtures on concrete compressive strength. In addition, the suppression of embedded rebar corrosion can also result from reduced concrete permeability rather than alteration of the electrochemistry of the corrosion process. Changes in the chloride permeability of the concrete were characterized to delineate this effect.

The objectives of this research were as follows:

1. Discover inhibitors with the potential to replace the best existing commercial products. The main goal of this project was to screen a series of compounds for their ability to prevent and suppress corrosion in high-quality concrete relative to the most popular commercial product.

2. Determine the effects of the inhibitors on the properties of the concrete. To examine this issue, the compressive strength of concrete cylinders containing inhibitors was measured. Negative effects on the compressive strength of concrete do not necessarily rule out the inhibitor as a potential inhibiting agent in concrete but certainly make it less desirable than another inhibiting agent with positive or no effect on the strength of concrete. In addition to mechanical properties, this study examined the effect of admixed compounds on the ionic permeability of concrete to delineate corrosion suppression by decreased diffusivity of chloride from

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electrochemical inhibition. Other concrete parameters such as the effect on set time, workability, and finishing were not evaluated in the present study.

METHODS AND MATERIALS

Overview

The corrosion properties of rebar in concrete with admixed inhibitors were evaluated by using a RCM that employed longitudinally cast 1040 steel wires. These steel wires had been heat treated such that the surface oxide emulated the surface oxide of as-received rebar. The polarization resistance of rebar in an SPS with added inhibitors and chlorides was examined using EIS. The results from the RCM and testing in solution using EIS were compared to determine the value of both testing procedures in evaluating inhibitors for use in concrete. Also, the concrete specimens were dissected to ensure corrosion was taking place on the steel wire within bulk concrete and not near the sample ends.

Other properties of concrete with admixed inhibitors examined in this project included compressive strength, specific gravity, and permeability to chlorides. Concrete cylinders and mortar cubes were produced to evaluate these properties of concrete with admixed inhibitors.

Inhibitors Tested

There are no known methods to accurately predict the success of a compound as a corrosion-inhibiting admixture based solely on its chemical structure. However, there are specific chemical species that have enhanced mobile electron densities and facilitate adsorption, a known prerequisite for adhesion. Inhibitor compounds were selected for this research because of prior success as inhibitors in concrete or another system, either commercially or as tested in research, or their possession of these known chemical species. The mode of inhibition, the pH range for inhibition, and the effect of the inhibitors on concrete properties are important attributes of the inhibitors being examined.

Calcium Nitrite (CN)

Nitrites are oxidizing, anodic inhibitors that are probably best classified as a passivator. Calcium nitrite is the active ingredient of one of the more prevalent commercial inhibitors used for embedded steel in concrete.[3,4,6] Calcium nitrite provides corrosion inhibition in the presence of chlorides. Research suggests that calcium nitrite may be an effective inhibitor up to a Cl^-/NO_2 ratio of 0.9.[3,4] Based on its successful application in the field, calcium nitrite was selected as a control compound in this investigation.

Although calcium nitrite has been proven an effective inhibitor for concrete through rigorous tests, the main concern lies in the anodic behavior and water solubility of the inhibitor.[11,12] With most anodic inhibitors, if the concentration drops below a threshold level and

the concrete chemistry is not maintained in its normal condition, passivity will not be maintained and corrosion could be greater than with no inhibitor at all. Research of sodium nitrite in high-pH cooling water systems and calcium nitrite in concrete has found that a critical concentration of nitrite ions is necessary to prevent pitting and that nitrite may contribute to the pitting of carbon steel if the concentration falls below a critical level.[11,13] The toxicity of calcium nitrite also presents concern about its application and suggests the need for research into new corrosion inhibitors for rebar.[7]

Lithium Nitrate (LN)

Although nitrites are used extensively in many corrosion-inhibition applications, the oxidized form of nitrite, nitrate, is thought to exhibit little or no inhibiting effect.[5,6] Lithium is also not typically used in corrosion-inhibition applications. However, lithium nitrate does have an effect on the concrete chemistry. Lithium nitrate has been shown to reduce expansion resulting from the alkali-silica reaction.[14,15] In the alkali-silica reaction, silica-bearing aggregates in the concrete may react with hydroxyl ions present in the concrete mix to produce a gel. This gel absorbs water and swells, placing pressure on the surrounding concrete to cause cracking. Lithium nitrate was selected for testing in this investigation to determine if it had any corrosion-inhibiting or exacerbating tendencies.

di-Sodium β-glycerophosphate (BGP)

Testing of β-glycerophosphate for cooling water corrosion control has shown that at near neutral pH, it acts as an inhibitor.[13] β-glycerophosphate has been shown to be an environmentally safe alternative to other more toxic inhibitors, including calcium nitrite.[7] Research has shown that β-glycerophosphate acts as a cathodic precipitating inhibitor whose performance can be improved by the addition of calcium ions.[7] Tests of β-glycerophosphate in SPSs have shown good inhibiting efficiency and protection against localized attack.[7,12] They have a pH around 12.5 with saturation of calcium hydroxide to imitate pore water extracted from concrete. Further testing found that the inhibitor efficiency of the β-glycerophosphate was equivalent to that of nitrite ions in a SPS.[7] Since β-glycerophosphate is believed to be a cathodic inhibitor, the lack of a critical threshold concentration to prevent accelerated attack allows β-glycerophosphate an advantage over nitrite-based inhibitors. Testing of β-glycerophosphate stems from the need for a nontoxic corrosion inhibitor for concrete application. This system has not been examined in concrete and thus was selected for testing in this study.

Orthoaminothiophenol (ATP)

Orthoaminothiophenol may be classified as an anodic inhibitor but is also thought to affect both the anodic and cathodic processes indirectly as an organic adsorber. Tests conducted by Srhiri et al. using a rotating cylindrical steel electrode found that orthoaminothiophenol produces a relatively thick and compact film on the surface of the steel.[16] The orthoaminothiophenol acts by greatly reducing the active area of the steel without modifying the chemistries of either the anodic or cathodic reactions. Testing also found that in a neutral pH,

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high-chloride solution, orthoaminothiophenol exhibits higher inhibitor efficiency than any other thiol compounds tested.[16] This compound was selected because of the high predicted adsorbing characteristics of the lone pair electrons on the thiol and amine as well as the pi electrons of the benzene.

Nitrilotrismethylene (or Aminotrimethylene) Phosphonic Acid (AMP or PA)

Phosphonic acids are used to prevent scale deposition and corrosion on industrial heat exchangers. The pH range of these systems is usually between 6.5 and 9.5. Research into cooling water systems indicates that AMP also has been used extensively in corrosion control to protect steel at high pH.[13] AMP protects ferrous metals through a mixed mode of inhibition, meaning it can affect the anodic and cathodic reaction processes. AMP is known to degrade in the presence of chloride to form orthophosphate, which is an alkaline inhibitor.[13] Zinc ions in conjunction with AMP have demonstrated effective corrosion inhibition in a SPS.[17]

The zinc ion, by itself, may precipitate a tenuous zinc hydroxide film at the cathodic site for limited corrosion inhibition. Above a pH of 7.5, however, the stability of the zinc ion in solution is low and may not be present in sufficient quantities for inhibition. The addition of phosphonates, including AMP, greatly increases the stability of zinc ions in solution. In addition, the degradation of AMP in the presence of chlorides does not take place when zinc ions are present. The increased stability of both zinc and AMP in solution when introduced together exhibits a synergism between the two inhibitors.[13] Because of the known benefit, zinc cations were used with AMP (PA).

Di-n-Butyl Sulfoxide (DS)

Di-n-butyl sulfoxide has been specifically listed as a theoretically sound corrosion inhibitor.[18] Organic molecules with sulfoxides represent a large group of compounds with the potential for corrosion inhibition through the presence of free electron pairs or a local negative dipole around the sulfur atom. Sulfoxides are generally considered to exhibit anodic inhibition, requiring a critical threshold concentration to preserve the inhibiting effect.[18] The two butane chains connected to the sulfur stabilize the electron density of the sulfoxide, allowing anodic inhibition.

Sodium Metasilicate (NA)

Metasilicates, when added to solution, produce a high pH environment and inhibit corrosion by forming a thin silicate film on the surface of the metal. Silicate ions are considered anodic inhibitors because initial silicate film deposition takes place at anodic sites. However, research indicates that the silicate film will proceed to cover cathodic sites in the presence of the silicate solution.[19] The reduced cathodic area acts to reduce the overall charge transfer available for localized attack, which may take place despite the passive film. The silicate film may precipitate at places on the metal formerly stripped of silicate film when in contact with silicate solution.

In addition to the promising characteristics of the silicates in solution, sodium metasilicate exhibits other admixture effects on reinforced concrete. Findings indicate that reinforced concrete specimens show reduced permeability when chromates or sodium metasilicate are admixed.[11] The combined qualities of reduced permeability and mixed corrosion inhibition show extreme promise for sodium metasilicate as a corrosion inhibitor in concrete.

Aminoethylethanolamine (AMA)

Aminoalcohols demonstrate adsorption inhibition and thus inhibit both the anodic and cathodic reactions at the metal interface. Aminoalcohols form a continuous film that inhibits by preferentially displacing chloride from the metal surface. Due to its mixed inhibitive action, aminoalcohols should not require a threshold concentration to avoid accelerated corrosion. Testing in concrete indicates that aminoalcohols cause a delay in the onset of corrosion and lower corrosion rates of rebar compared to the use of no inhibitive admixture.[20] In addition, research suggests aminoalcohols do not alter concrete strength, air entrainment, or setting time.[20] The concrete admixed with aminoalcohols should be of good quality, considering the absence of observable ill effects from the admixture.

Resistance Change Method

Use of the RCM allows the determination of corrosion status, i.e., whether corrosion is occurring or not, as well as relative corrosion rates of an embedded wire in concrete. Essential to this measurement are the sensitivity of the resistance of the embedded wire to mass loss, similarity of surface conditions on the test wire to rebar surface chemistry, and assurance that corrosion of the embedded wire takes place within the bulk of the concrete and not at the ends. In addition, temperature fluctuations of the wire must be compensated for in the resistance measurement to delineate corrosion-induced resistance change from temperature-induced resistance change. In order to ensure quality measurements, a wire/rod system was developed to meet the mentioned requirements, and a reference wire system was developed to account for temperature fluctuations.

Concrete batches containing different concentrations of inhibitors were developed to allow assessment of the relative inhibiting efficiency of those inhibitors in concrete. The concrete blocks were constructed with ponding dams to allow diffusion of aggressive species from the top of the block. By cycling the blocks between a 0.6 M chloride solution and dry conditions, accelerated corrosion was observed. This allowed for rapid screening of suitable corrosion inhibitors for concrete.

Preparation of Wire/Rod System

The construction of the wire/rod system for placement in concrete requires several stages:

1. The wire is heat treated to produce a surface oxide that emulates that of rebar.

2. The wire is fastened between thick steel rods that are capable of withstanding corrosion without affecting the wire resistance measurements. The wire attaches to the rod at the bottom of a hole milled on the end of the rod that is 0.508 cm (0.2 in) deep.

3. The steel end rods are coated with an epoxy paint and the wire/rod connection is backfilled with cement to slow corrosion near the rod/wire connection, as shown in Figure 1.

4. A wire/rod system is placed into a Plexiglas tube and filled with mortar for use as a temperature reference for each block.

The as-received wire for the resistance change test is altered in surface composition by heat treatment. This is done to allow the corrosion initiation condition to be similar to that of commercial rebar. A 1040 steel wire (diameter 0.009 in (228.6 μm)) was purchased from Mt. Joy Wire Company (Mt. Joy, PA). The wire was placed in a computer-controlled electric furnace for 1 hour at 538°C (1000°F) following a procedure established previously.[8] X-ray photoelectron spectroscopy (XPS) was conducted previously to compare the surface composition of the heat-treated wire and typical No. 5 rebar. The XPS results are shown in Figure 2, where the peaks represent the counts of characteristic values of inner shell ionization of target atoms and illustrate a suitable match of surface chemistry between the heat-treated wire and the No. 5 rebar.

Steel rods that are to be connected to the heat-treated wire must be capable of withstanding significant corrosion and must have a diameter suitable to fit in concrete molds without affecting the total resistance of the wire/rod system. The rods used for connectors to the heat-treated wire were 1045 steel (McMaster-Carr). The rod was 0.25 in (0.635 cm) in diameter good for fitting in concrete molds and capable of withstanding corrosion should it occur at the block ends without affecting the resistance measurement of the wire. The rod was cut into pieces 3.94 in (10 cm) long. A center hole, 0.11 in (0.28 cm) in diameter and 0.2 in (0.508 cm) deep, was then milled in one end of the rod for connection to the wire. This milled region
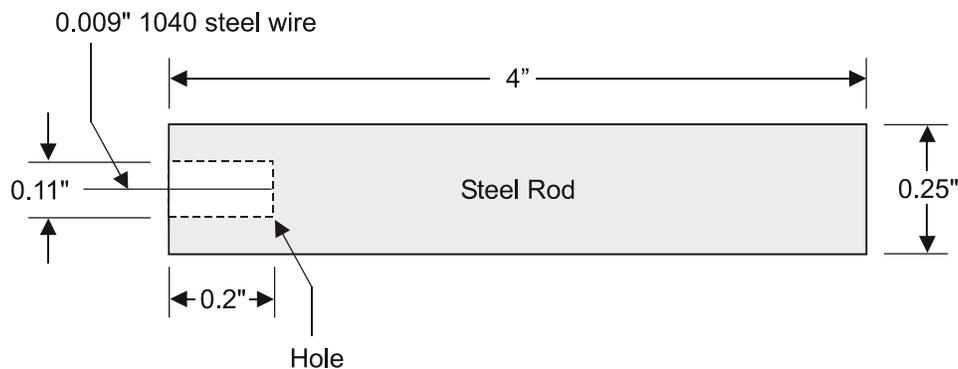
Figure 1. Schematic of wire/rod attachment with backfilled mortar hole.
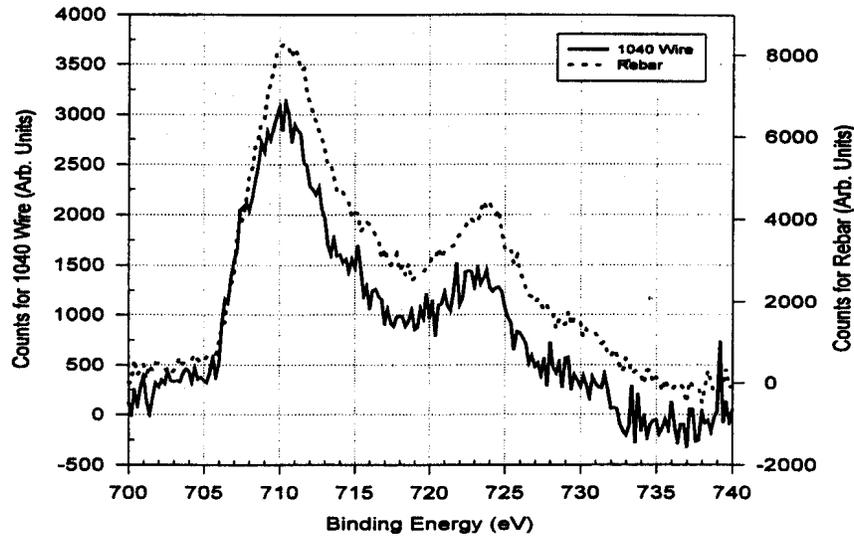
Figure 2. Iron detail of XPS scan of the surfaces of No. 5 rebar and heat treated 1040 steel wires with backgrounds removed. ©NACE International 2000.

provided a chloride shield for the wire connection points. A finite element model determined that the steel rod would need to undergo uniform corrosion over 0.0004 in (0.01 mm) deep and over 1 in (2.54 cm) of its length to affect the fourth decimal place of the resistance measurement.[8] This was an order of magnitude less than the sensitivity of the RCM method. Localized corrosion would need to be much deeper.

The wire was connected to the rods using lead-based solder (X-ergon). The rod was heated with a needle torch to melt the solder. The Pb-Fe galvanic couple is not severe and has an estimated corrosion rate of 60 $\mu A/cm^2$ in an aerated 3% NaCl solution.[21] The expected corrosion is much less than this estimation, since the solder is present in limited amounts, thus producing a small cathode–to–large anode area ratio, a favorable situation. Once the connection between the wire ends and two rods was made, mortar was placed in the recessed groove containing the wire/rod connection to add strength and extra corrosion protection to the wire/rod connection.

The surface region of as-cast concrete has increased availability of oxygen and chlorides and thus provides an environment more conducive to corrosion. Therefore, coatings were placed on the steel rods to provide additional corrosion protection of the wire/rod connection that transected the block surface. These coatings were applied as follows:

1. The steel rods of an assembled wire/rod system were cleaned in an alkaline cleaner bath for 5 min at 57 °C (86.85 g/L of tri-sodium phosphate + 22.5 g/L of sodium carbonate). This cleaner bath will remove contaminants such as machining oil from the rods.

2. Rinse.

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3. Immerse rods in a Zn-phosphate bath (Electrochemical Products, Inc.) for 10 minutes at 60 $^\circ$C. As the acid bath reacts with the metal, neutral solution is formed locally at the rod/solution interface. Metal phosphates precipitate out in neutral solution at cathodic sites on the metal. The coating has a small crystal size and low porosity with an average coating weight of 0.646 to 0.969 mg/cm^2. Although this coating allows limited protection of the steel, it serves well as a base for a more corrosion-resistant epoxy coating.

4. Apply a two-part epoxy coating (Carboline Company). This coating required 24 hours to cure after application to the zinc phosphate-coated steel rods. The epoxy was applied by dipping the rods in epoxy and then brushing the remaining steel rod surfaces with epoxy. The average epoxy coating thickness was ca. 1 mm (0.0393 in) and adhered tightly to the zinc-phosphate coating, providing an effective barrier to moisture and underfilm corrosion. Care was taken when applying both coating systems to avoid coating the 1040 steel wire.

Wire/rod assemblies that were used as temperature references were placed in a Plexiglas tube 26.7 cm (10.5 in) long having an outer diameter of 1.27 cm (0.5 in) and a 0.16 cm (1/16 in)wall thickness. The Plexiglas tube, now containing the wire/rod assembly, was filled with mortar having a water/cement (w/c) ratio of 0.45. In the production of the resistance measurement blocks, mortar was forced into one end of the Plexiglas tube containing the wire/rod assembly until the tube was full. This method of producing temperature reference wires lead to loss of wire/rod continuity in some samples. After the mortar or cement was allowed to cure for 24 hours, silicone caulk was applied to the ends of the tube to seal against moisture and aggressive species. In principle, the reference wire will not be exposed to aggressive species and thus will not undergo corrosion. This wire can then be used as a temperature reference since the fluctuation of the resistance of the reference wire may be attributed solely to temperature changes and not to changes caused by corrosion of the wire.

Casting and Preparation of the Concrete Specimens for the RCM

Once the steel rod/wire assembly was ready for placement into the concrete, the batch ingredients, added inhibitors, and concrete molds were prepared for casting RCM concrete specimens.

Post and rail overlay mix with a w/c ratio of 0.45 was used for casting the specimen blocks. This mix is identical with a standard VDOT Type A4 concrete mixture with the exception of the coarse aggregate size. No. 4 coarse aggregate was used to ease the pouring of the concrete into molds containing the fragile rod/wire assemblies. The batch ingredients and amounts of each for a standard batch without inhibitors were as follows:

Post and Rail Overlay Mix	Batch Proportions
6.135 lb Type I/II Roanoke cement	663 lb/yd^3
14.352 lb fine aggregate (sand)	1550 lb/yd^3
14.55 lb coarse aggregate (No. 4)	1571 lb/yd^3
2.76 lb water at room temperature	298 lb/yd^3 (w/c = 0.45)

The coarse and fine aggregates were water saturated for 24 hours and then drained for 48 hours to obtain a consistent moisture condition. The amount of water batched on several mixes was adjusted to account for the water content of the inhibitor admixture and maintained the 0.45 w/c ratio. The amount of inhibitor added, change in water content of the batch, and other information regarding the resistance measurement blocks produced is listed in Table 1.

A table-top mixer was used for all concrete batches. First, inhibitive admixtures were added to either the cement or mix water prior to being placed in the mixer. Solid admixtures were added to the bag of cement and shaken thoroughly. Liquid admixtures were added to the mix water and stirred. Second, the coarse aggregate and half the amount of mix water were added to the mixer. Third, the fine aggregate, cement, and remaining mix water were added to the mixer. All ingredients were mixed at low speed (140 ± 5 rpm) for 3 minutes and then allowed to rest for an additional 3 minutes. During the rest period, the mix was covered with a wet towel to prevent evaporation of the mix water. Fourth, the admixture was mixed for an additional 2 minutes at a medium speed (285 ±10 rpm).

Once the concrete was mixed, wire/rod assemblies were placed longitudinally in the concrete molds before the concrete was placed. First, the reference wire was positioned on the lowest placement level on the mold and concrete was spooned in around it. Next, if an intermediate level of rod/wire assemblies was to be installed, they were placed on the level above

Table 1. Concentration of Inhibitors Used in Resistance Change Measurement Blocks

Chemical Compound	Abbrev.	Concrete Conc. (mol/ft^3)	No. Samples	Amount per 0.25 ft^3 Concrete	Less H$_2$O in Batch	Source
β-glycerophosphate	BGP-1	0.815	3	62.4 g	125 ml	Alfa Aesar
	BGP-2	0.283	3	21.7 g		
Control	Co-1		3			
	Co-2		3			
Calcium Nitrite	CN	0.815	4	70 ml	44.5 ml	WR Grace
Lithium Nitrate	LN	0.815	4	14.05 g		Fisher
2-aminothiophenol	ATP-1	0.815	4	21.8 ml		Fluka
(99% pure)	ATP-2	0.283	4	7.6 ml		
	ATP-3	2.832	4	75.8 ml		
Phosphonic acid	PA	0.815	4	30.5 g AMP		Fluka
				56 g zinc salt		
Dibutyl Sulfoxide	DS-1	0.815	4	33.01 g		Aldrich
	DS-2	0.283	4	11.46 g		
	DS-3	2.832	4	114.62 g		
Sodium Metasilicate	NA-1	0.815	4	24.87 g		Fluka
	NA-2	0.283	4	8.64 g		
	NA-3	2.832	4	86.36 g		
Aminoethylethanolamine	AMA-1	0.815	4	20.6 ml		Fluka
(97% pure)	AMA-2	0.283	4	7.2 ml		
	AMA-3	2.832	4	71.6 ml		

Note: This concentration of CN is the lowest recommended dosage without consideration of the chloride content of the concrete. All inhibitors were tested under similar conditions to examine the relative effectiveness.
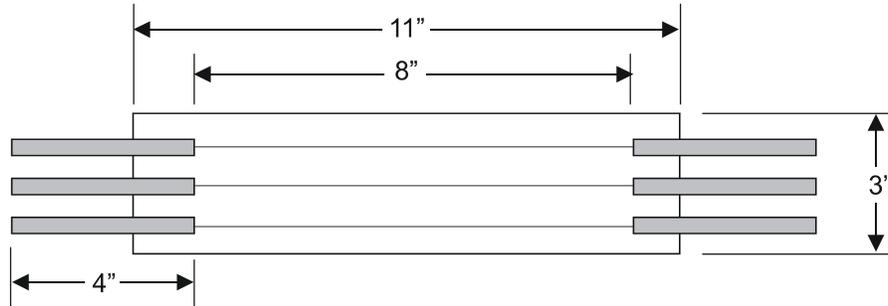
Figure 3. Schematic of wire placement in sample block (overhead view).

the reference wire, and concrete was carefully spooned in around and then over them. This step was then repeated for the top level of the rod/wire placement. An overhead view of the sample block with top-level wire placement is shown in Figure 3.

The segmented mold ends fitting around the rods were then tightened using wing nuts to maintain the rod/wire placement. A schematic of the mold demonstrating the sizes of the parts and how they fit together is shown in Figure 4. Next, the mold was filled with concrete, vibrated to consolidate the concrete, and given a wood float top surface finish by pushing a rectangular piece of wood across the top of the mold to even out the concrete surface. The concrete-filled molds were covered with plastic to prevent evaporation of water and allowed to cure at room temperature for 24 hours. Finally, the blocks were removed from the concrete molds and placed in a moist room to cure for 28 days at a temperature of 23 $^{\circ}$C (72 $^{\circ}$F).

When the concrete measurement blocks were finished curing, the blocks were removed from the moisture room and prepared for testing by skiving the top ¼-in surface layer of concrete using a wet diamond saw blade. This was done to eliminate surface effects on permeability and to reduce the time for corrosion initiation. The blocks were further prepped by attaching RCA connecters to the ends of rods to facilitate electrical lead connection and by attaching Plexiglas™ ponding dams to the top of the blocks.

The ends of the steel rods were exposed using a wire brush, and RCA connectors (Switchcraft) were attached using a silver-filled conductive epoxy. The conductive adhesive (McMaster-Carr) had a resistivity less than 0.0001 ohms-cm^2. After the silver epoxy had cured for 24 hours, epoxy (Carboline) was placed over the attachment area of the leads to prevent corrosion from taking place at this sensitive connection. RCA plugs allowed ready attachment of electrical leads for 4-point resistance measurement.

Finally, ponding dams were constructed from Plexiglas™ strips (0.25 in thick, 1 in tall) glued together with acrylic adhesive and attached to the top of the blocks using silicone caulk. A schematic demonstrating the size and setup of the ponding dam is shown in Figure 5.

½"
½"
½"
1 ½"

holes for
steel rods
5/16" dia

4"

End View

3"
0.5"
12"

Side View

3"
0.5"
11"

Top View
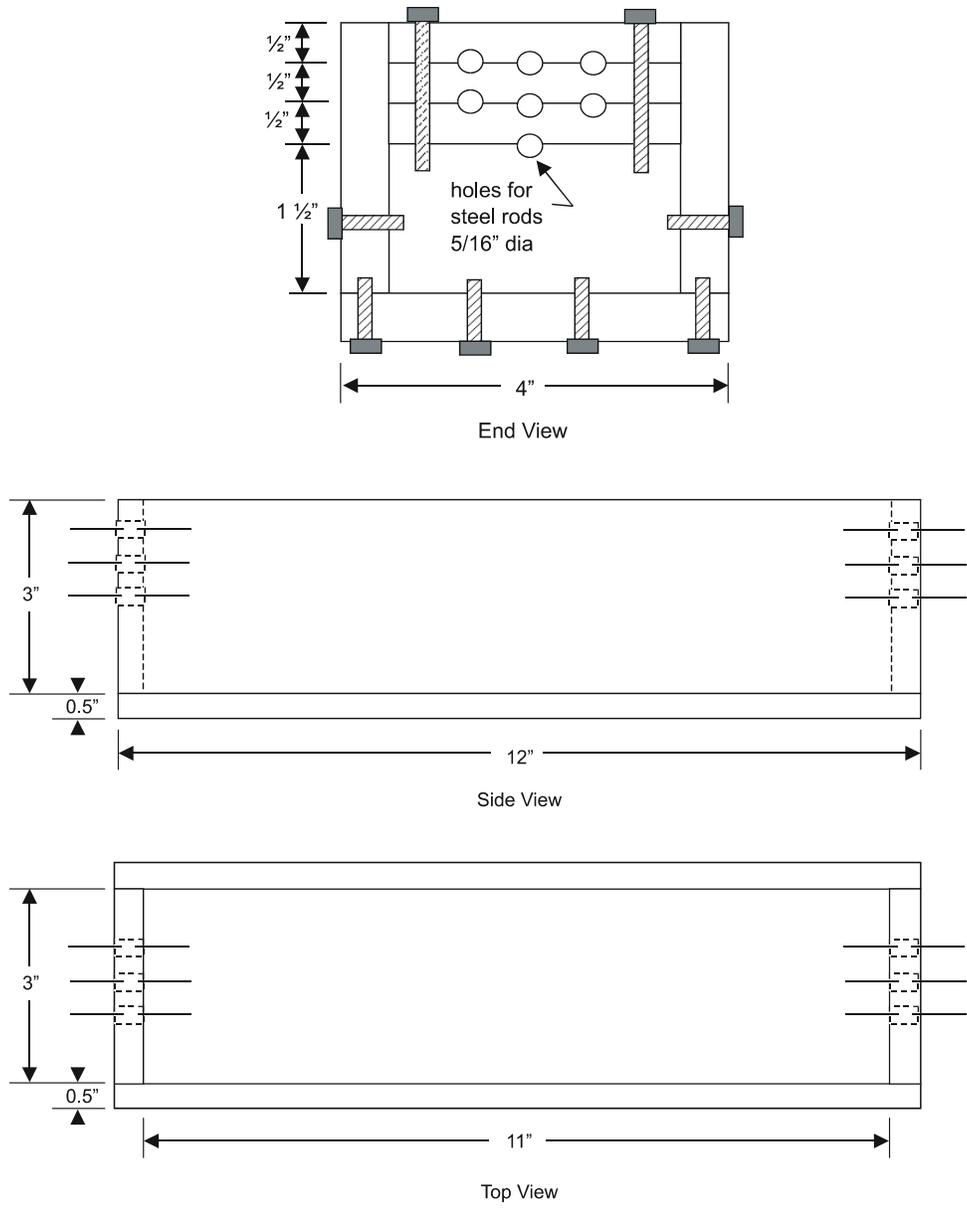
Figure 4. Schematic of concrete mold.   All sheets are ½-in Plexiglas.

Ponding Dam

1"

Sample Block

10.5"

3.0"

2.5"

11.0"
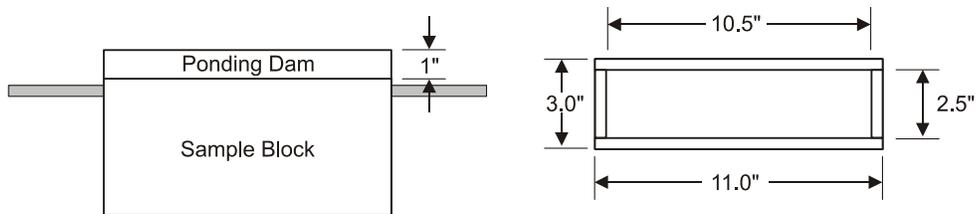
Figure 5. Ponding dam schematic.

Testing Specimens Using the Resistance Change Method

When the resistance measurement blocks were ready for testing, chloride was added to the blocks through a ponding cycle to expedite wire corrosion for more rapid assessment of the relative efficiency of the various corrosion inhibitors. A 7 days wet/14 days dry ponding cycle was followed using 0.6 M (3.5 wt%) NaCl solution. The ponding dams were filled with the salt solution on the first day of measurements and then emptied on the next week prior to taking measurements.

Resistance change measurements of the test blocks were conducted once a week using a Keithley 2001 digital multimeter. The Keithley 2001 digital multimeter was set to a four-wire resistance mode to eliminate lead resistance values from the desired wire resistance. RCA plugs were attached to the multimeter in five channels, one for each wire, and to the block on each end of the wire/rod system at the RCA connectors. Each block was placed in a black Plexiglas™ box and allowed to sit for 10 minutes before measurements were taken to allow the temperature measurement system to equilibrate. Thirty resistance values were measured for each channel over a period of 5 minutes, and the values were averaged to obtain a resistance measurement. The resistance values of each test wire were then divided by the resistance of the temperature reference wire for that block (if available) to obtain a unitless temperature-corrected "resistance" value.

Dissections of Resistance Change Concrete Specimens

Based on the significant time required to conduct a dissection, several RCM concrete specimens were randomly selected for analysis after all the test wires for the corrosion study had reached an infinite resistance. This open circuit condition indicated that the wires had corroded completely through their cross section. The purpose of the dissections was twofold. First, the dissection and analysis was conducted to ensure that the test wire had indeed corroded through at some point within the bulk of the concrete. Second, the dissection and analysis were performed to examine at what distance from the end in the concrete the wire had corroded through. This examination was conducted to ensure that corrosion was not taking place merely at the wire/rod interface, which would imply that the sample construction method was affecting the test results.

Dissection Method

The block was labeled in nine equal sections that represented transverse slices on the longitudinal axis. The sections were 2.54 cm (1 in) thick starting at 5.08 cm (2 in) from the ends. After labeling, the top layer of concrete (top 7/8 in) containing the rod/wire system was removed using a diamond tipped saw. This layer was then sectioned into the nine transverse pieces, and the surfaces were rinsed to reveal the wire ends area.

Analysis of Corrosion in Dissection

The sections were analyzed by placing voltmeter leads on each end of the exposed wire in the concrete section and measuring the resistance. Infinite resistance indicates that the wire in

that section was no longer continuous. To facilitate voltmeter probe contact, the exposed wire ends were coated with a conductive copper paint.

Measurements in Simulated Pore Solution

The electrochemical behavior of the inhibitors were examined in SPS. SPS simulates the concrete chemistry and allows the use of conventional electrochemical methods. Inhibitor effectiveness was quantified using EIS to determine the polarization resistance (R_p) of rebar in SPS containing chlorides and test inhibitors. These electrochemical measurements complemented the RCM results by delineating those compounds that intrinsically affect the electrochemical reaction kinetics (actual corrosion inhibitors) from those that alter the chloride permeability of concrete.

Experimental Cell

Electrochemical tests were conducted in a polymethylpentene cell to avoid caustic attack of a glass cell. A separate reservoir with a Luggin probe was used to protect the saturated calomel reference electrode (SCE). The working electrode consisted of steel rebar 5 cm (2 in) long by 1.27 cm (0.5 in) diameter; the counter electrode consisted of a concentric cylindrical platinized niobium mesh surrounding the working electrode. A schematic of the electrochemical cell setup demonstrating placement of the electrodes is displayed in Figure 6.
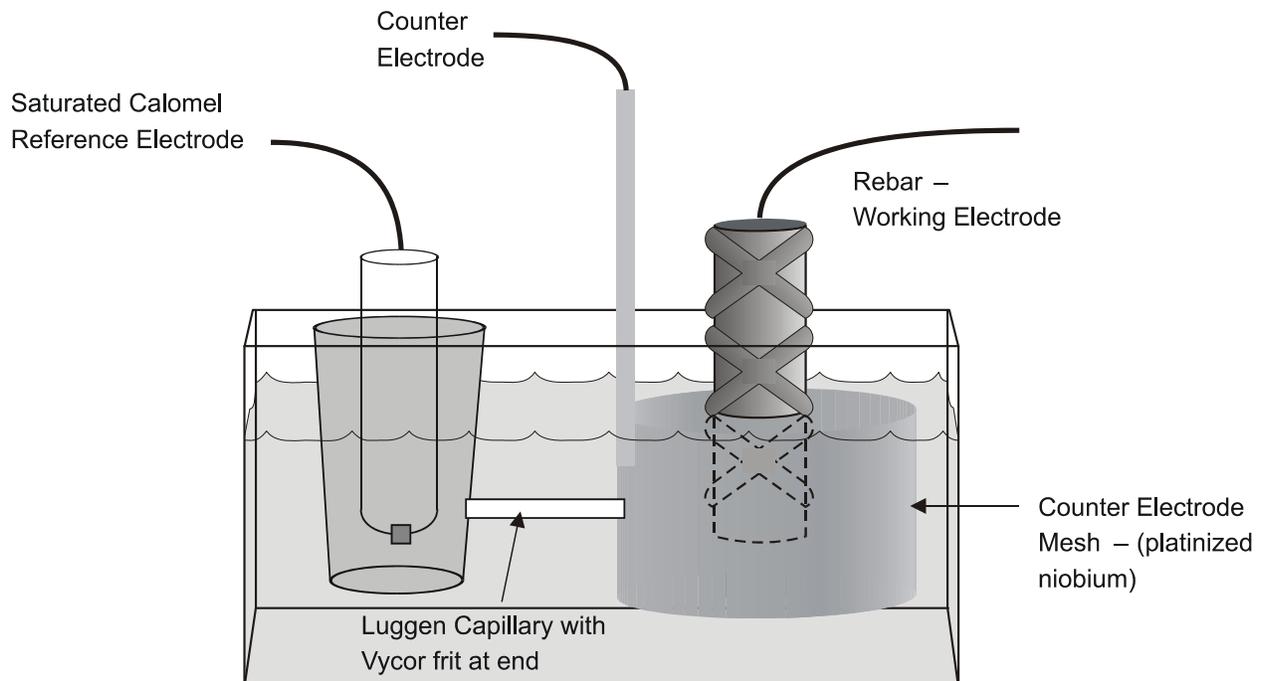
Figure 6. Schematic of electrochemical cell.

The rebar was prepared for testing by cleaning ultrasonically in hexane. A Teflon washer was attached to the end to prevent corrosion attack and restrict the electrochemical results to the rebar surface. A hole 1.905 cm (0.75 in) deep was drilled and tapped on the rebar end for attachment of the washer. The Teflon washer was attached using a nylon screw to the end of the rebar to be immersed. The area around the nylon screw and the Teflon washer were then sealed with silicone caulk to prevent crevice corrosion at the Teflon/steel junction.

Methodology for Solution Testing

SPS consisted of saturated calcium hydroxide. Following cleaning and washer attachment, the rebar was immersed in the SPS (as shown in Figure 6) under ambient aeration and allowed to reach a stable open circuit potential (OCP) prior to EIS testing. Following inhibitor addition, the rebar was allowed to equilibrate for 72 hours prior to conducting OCP measurements and EIS testing.

After 72 hours of immersion and subsequent testing by EIS, sodium chloride was added to the solution to reach a 0.3 M concentration. The addition of inhibitor to the solution followed by the addition of chloride simulated the sequence of events in field exposure. The sample was allowed to stabilize for another 12 hours, as assessed by the OCP, before another impedance scan was conducted. Sodium chloride was then added again to bring the final chloride concentration of the solution to 0.6 M. The sample was allowed to equilibrate for 12 hours again before EIS testing. The inhibitor concentrations tested are listed in Table 2.

The EIS measurement was conducted using a 10 mV root-mean-square sine wave voltage excitation imposed on a DC potential set at the OCP. The voltage excitation was varied in frequency from 65 kHz to 0.01 Hz. Measurements were conducted using a Solartron 1286 Electrochemical Interface and a Solartron 1255 Frequency Response Analyzer, both under software control. All instruments were calibrated.

Table 2. Inhibitor Dosages for Electrochemical Impedance Scans (n = 1)

Chemical Compound	Dosage	Amount/L
β-glycerophosphate	0.01M	3.06 g
Control	n.a.	n.a.
Calcium nitrite	0.01M	3.44 ml
Lithium nitrate	0.01M	0.69 g
2-aminothiophenol	0.01M	1.07 ml
Phosphonic acid	0.01M	2.99 g
Dibutyl sulfoxide	0.01M	1.62 g
Sodium metasilicate	0.01M	1.22 g
Aminoethylethanolamine	0.01M	1.01 ml

Characterization of Admixed Concrete

The addition of chemical compounds (e.g., corrosion inhibitors) to concrete paste could have adverse effects on other properties of the concrete. To this end, the effect of the test

inhibitors on the compressive strength of admixed concrete was examined. In addition, density and permeability measurements were made on concrete cylinders to obtain additional data on the effects of the inhibitors on concrete properties.

Preparation of Concrete Compressive Cylinders

Concrete cylinders were produced to test the effect of all inhibitors studied in this project on concrete properties. The compressive strength and density were recorded for the concrete cylinder. In addition to these properties, concrete cylinders were also produced for chloride permeability testing. The batch ingredients for the concrete cylinders were batched separately yet identical with the batch ingredients for the resistance change measurement blocks. The inhibitor amounts and water corrections for the concrete compressive cylinders are listed in Table 3.

The batch ingredients were mixed using the same procedure as the RCM blocks except for the molds used. The concrete was cast in a disposable plastic cylinder 4 in (10 cm) in diameter and 8 in (20 cm) in height. The concrete was placed into the molds and then vibrated to consolidate. The tops of the molds were given a wood float top surface finish and then covered with a plastic cap. The entire mold was covered with a plastic sheet to minimize water evaporation. The concrete was allowed to cure for 24 hours and then demolded. Concrete containing some admixture was still green after 24 hours. These were demolded at a later age when it could be accomplished without damaging the cylinder. Upon removal from the molds, the concrete cylinders were placed in a moisture room maintained at 72 $^{\circ}$F (23 $^{\circ}$C) and 100 percent relative humidity and allowed to cure for 28 days before testing.

Table 3. Inhibitor Dosages for Concrete Cylinders

Compound	Abbrev.	Dosage (mol/ft^3 concrete)	No. Samples	Amt./ 0.25 ft^3 concrete	Less H$_2$O in Batch	Source
β-glycerophosphate	BGP-1	0.283	4	21.7 g		Alfa Aesar
	BGP-2	0.815	4	62.4		
Control	Co-1		4			
Calcium nitrite	CN-1	0.283	4	24.56 ml	15.6 ml	WR Grace
	CN-2	0.815	4	70.8 ml	45 ml	
Lithium nitrate	LN-1	0.283	4	4.88 g		
	LN-2	0.815	4	14.05 g		
2-aminothiophenol	ATP-1	0.283	4	7.6 ml		Fluka
	ATP-2	0.815	4	21.8 ml		
Phosphonic acid	PA-1	0.283	4	10.6 g		Fluka
	PA-2	0.815	4	30.5 g		
Dibutyl sulfoxide	DS-1	0.283	4	11.46 g		Aldrich
	DS-2	0.815	4	33.01 g		
Sodium metasilicate	NA-1	0.283	4	8.64 g		Fluka
	NA-2	0.815	4	24.87 g		
Aminoethylethanolamine	AMA-1	0.283	4	7.2 ml		Fluka
	AMA-2	0.815	4	20.5 ml		

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Determination of Density of Cylinders

The density of the concrete is needed to normalize the compressive strength measurements. Density was determined by obtaining the weight of the concrete or mortar in air and in water. The concrete cylinders were weighed in air on a digital scale and then weighed in water using a suspended stage attached to a digital scale. The density was calculated by dividing the weight of the cylinder in air by the difference between its weight in air and its weight in water.

The density was used as an approximation of the air content of the concrete, which is useful in correcting for the effect of air content on compressive strength. Typical air content corrections for compressive strength use a 1 percent larger air content, leading to a 5 percent reduction in compressive strength.[22] Thus, the air content effects on strength for the inhibitor doses can be normalized to the control air content by adjusting air content and strength. The air content of the concrete was determined from the following equation[22]:

$$\text{Air content} = ((\text{Air free density}) - ((W_{air})/(W_{air} - W_{water})))/(\text{Air free density}) \qquad (1)$$

where W_{air} corresponds to the weight of the object in air and W_{water} corresponds to the weight of the object in water. The air free density may be calculated by the following equation[33]:

$$\text{Air free density} = \Sigma((m_i)/(\rho_i))/(\Sigma((m_i)/(\rho_i)))*(\rho_i) \qquad (2)$$

where m_i corresponds to the mass of the batch ingredient, i, and ρ_i corresponds to the density of the batch ingredient, i. The formula is summed over all the batch ingredients.

Mechanical Testing of Cylinders

Compressive strength testing was conducted on a Baldwin Tate-Emery Load Indicator with load pacer. The force was applied at a continuous rate using a hydraulic press until the force reached a maximum. At this point the concrete or mortar fractured and the force applied decreased abruptly. The maximum compressive strength was recorded and then corrected for air content.

Chloride Permeability Testing

The concrete samples were tested for chloride permeability using the Electrical Indication Test (ASTM C 1202).[23] Testing of permeability was conducted on the concentrations of the inhibitors listed in Table 4.

Table 4. Admixed Compounds and Concentrations Tested for Concrete Permeability to Chloride (n = 1)

Admixed Compound	Abbrev.	Dosage (mol/ft^3 concete)
Aminoethylethanolamine	AMA-1	0.283
	AMA-2	0.815
2-aminothiophenol	ATP-1	0.283
	ATP-2	0.815
Di-sodium β-glycerophosphate	BGP-1	0.15
	BGP-2	0.283
	BGP-3	0.3
	BGP-4	0.45
	BGP-5	0.815
None	Control	
Calcium nitrite	CN-1	0.283
	CN-2	0.815
	CN-3	1.63
	CN-4	2.47
Di-n-butyl sulfoxide	DS-1	0.283
	DS-2	0.815
Fly ash	FA-1	Replace 20% cemt.
Lithium nitrate	LN-1	0.283
	LN-2	0.815
	LN-3	1.63
	LN-4	2.47
Sodium metasilicate	NA-1	0.283
	NA-2	0.815
Nitrolotrisphosphonic acid	PA-1	0.283
	PA-2	0.815

RESULTS AND DISCUSSION

Overview

The results of this project are presented and discussed in four parts: (1) RCM, (2) electrochemical tests in SPS, (3) compressive strength testing, and (4) chloride permeability tests. The results and information from these experiments are initially presented and then subsequently discussed in greater detail. The results of the resistance measurements, testing in pore solution, and measurements of concrete properties all contributed to a broader understanding of the inhibitors studied in this project and the inhibitor evaluation process.

Resistance Change Method Results

The RCM allowed the determination of the change in wire resistance over time and the amount of time necessary for a wire to corrode through. The amount of time necessary for wires to corrode through allowed unambiguous comparison of the inhibitor performance at the various

concentrations used. The change in wire resistance over time permitted further insight into the effectiveness of each inhibitor and concentration.

Examination of RCM Data

The measured resistance from each wire was plotted versus the week the measurement was taken. Each resistance value was first divided by the reference wire resistance to correct for temperature fluctuations. However, in many cases, the reference wire resistance was either unstable, possibly due to poor electrical contact, or infinite, due to complete loss of wire conductivity. The resistance values, either temperature corrected or not, were then selected for linear regression analysis.

The consistency of the uncorrected resistance values was less than for the temperature corrected values since fluctuations in temperature independently cause fluctuations in resistance. However, a comparison of the linear regression slopes of the same wire, both referenced and not, showed that the nonreferenced wires were associated with the same or very similar corrosion rate as was the referenced wire and are reasonable to consider in evaluation of the inhibitors. Examples of the validity of the nonreferenced data are presented in Table 5, and the graphs corresponding to these data may be found in Chambers.[24]

The wires used in the resistance measurement graphs are referred to by number according to their respective location in the concrete. Figure 7 shows the relative location of the wires in concrete. The circles representing the wire location actually represent the cross-sectional area of the steel rods connected to the wires if Figure 7 is to be considered to scale.

Table 5. Comparison of Referenced vs. Nonreferenced Change in Resistance Measurements

BLOCK	Wire	Time Period of Measurement (weeks)	Referenced? (y/n)	Corrosion Rate (Ω/Ω-wk)	(Ω/wk)	Time to Open Circuit	Current Status of Wire
BGP-2, #3 (0.283 mol/ft^3)	4	35-62	y	0.0203			
	4	38-62	n		0.0231		Active (unbroken)
NA-1, #1 (0.815 mol/ft^3)	1	43-55	y	0.005			
	1	43-55	n		0.0052		
	1	55-90	y	0.0002			
	1	55-90	n		0.0002		Active (unbroken)
	2	48-93	y	0.0146			
	2	52-102	n		0.103		Active (unbroken)
AMA-1, #3 (0.815 mol/ft^3)	4	30-48	y	-0.0009			
	4	37-48	n		-0.0008		
	4	48-62	y	0.0653			
	4	48-62	n		0.0525	64	Open (broken)
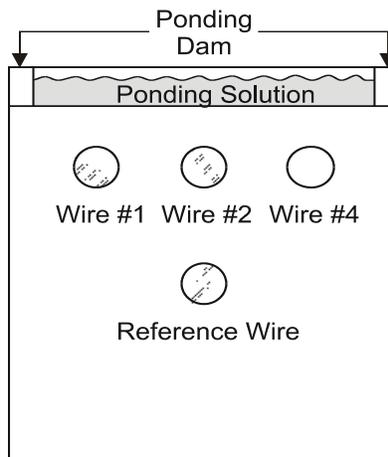
Figure 7. Wire placement and numbering used in resistance measurement blocks.

Chloride seepage from the ends of most blocks eventually corroded the RCA connector leads at the ends of the steel rods. This corrosion product buildup was believed to be the source of outlier resistance data. A conductive grease was applied to the connectors and eliminated much of the noise; however, significant outliers were excluded from subsequent analysis. Lines were fit to the selected data using linear regression in Microsoft Excel. The slopes of the resistance change in ohms per week are shown on each graph along with the linear correlation coefficient, R^2 (1 represents a perfect fit) near the line to which they correspond. Example graphs showing blocks with a consistent reference wire (Figures 8 and 9), unstable reference wire (Figures 10 and 11), and nonfunctioning reference wire (Figures 12 and 13) are shown.

Example graphs of resistance ratios corrected for temperature fluctuations are shown in Figures 8 and 9. The values of resistance ratios given in these plots were presented in temperature-corrected resistance units where the resistance of the test wire was divided by the resistance of the reference wire. These figures present the resistance ratios measured over the different testing periods for a specific calcium nitrite block (block 2) at 0.815 mol/ft^3. Figure 8 shows the resistance ratios versus time data of wires 1 and 2 for this calcium nitrite block. Figure 9 shows the resistance ratios versus time data of wire 4 for this calcium nitrite block. Note that the resistance change occurs in different stages; small changes in resistance are usually seen over a large time period, indicating a low corrosion rate. Large changes in resistance ratios typically occur over smaller time periods indicating localized corrosion taking place at some point on the wire.

The graphs of resistance ratios change versus time for stable, active reference wires are considered to represent the most accurate corrosion rate data in this project. Figures 8 and 9 display the temperature-corrected resistance ratios versus time for block 2 of calcium nitrite at a concentration of 0.815 mol/ft^3. The resistance ratios of wire 1 did not increase rapidly for the first 44 weeks but increased rapidly over the next 5 weeks until the wire corroded through. At this point, no current could pass through the wire. Wire 2 of the same block remained at a low corrosion rate for the first 40 weeks of testing and then corroded rapidly for the next 13 weeks until it corroded through. Wire 4 of the block, shown in Figure 9, corroded slowly for the
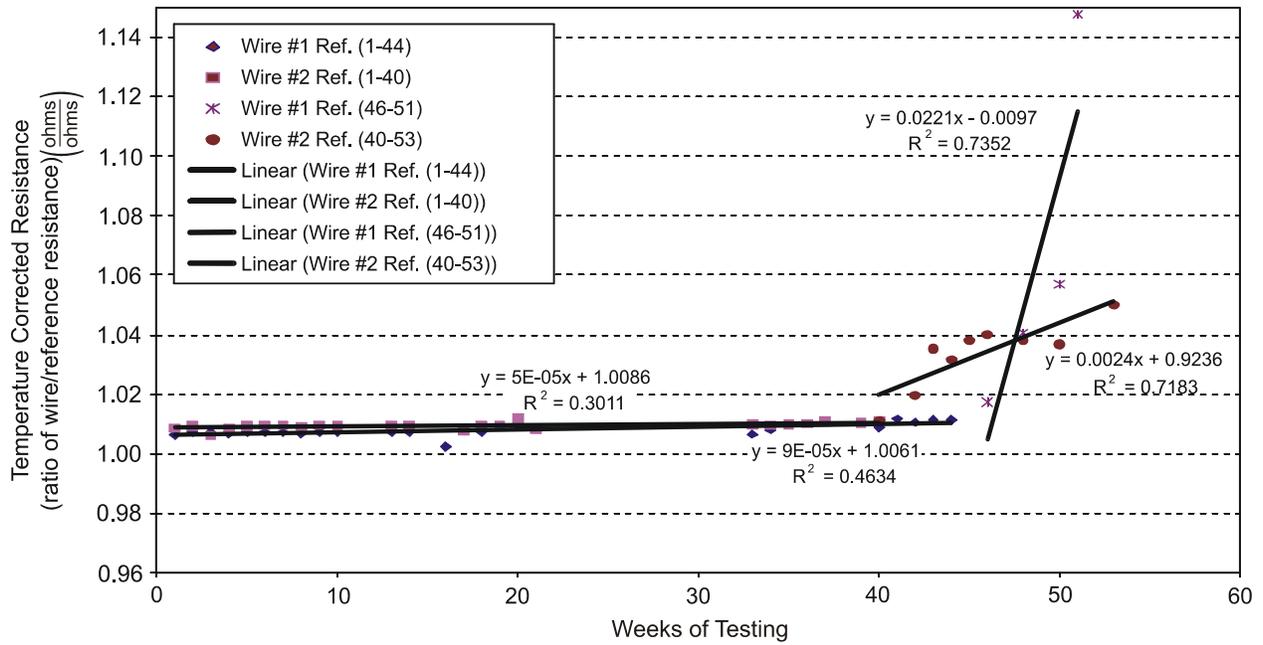
20

Chart axes:
- Y-axis: Temperature Corrected Resistance (ratio of wire/reference resistance) $\left(\frac{ohms}{ohms}\right)$
- X-axis: Weeks of Testing

Legend:
- ◆ Wire #1 Ref. (1-44)
- ■ Wire #2 Ref. (1-40)
- ✳ Wire #1 Ref. (46-51)
- ● Wire #2 Ref. (40-53)
- — Linear (Wire #1 Ref. (1-44))
- — Linear (Wire #2 Ref. (1-40))
- — Linear (Wire #1 Ref. (46-51))
- — Linear (Wire #2 Ref. (40-53))

Equations on chart:
$y = 0.0221x - 0.0097$
$R^2 = 0.7352$

$y = 5E{-}05x + 1.0086$
$R^2 = 0.3011$

$y = 0.0024x + 0.9236$
$R^2 = 0.7183$

$y = 9E{-}05x + 1.0061$
$R^2 = 0.4634$

Wire	Time Period (weeks)	Referenced? (y/n)	Corrosion Rate (ohms/ohm-week)	Week went open	Current Status of wire
1	1-44	y	9.00E-05		
1	46-51	y	2.21E-02	52	Open
2	1-40	y	5.00E-05		
2	40-53	y	2.40E-03	53	Open

Figure 8. Graph of temperature corrected resistance versus week of testing for calcium nitrite block 2. Data are for wires 1 and 2.
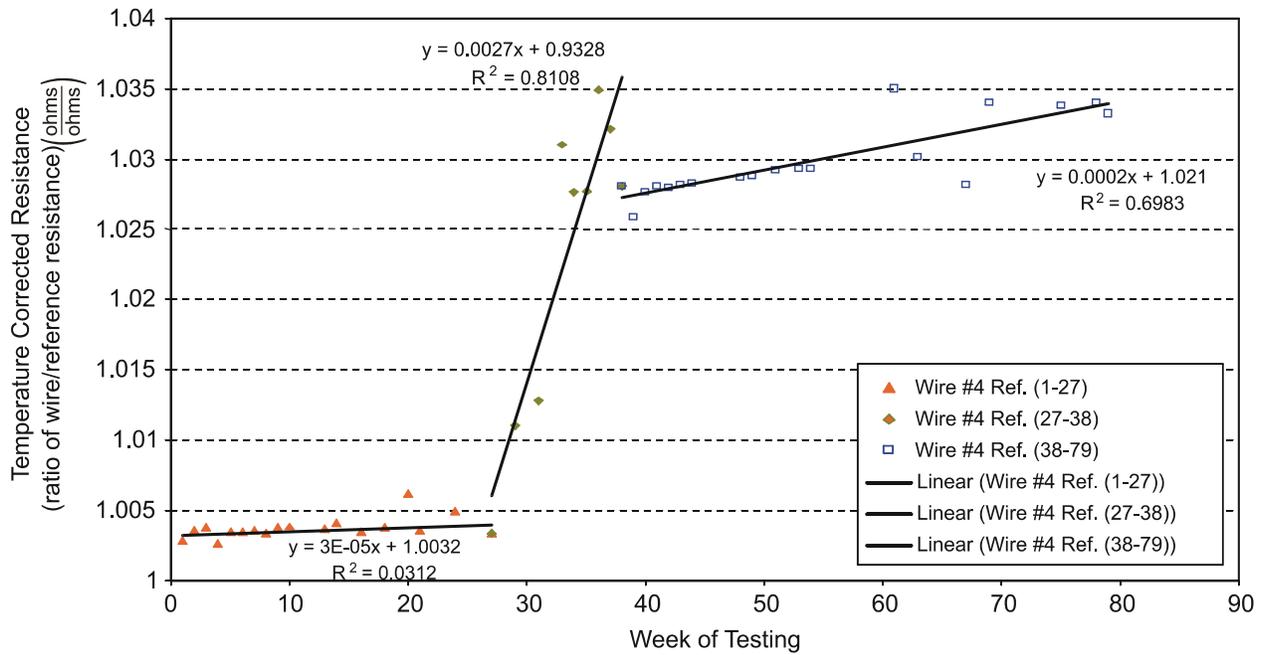
y = 0.0027x + 0.9328
R^2 = 0.8108

y = 0.0002x + 1.021
R^2 = 0.6983

y = 3E-05x + 1.0032
R^2 = 0.0312

Temperature Corrected Resistance
(ratio of wire/reference resistance) $\left(\frac{ohms}{ohms}\right)$

Week of Testing

▲ Wire #4 Ref. (1-27)
◆ Wire #4 Ref. (27-38)
□ Wire #4 Ref. (38-79)
—— Linear (Wire #4 Ref. (1-27))
—— Linear (Wire #4 Ref. (27-38))
—— Linear (Wire #4 Ref. (38-79))

Wire	Time Period (weeks)	Referenced? (y/n)	Corrosion Rate (ohms/ohm-week)	Week went open	Current Status of wire
4	1-27	y	3.00E-05		
4	27-38	y	0.0027		
4	38-79	y	0.0002	79	Open

Figure 9. Graph of temperature corrected resistance versus week of testing for calcium nitrite block 2. Data are for wire 4.

Figure 10. Graph of resistance (corrected and not temperature corrected) versus week of testing for di-sodium β-glycerophophate block 3 at 0.283 mol/ft^3. Data are for wires 1 and 2. *Note the different units for referenced and nonreferenced wires.

Chart elements:

Y-axis: Resistance (ohms) or $\left(\frac{ohms}{ohms}\right)$ *

X-axis: Weeks of Testing

Legend:
- Wire #1 Ref. (1-56)
- Wire #2 Ref. (1-4)
- Wire #1 NonRef. (1-101)
- Reference Wire (1-62)
- Linear (Wire #2 Ref. (1-4))
- Linear (Wire #1 Ref. (1-56))
- Linear (Wire #1 NonRef. (1-101))
- Linear (Reference Wire (1-62))

Equations on chart:
- $y = 0.0163x + 0.918$ $R^2 = 0.7094$
- $y = 0.0015x + 0.9138$ $R^2 = 0.7822$
- $y = -0.0014x + 0.968$ $R^2 = 0.9249$
- $y = -8E-06x + 0.8838$ $R^2 = 0.0016$

Wire	Time Period (weeks)	Referenced? (y/n)	Corrosion Rate	Week went open	Current Status of wire
1	1-56	y	-0.0014 (ohms/ohm-week)		
1	1-101	n	-8.00E-06 (ohms/week)		Active
2	1-4	y	0.0163 (ohms/ohm-week)	5	Open

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Legend
▲ Wire #4 Ref. (1-35)
■ Wire #4 Ref. (35-62)
● Wire #4 NonRef. (38-62)
◆ Wire #4 NonRef. (62-102)
▬ Linear (Wire #4 Ref. (1-35))
▬ Linear (Wire #4 Ref. (35-62))
▬ Linear (Wire #4 NonRef. (62-102))
▬ Linear (Wire #4 Ref. (35-62))
▬ Linear (Wire #4 NonRef. (38-62))

Chart annotations:

$y = 0.0016x + 1.6206$
$R^2 = 0.5415$

$y = 0.0231x + 0.0778$
$R^2 = 0.9245$

$y = 0.0203x + 0.2284$
$R^2 = 0.9268$

$y = -0.0009x + 0.9708$
$R^2 = 0.8725$

Axis labels: Resistance (ohms) vs. Weeks of Testing

Wire	Time Period (weeks)	Referenced? (y/n)	Corrosion Rate (ohms/week)	Week went open	Current Status of wire
4	1-35	y	-0.0009		
4	35-62	y	0.0203		
4	38-62	n	0.0231		
4	62-101	n	0.0016		Active

Figure 11. Graph of resistance (corrected and not temperature corrected) versus week of testing for di-sodium β-glycerophophate block 3 at 0.283 mol/ft³. Data are for wire 4. *Note the different units for referenced and nonreferenced wires.

Figure 12. Graph of resistance (not temperature corrected) versus week of testing for minoethylethanolamine block 2 at 0.283 mol/ft^3. Data are for wires 1 and 2.

				y = 0.0386x + 4.0933
Wire	Time Period	Referenced?	Corrosion Rate	Week went	Current Status
	(weeks)	(y/n)	(ohms/week)	open	of wire
4	1-24	n	0.001		
4	24-74	n	0.0957		
4	74-90	n	0.0144		
4	90-93	n	0.6775		
4	93-102	n	0.0386		Active

Figure 13. Graph of resistance (not temperature corrected) versus week of testing for aminoethylethanol-amine block 2 at 0.283 mol/ft^{3}. Data are for wire 4.

first 27 weeks of testing and then corroded rapidly for the next 11 weeks until it stabilized to a low corrosion rate until week 79 of testing, when it corroded through. The suspected cause of the rapid corrosion rates was pitting caused by chloride depassivation. The stabilization of the temperature-corrected resistance ratios of wire 4 back to a low corrosion rate indicated that repassivation had taken place. The variability of these data also revealed heterogeneities not only within the concrete block but also within centimeters of the same block of concrete. This heterogeneity is characteristic of concrete testing.

Many of the blocks did not have stable reference wires. An example of a resistance measurement block with a reference wire that went from stable to unstable is presented in Figures 10 and 11. The reference wire resistance for the di-sodium β-glycerophosphate block is displayed in Figure 10 and had a resistance change of 0.0015 ohms/week. This resistance change was assumed to result from corrosion that would explain the reference wire instability. Notice that wires 1 (Figure 10) and 4 (Figure 11) have negative slopes for their temperature-corrected resistance ratio since the reference wire was corroding faster than the test wires. A comparison of the trends in the slope of wire 4 (Figure 11) in temperature-corrected units (ohms/ohm) and uncorrected units (ohms) is displayed for weeks 38 through 52. However, in this case, the high corrosion rate of the test wires relative to the reference wire created a condition for relative similitude between referenced and nonreferenced data.

Many of the blocks had reference wires that were either unstable during the majority of testing or were not intact at all. The graph of aminoethylethanolamine block 2 having a concentration of 0.283 mol/ft^3 is shown in Figures 12 and 13. The reference wire for the block was not intact from the first week of measurement and, therefore, none of the resistance values could be temperature corrected. The trends in the resistance ratio were still fit using linear regression, which gave a reasonable estimate of the relative corrosion rate.

Wire 1 for the block mentioned had a negative slope in the uncorrected resistance ratio versus time plot for 36 weeks of testing. Such a negative slope would indicate that the resistance ratio of the wire had actually decreased over time, a highly unlikely event. These negative slopes were considered to represent a drift in temperature, but might represent deposition of conductive films on the wire that could contribute to increased conductivity.[8] Wire 1 then experienced rapid corrosion and corroded through on week 42.

Comparison of Inhibitors Using Resistance Measurement Data

Comparisons of the corrosion-inhibiting efficiency of the different inhibitors and different concentrations were made using two metrics: (1) the estimated linear regression slopes, and (2) the number of weeks the wire maintained electrical conductivity (or time-to-open-wire conditions). Plots were constructed to show the percentage of wires active over time. By comparing the percentage of wires with remaining continuity versus time, the corrosion performance of the different inhibitors could be compared. The inhibitors with better inhibiting efficiencies retained higher percentages of active wires on the plot. The percentages of active wires, or wires that had not corroded through, compared to total number of wires for a given inhibitor and given concentration, versus weeks of testing are presented in Figures 14 through 19. A summary showing the percentage of active wires after 100 weeks is presented in Figure 20. Graphs of the percentage of time a set of wires would have an associated a low-corrosion rate (<0.0002 temperature corrected resistance ratio units/week)(TCRUs/week) were also examined to compare inhibitor efficiency.

The wire survivability plots for the various inhibitors and dosages were used to delineate inhibitor quality. Of the compounds and concentrations tested, the best performers (based solely on wire survivability) were the blocks containing 0.815 mol/ft^3 of sodium metasilicate, di-n butyl sulfoxide, lithium nitrate, and sodium β-glycerophosphate. The best performer in wire survivability was sodium β-glycerophosphate at a concentration of 0.283 mol/ft^3. Phosphonic acid and 2-aminothiophenol performed worse than the control samples at almost any point in time in the testing and, more important, performed worse in the latter weeks. Also, di-n butyl sulfoxide concentrations of 0.283 and 0.815 mol/ft^3 and aminoethylethanolamine at a concentration of 0.815 mol/ft^3 performed better than the calcium nitrite at a concentration of 0.815 mol/ft^3. Although this dosage is the minimum dosage recommended by W.R. Grace Construction for concrete with chloride exposure, all compounds were tested under identical conditions.
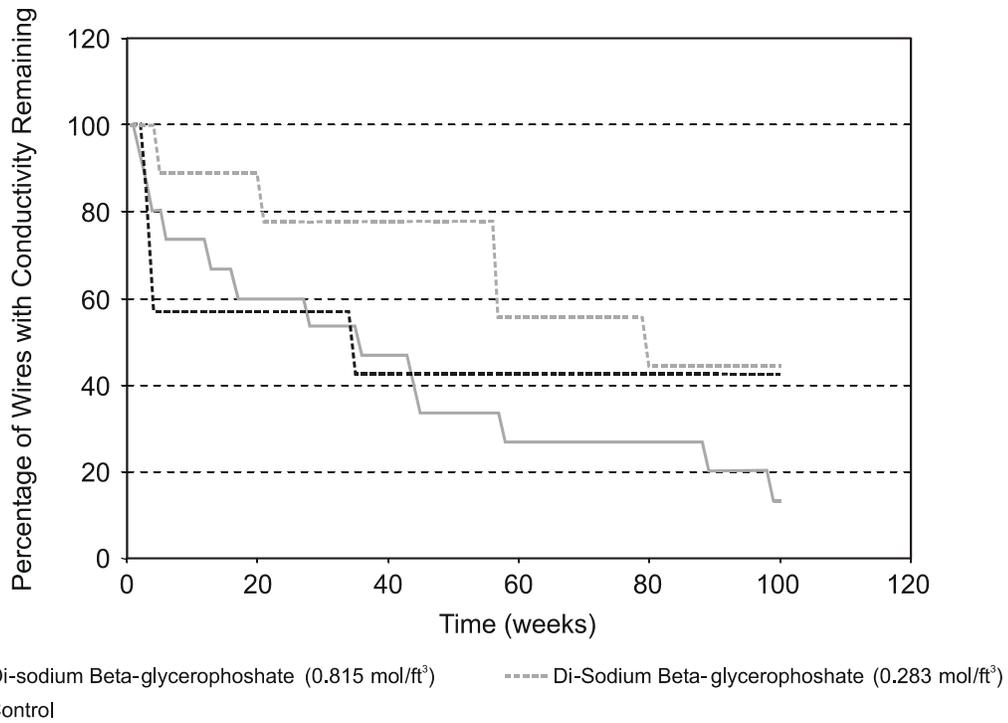
Figure 14. Percentage of wires active in resistance measurement over time for di-sodium beta-glycerophosphate admixed concrete.
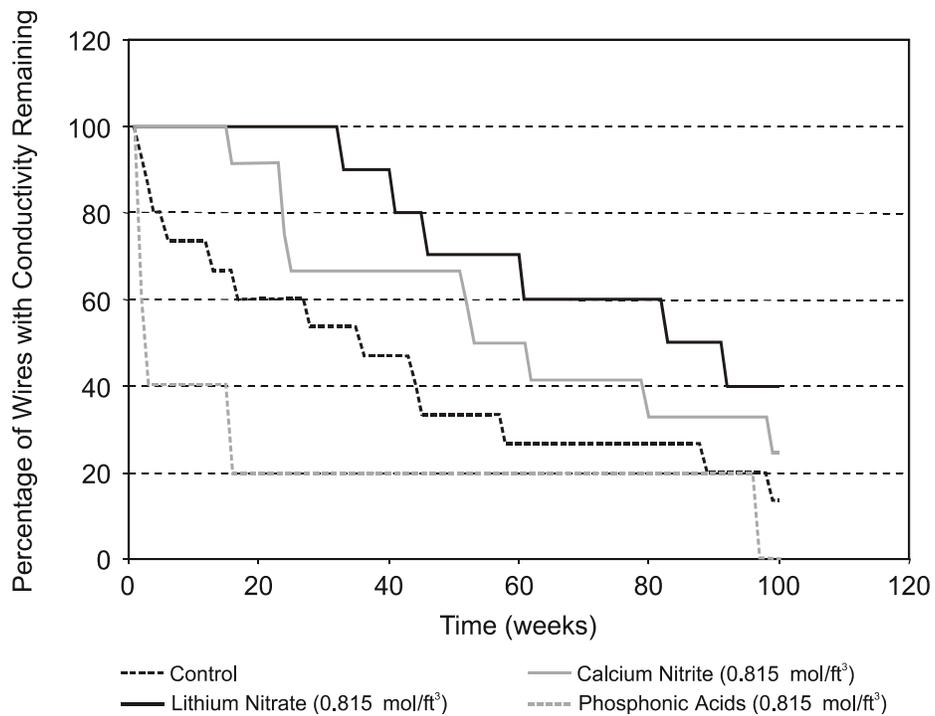
Figure 15. Percentage of wires active in resistance measurement over time for calcium nitrite, lithium nitrate, nitrilotrismethylene phosphonic acid admixed concrete.
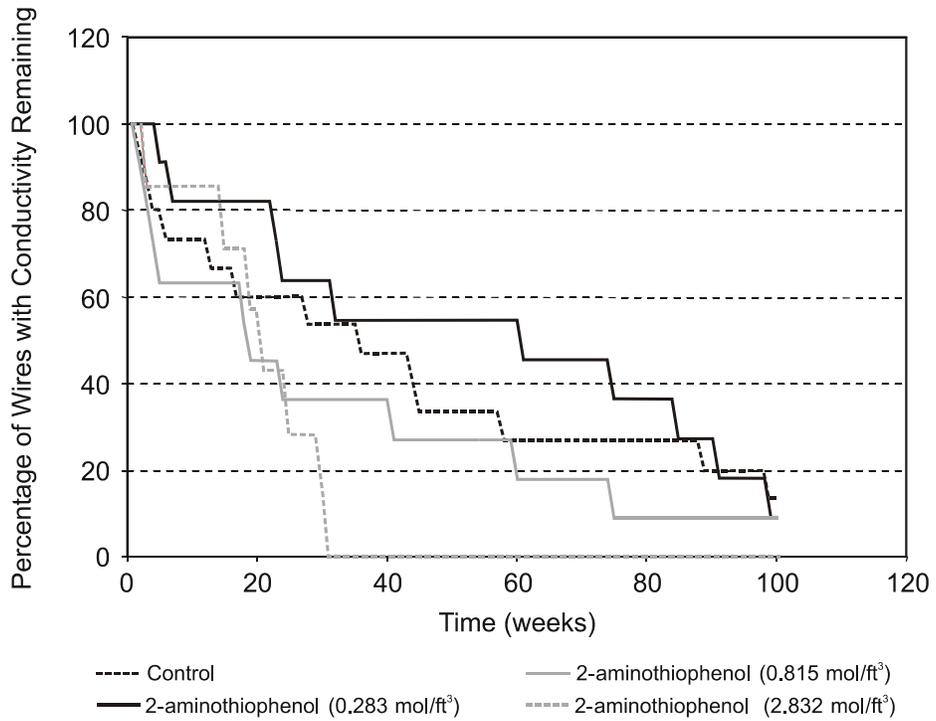
Figure 16. Percentage of wires active in resistance measurement over time for 2-aminothiophenol admixed concrete.
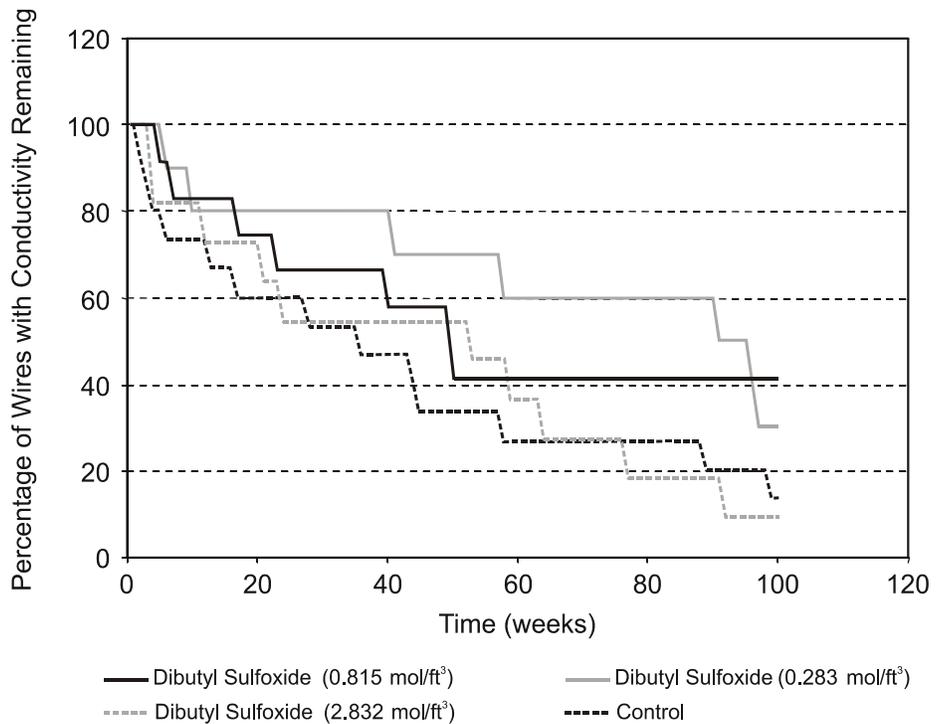
Figure 17. Percentage of wires active in resistance measurement over time for di-butyl sulfoxide admixed concrete
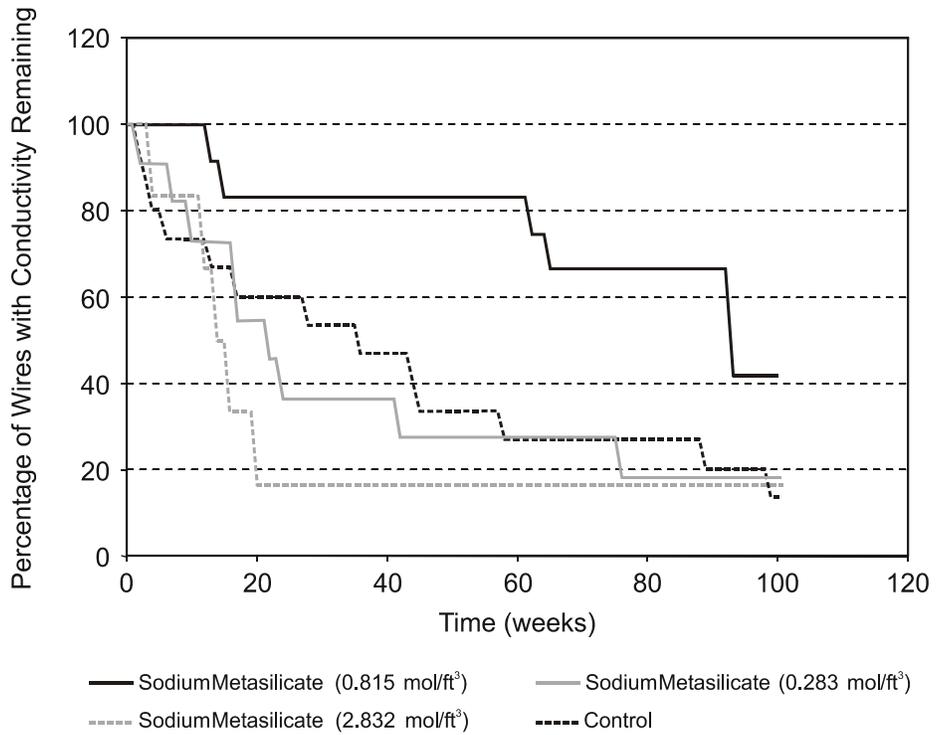
Figure 18. Percentage of wires active in resistance measurement over time for sodium metasilicate admixed concrete.
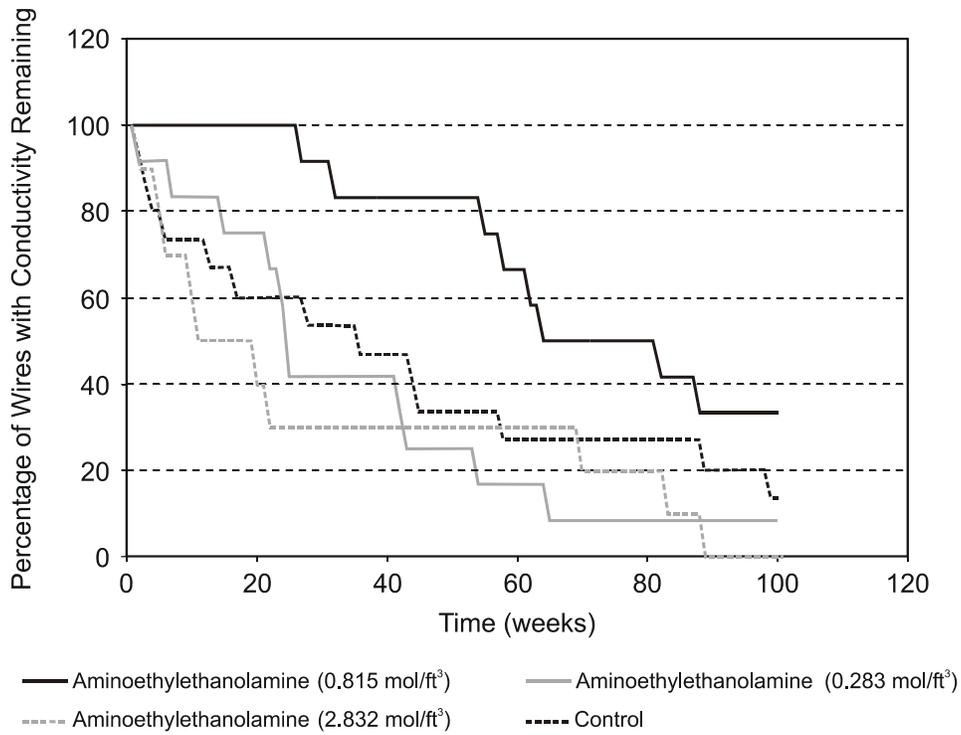
Figure 19. Percentage of wires active in resistance measurement over time for aminoethylethanolamine admixed concrete.

30
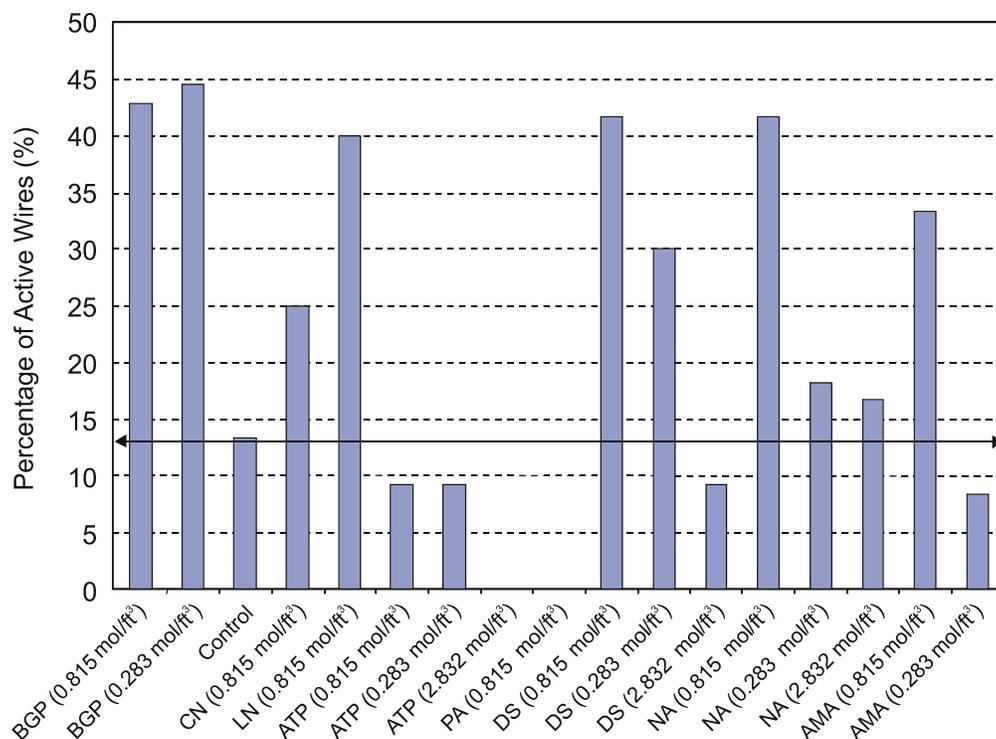
Figure 20. Percentage of wires active after 100 weeks of measuring resistance change for all admixed concrete. Line (arrows) represents control.

The intermediate concentration (0.815 mol/ft^3) of all inhibitors tested performed better than either the low (0.283 mol/ft^3) or high concentration (2.832 mol/ft^3) with the exception of the 2-aminothiophenol and the sodium β-glycerophosphate. For these inhibitors, the low concentration performed best, although only a slight difference between the low and intermediate concentrations can be seen in Figure 20. All inhibitors tested with a dosage of 2.832 mol/ft^3 demonstrated that this high concentration performed worse than either the low or intermediate concentrations. This downturn in performance at high inhibitor concentrations suggests that other properties of the concrete (e.g., permeability) were detrimentally affected by the dosage. This finding points to the complex interaction between corrosion inhibitors and concrete and the fact that total performance cannot be predicted by electrochemical characterization alone.

The other criterion for determination of inhibitor effectiveness was resistance change over time. The resistance change over time was determined by linear regression of selected regions of resistance measurement data points. The resistance change was translated into general corrosion penetration depth using a finite element model created by Cella[8] that is summarized in Figure 21. A resistance change of 0.0002 ohms/week was selected as the maximum acceptable corrosion rate to be considered low because it translated to 0.002 mm/yr (0.078 mils/yr), assuming uniform corrosion over the length of the wire. This rate is the maximum expected corrosion rate for rebar in concrete without admixed or ponded chloride.[25] Since there is no nondestructive technique to determine whether these low resistance changes were due to pitting or passive corrosion, all resistance changes of 0.0002 ohms/week or less were considered low
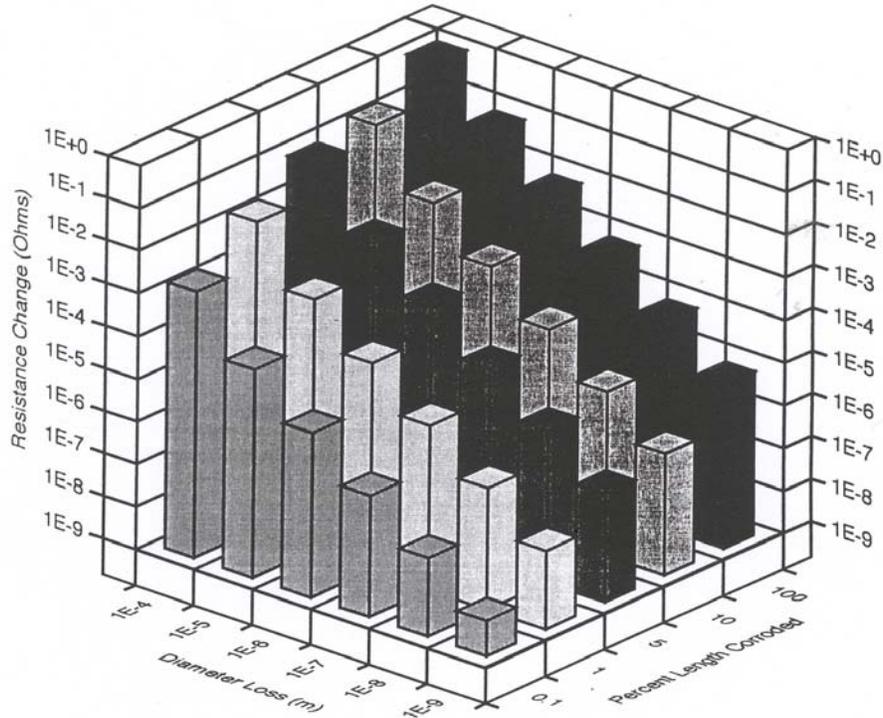
Figure 21. Resistance change due to corrosion as a function of percent original length affected and corrosion depth in a 20 cm long, 228.6 μm diameter 1040 steel wire. ©NACE International 2000.

corrosion rates. For the length and diameter of the wire used, a sensitivity of 1 μΩ was possible using the Keithly electrometer. The percentage of time that the wires were associated with "low" corrosion rates is shown in Figure 22 for the various inhibitors.

The percentage of time that each wire was associated with a low corrosion rate (< 0.0002 TCRUs/week) was estimated by taking the entire number of weeks that a certain wire spent at low corrosion rate and dividing that by the possible number of weeks. The possible number of weeks was simply the summation of the number of weeks that each block was ponded summed over every wire. The chart of the percentage of weeks at low corrosion rate for each inhibitor and concentration is shown in Figure 22.

The obvious standout for a low corrosion rate was the set of blocks with lithium nitrate as an inhibitor. Other inhibitors and dosages that performed well with respect to time at a low corrosion rate were aminoethylethanolamine at 0.815 mol/ft^3, sodium metasilicate at 0.815 mol/ft^3, and sodium β-glycerophosphate at 0.283 mol/ft^3. Inhibitors and dosages that were not outstanding but significantly better than the control specimens with regard to corrosion rate were di-n butyl sulfoxide at 0.283 and 0.815 mol/ft^3, 2-aminothiophenol at 0.283 mol/ft^3, calcium nitrite at 0.815 mol/ft^3, and sodium β-glycerophosphate at 0.815 mol/ft^3.
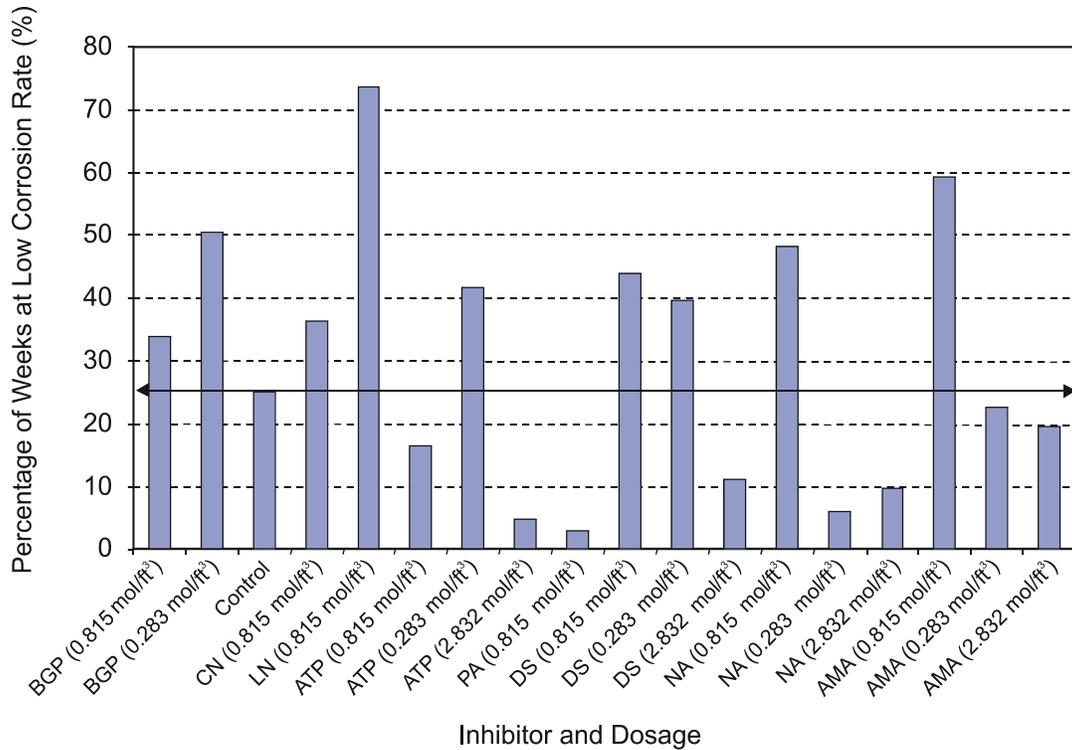
Figure 22. Percentage of time wires spent at "low" corrosion rate (less than 0.0002 TCRUs/week).

Similar to the active wire status graphs, the graphs of percentage of weeks at a low corrosion rate clearly showed that the intermediate concentration performed better than the low concentration with the exception of sodium β-glycerophosphate and 2-aminothiophenol. These inhibitors performed better at a low concentration than at intermediate concentration in both the percentage of weeks at a low corrosion rate and the percentage of active wires.

Dissections of Resistance Change Specimens

Dissections were conducted on several of the randomly selected resistance change specimens to verify that the wire was corroding within the bulk of the concrete and not at the connections to the steel rods. The results of this test are not to be construed to indicate inhibitor performance. Rather, these analyses were conducted to determine whether wire corrosion was a result of the materials tested (concrete, inhibitors) and not the specimen construction method. The dissections were carried out by cutting the block into nine sections. The sections cut from the two ends of the block were 2 in wide to accommodate the steel end rods, and the sections in between were cut 1 in wide. A schematic of the labeling of the dissected block sections is shown in Figure 23. The results of the dissection analysis are presented in Table 6.
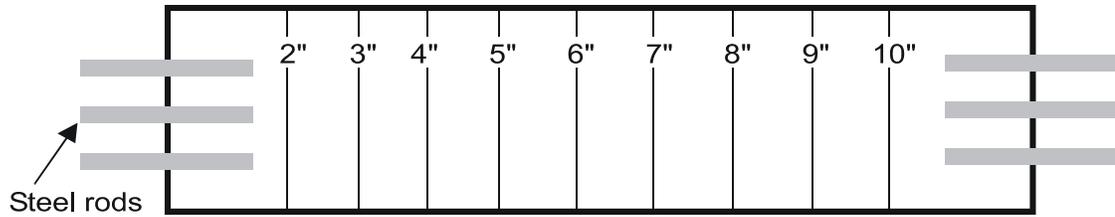
Figure 23. Labeling of sections from dissected concrete block.   Distances are from the left end to the cut.

Table 6. Conductivity of Dissected Portions of Resistance Change Blocks

Block	Wire	Inches from one end of the block								
		2	3	4	5	6	7	8	9	10
CO #4	1	Intact	Intact	Broken	Broken	Broken	Intact	Intact	Broken	Broken
	2	Intact	Intact	Broken	Intact	Broken	Intact	Intact	Broken	Broken
	4	Intact	Intact	Intact	Broken	Broken	Intact	Broken	Broken	Broken
ATP-3 #2	1	Intact	Broken	Intact	Intact	Intact	Intact	Intact	Intact	Intact
ATP-3 #3	1	Broken	Intact	Intact	Intact	Intact	Intact	Intact	Intact	Broken
PA #2	2	Intact	Broken	Intact	Intact	Intact	Intact	Intact	Intact	Intact
	4	Intact	Broken	Intact	Intact	Intact	Intact	Intact	Intact	Intact
PA #3	4	Intact	Intact	Broken	Intact	Intact	Intact	Intact	Intact	Intact
DS-3 #3	1	Intact	Intact	Intact	Broken	Intact	Intact	Intact	Broken	Broken
	2	Broken	Intact	Broken	Intact	Broken	Broken	Intact	Broken	Intact
NA-3 #1	1	Intact	Intact	Intact	Intact	Broken	Intact	Intact	Intact	Intact
	2	Intact	Broken	Intact	Intact	Intact	Intact	Intact	Intact	Intact
NA-3 #3	2	Intact	Intact	Intact	Intact	Broken	Broken	Broken	Broken	Broken
	4	Broken	Broken	Broken	Intact	Broken	Broken	Intact	Broken	Intact
NA-3 #4	2	Intact	Intact	Broken	Intact	Broken	Intact	Intact	Intact	Intact
BCAP #3	1	Intact	Intact	Broken	Intact	Intact	Broken	Intact	Intact	Intact
	4	Intact	Intact	Intact	Intact	Intact	Intact	Broken	Intact	Intact

These dissections indicated that almost half of the wires corroded through at the ends. However, many of the wires corroded through in more than one location away from the block ends. The multiple points of discontinuity in the wires were most likely due to the continued ponding of blocks containing wires that had reached infinite resistance because other wires in the concrete block were still active. Also, all these dissected samples sat for at least 1 month after infinite resistance was reached in the last wire before the dissection was performed. Since the blocks with only one active wire at the beginning of testing show no preferential location for corrosion and the blocks that did corrode at the ends also corroded in other locations on the wire, it is reasonable to assume that the wire ends were not preferential locations for corrosion.

Results of Testing in Simulated Pore Solution

Electrochemical testing in a SPS was conducted to evaluate the inhibitor effect on rebar corrosion rate. This was evaluated using EIS to determine the polarization resistance (R_p). The EIS results are presented here.

The impedance of rebars immersed in saturated calcium hydroxide + inhibitors was measured under potentiostatic conditions using a 10 mV ac voltage excitation between 65 kHz and 0.01 Hz. The values of R_p were determined by fitting the data to equivalent circuit analogues. With the exception of the phosphonic acid impedance data, all inhibitors were fit using a single time constant (simplified Randles) circuit with a constant phase element (CPE) to represent capacitive elements (e.g., the double layer and oxides). The phosphonic acid impedance data were fit using a two-time constant equivalent circuit with CPEs. These circuits are shown in Figure 24.

A typical method to determine if the impedance data have one or more time constants is to examine the number of peaks that appear on the phase angle plot. Each peak on the phase angle plot typically corresponds to a time constant.

An example set of impedance data from the results of di-n-butyl sulfoxide with no chloride, 0.3 M chloride, and 0.6 M chloride in solution is presented in Figure 25. The two graphs on the left are the Bode magnitude (top) and phase angle (bottom) representation of the impedance data. The graph on the right is the complex plane (Nyquist plot) representation of the data.

The R_p values determined from tests in SPS (saturated calcium hydroxide) with inhibitor before chloride addition are presented in Figure 26. R_p values in the presence of 0.3 M chloride and 0.6 M chloride additions to the inhibitor and calcium hydroxide solution are presented in Figures 27 and 28, respectively. Recall that the corrosion rate is inversely proportional to R_p; thus a large R_p value is favorable with regard to the inhibition of corrosion.

CPE- Constant Phase Element   R - Resistor
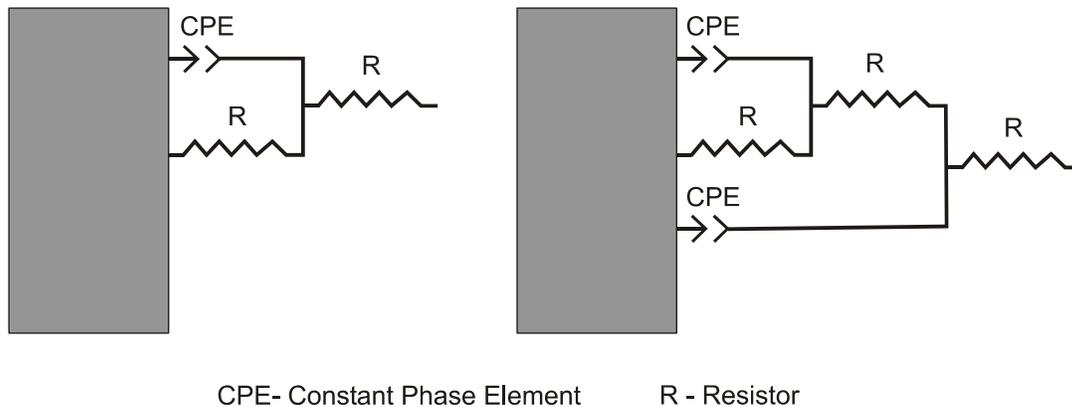
Figure 24. Single (left) and two-time constant (right) equivalent circuits used to fit impedance data.
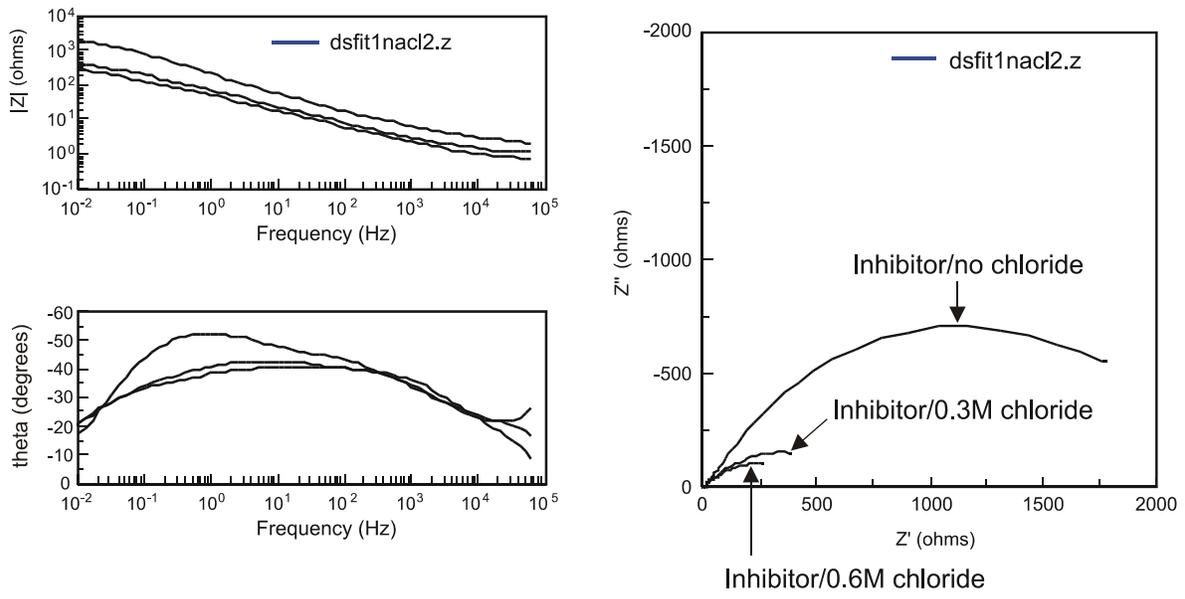
Figure 25. EIS results of di-n-butyl sulfoxide in saturated calcium hydroxide.
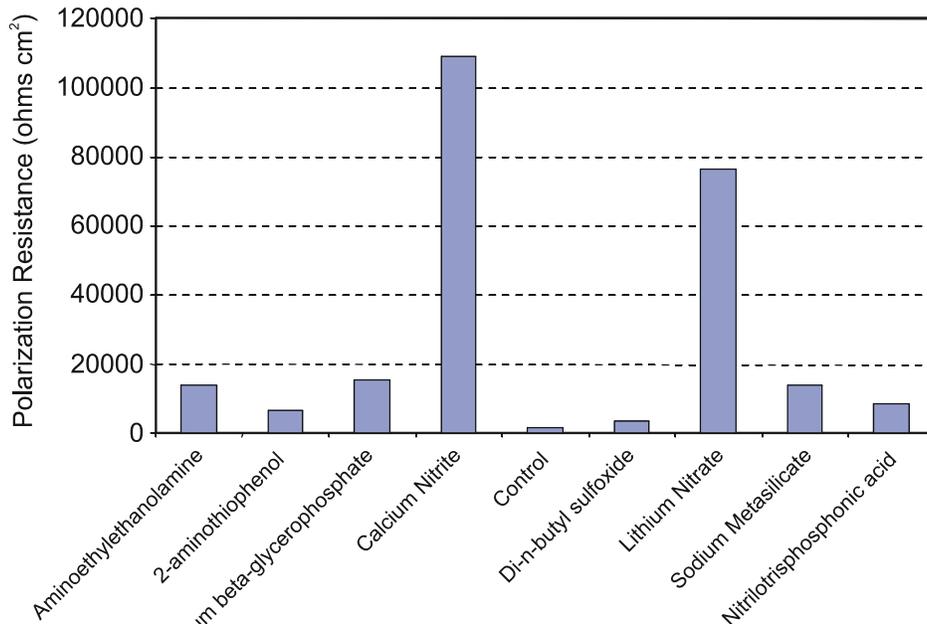
Figure 26. Polarization resistance of rebar in saturated calcium hydroxide and 10 mM inhibitor.
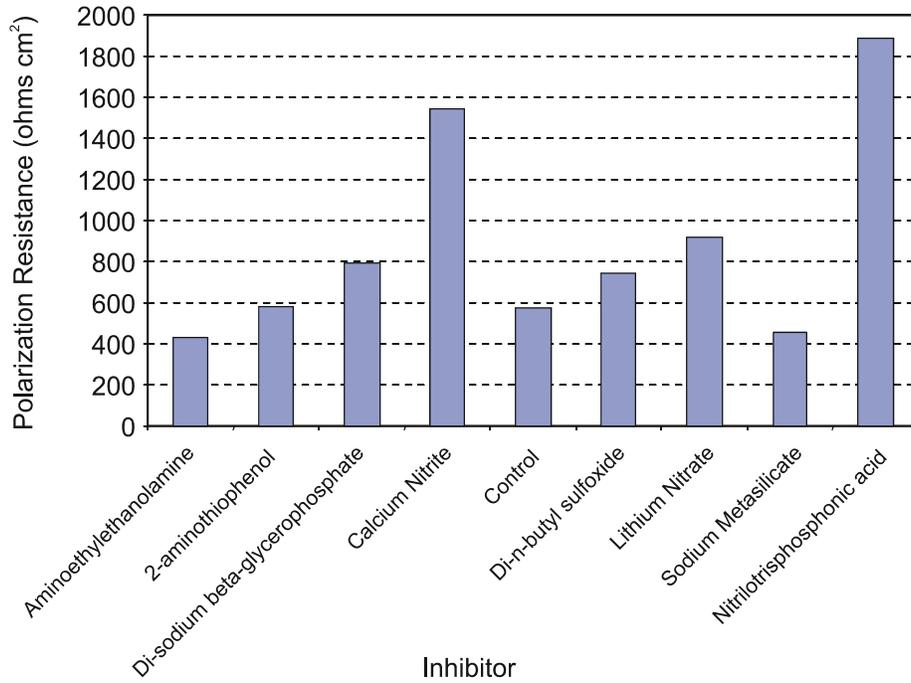
Figure 27. Polarization resistance of rebar in saturated calcium hydroxide and 10 mM inhibitor after addition of 0.3 M of sodium chloride.
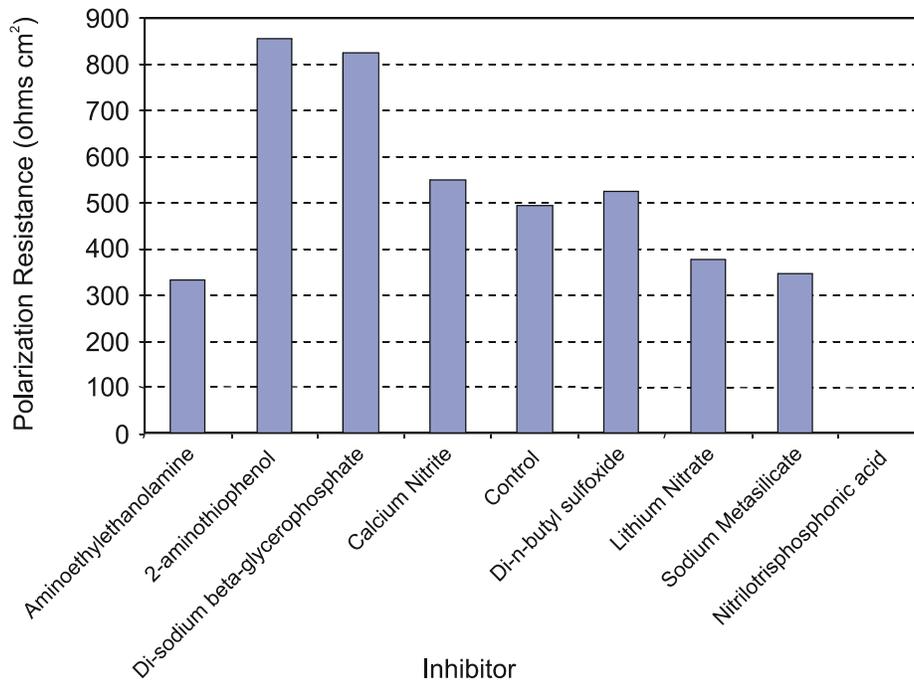
Figure 28. Polarization resistance of rebar in saturated calcium hydroxide and 10 mM inhibitor after addition of 0.6 M of sodium chloride.

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In Figure 26 it can be seen that when no chlorides are present, the highest polarization resistance is achieved when using calcium nitrite and lithium nitrate. All of the inhibitors tested performed better than the control with the exception of phosphonic acid, which exhibited two time constant behavior suggesting a breakdown of the passive film. The significant corrosion of the rebar in phosphonic acid in saturated calcium hydroxide may have been due in part to a drop in pH from 12.3 to 5 caused by the phosphonic acid. The pH of 5 creates an active corrosion condition for steel in solution.

The R_p data in Figure 27 were obtained 12 hours after the addition of 0.3 M sodium chloride to the inhibitor and saturated calcium hydroxide solutions. Similar to the data in Figure 26, the calcium nitrite and lithium nitrate inhibitors performed well. Nitrilotrisphosphonic acid and Di-sodium β-glycerophosphate also performed very well.

R_p data were collected following the addition of 0.6 M sodium chloride to the solution containing saturated calcium hydroxide and inhibitors, as shown in Figure 28. After 12 hours in the higher chloride environment, all of the inhibitors ranked close to the control in R_p with the exception of 2-aminothiophenol and di-sodium β-glycerophosphate.

Properties of Concrete Containing Inhibitors

The results of testing the compressive strength of mortar cubes and concrete cylinders and the permeability of concrete cylinders are discussed in this section. The purpose of testing the properties of concrete containing the inhibitors was to discover the effects, if any, the inhibitors had on the concrete. The mechanical testing of the concrete was important to determine the feasibility of employing the inhibitive admixtures in concrete structures. The results of permeability testing, when compared with the results from the testing of resistance measurement blocks, assisted in distinguishing the corrosion inhibition due to the electrochemical effects of the inhibitors from the effects on permeability.

Results of Compressive Testing of Concrete Cylinders

Compression testing of concrete cylinders was conducted at an age of 28 days to determine the effects of the inhibitors on this important property. The compressive strengths of cylinders containing inhibitors with values near the control specimen (no inhibitor) suggested little or no effect of the inhibitor addition on concrete strength. This study did not examine the effects of inhibitor additions on slump, setting time, or strength gain over time, which would be needed to determine any additional effects on concrete. The compressive strengths were normalized for air content to match the control samples and are presented in Figure 29. The compressive strengths were adjusted by increasing the compressive strength by 5 percent for every 1 percent air content greater than that of the control sample.[22] Di-n-butyl sulfoxide had a lower compressive strength than did the control cylinders, and its compressive strength decreased with increasing concentration. Cylinders containing phosphonic acid had significantly lower compressive strengths than did the control and decreased with increasing concentration. The effect of phosphonic acid on the strength of concrete may be due to the complexing of phosphonic acid with calcium hydroxide that results in a severe reduction in pH with consequent

attack of the calcium silicate hydrates. All other inhibitors had higher compressive strengths than did the control. High concentrations of aminoethylethanolamine and 2-aminothiophenol and both concentrations of calcium nitrite had statistically higher compressive strengths than did the control but were of small magnitudes.
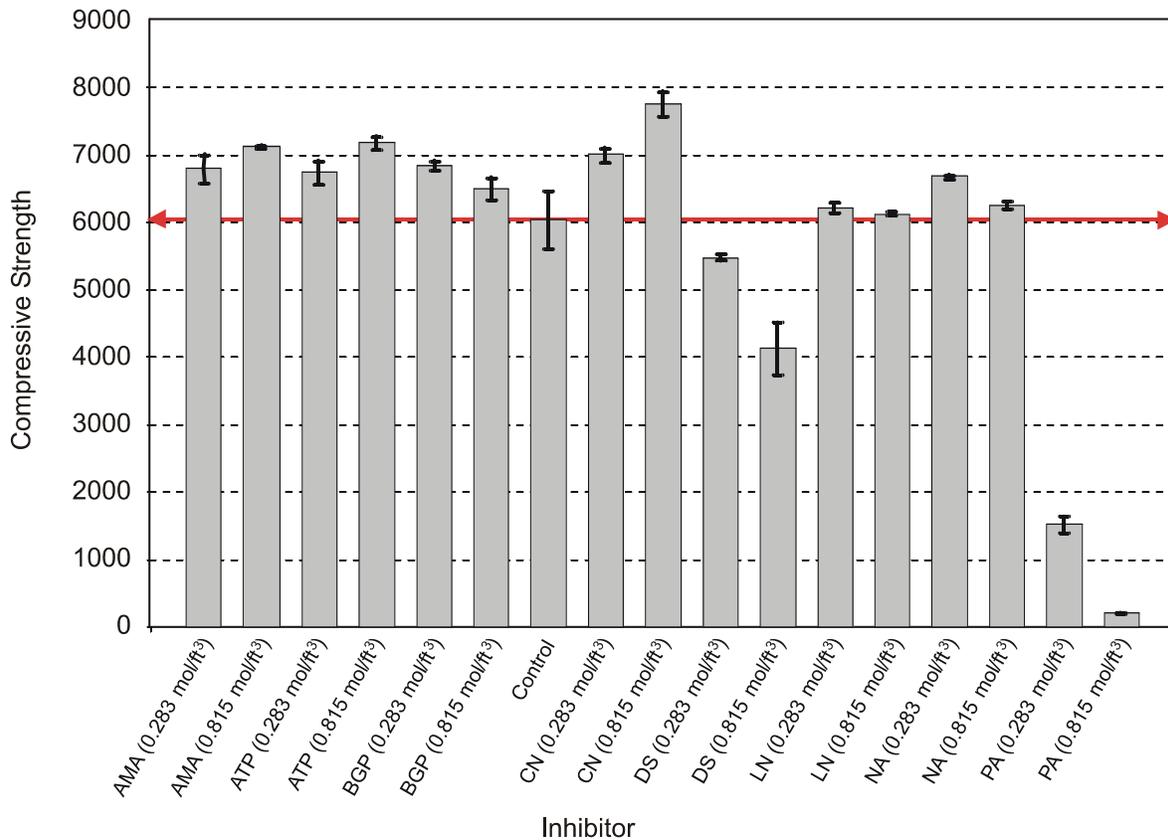
Figure 29. Compressive strengths of concrete cylinders containing inhibitors.

Permeability of Concrete Cylinders

Rapid chloride permeability screening tests were conducted on one concrete cylinder for each inhibitor dose available. The permeability was measured in coulombs of charge passed through the cylinder, where the charge will increase as the amount of chloride or other ions that pass through the concrete increases. A higher permeability to chloride ions translates into poorer quality concrete for preventing corrosion, since more chlorides may reach the embedded steel more quickly. Values of permeability in units of charge that were less than the control represented quality concrete for preventing chloride diffusion, whereas values greater than the control represented a poor concrete that would allow chloride to penetrate the concrete at greater rates. The total amount of charge in coulombs was measured over 6 hours of testing and is presented in Figure 30. The permeability results were not corrected for air content since the air content has little practical effect on permeability.[22]
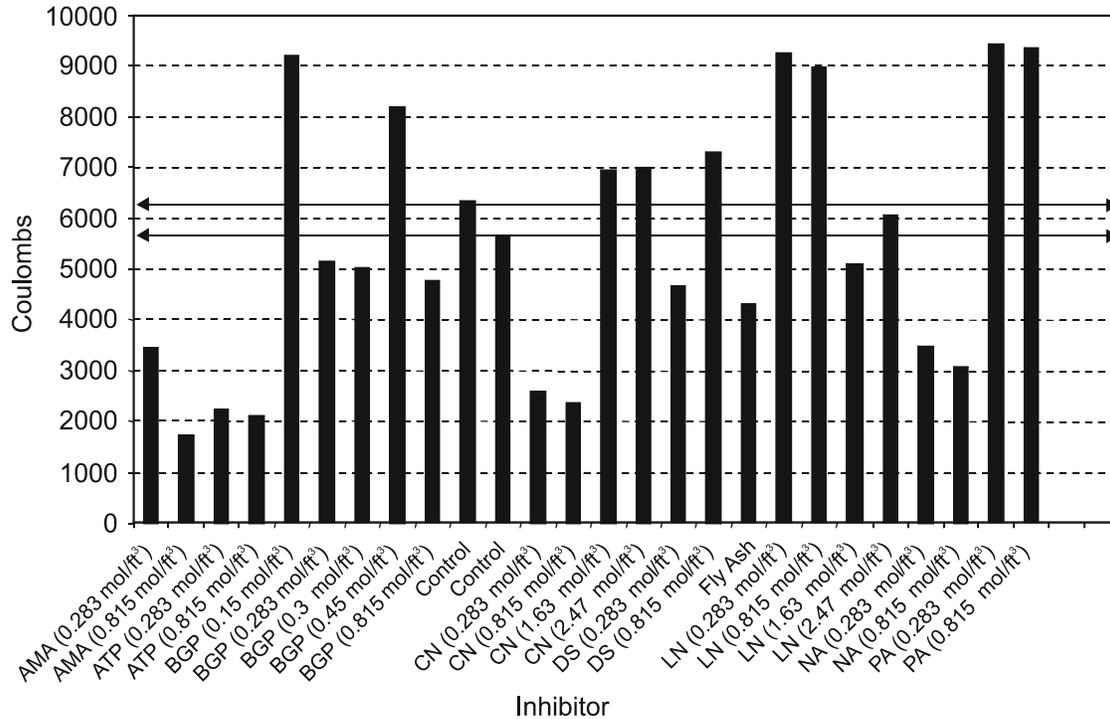
Figure 30. Permeability of concrete to chloride.

It must be noted that the permeability test results in a confounded measurement in that an admixture could change the ionic resistance of the concrete by changing either the pore structure or the resistivity of the pore solution. Nonetheless, permeability data can begin to allow one to delineate the electrochemical behavior of the inhibitor from the physical effects of the inhibitor on the concrete, as discussed further in a subsequent section.

Permeability results from cylinders containing aminoethylethanolamine, 2-aminothiophenol, and sodium metasilicate showed significantly lower permeability than that of the control samples for the 0.283 mol/ft^3 and 0.815 mol/ft^3 dosages. These dosages were associated with nearly equivalent permeability for the 2-aminothiophenol and sodium metasilicate admixtures, suggesting no dependence of permeability with concentration. The permeability results for aminoethylethanolamine, however, indicated a much lower permeability in the 0.815 mol/ft^3 dosage compared to the 0.283 mol/ft^3 dosage, which suggests an inverse dependence of permeability with aminoethylethanolamine concentration. It should be noted, however, that additional concentrations and multiple samples would need to be examined to confirm the dependence of permeability on concentration for all the inhibitors tested. The results presented are to be considered preliminary indications.

Permeability results from concrete samples containing di-sodium β-glycerophosphate, calcium nitrite, lithium nitrate, and di-n-butyl sulfoxide showed that different concentrations of these inhibitors had dramatically different effects on permeability. The permeability results for di-sodium β-glycerophosphate at 0.15 mol/ft^3 and 0.45 mol/ft^3 indicated a high permeability to chloride, whereas the concentrations of 0.283, 0.3, and 0.815 mol/ft^3 were associated with

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permeabilities similar to that of the control sample. The permeability results for di-n-butyl sulfoxide indicated that the 0.283-mol/ft^3 dosage was associated with a lower permeability than that of the control, whereas the 0.815-mol/ft^3 dosage was associated with a high permeability when compared to that of the control specimens. Permeability results for calcium nitrite indicated a high chloride permeability at higher dosages, 1.63 and 2.47 mol/ft^3, but a low permeability at low dosages, 0.283 and 0.815 mol/ft^3. The permeability at lower dosages was much lower than the control permeability, and the permeability at higher dosages was nearly equivalent to the control permeability. The permeability results for lithium nitrate indicated the opposite dependence on concentration compared with that of the commercial calcium nitrite mix. The permeability for lithium nitrate was greatly increased at low dosages, 0.283 and 0.815 mol/ft^3 but was equivalent to that for the control at higher concentrations, 1.63 and 2.47 mol/ft^3.

The permeability test conducted on concrete samples containing phosphonic acid at 0.283 mol/ft^3 indicated the highest permeability listed on the chart in Figure 30. The testing of the permeability of the phosphonic acid dosage of 0.815 mol/ft^3 led to a spike in current in the permeability cell within 1 hour of testing that was 5 times the amount of current of the maximum of any other specimen. After the current spiked, the phosphonic acid specimen with high dosage split in half under the heat and pressure caused by the experiment. If the rise in current had not caused the destruction of the sample and the current had maintained the maximum level for the rest of the test, the permeability of the phosphonic acid at 0.815 mol/ft^3 would have registered above 40,000 coulombs. Data from the measured current over time for both control samples and both dosages of phosphonic acid are shown in Figure 31.
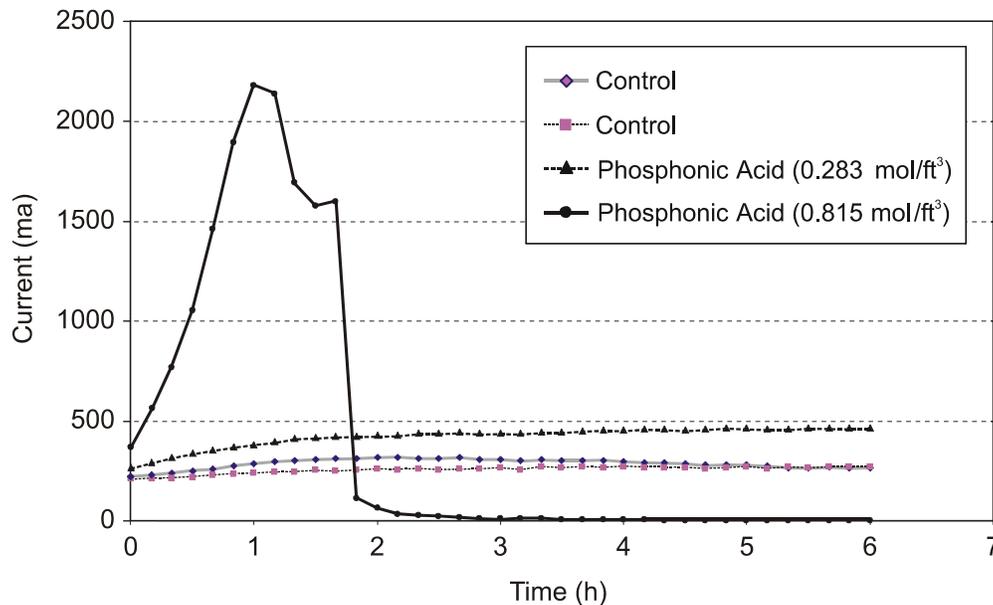
Figure 31. Measured current over time to determine permeability of concrete to chloride for control and phosphonic acid concrete samples.

Summary of Results and Discussion

Inhibitor performance was ranked using a variety of metrics. Figure 32 shows 60 percent correlation between the two metrics used to assess resistance change data, i.e., wire survivability and time at a low corrosion rate. A good correlation of these two metrics provided more confidence in the results of the resistance measurements.
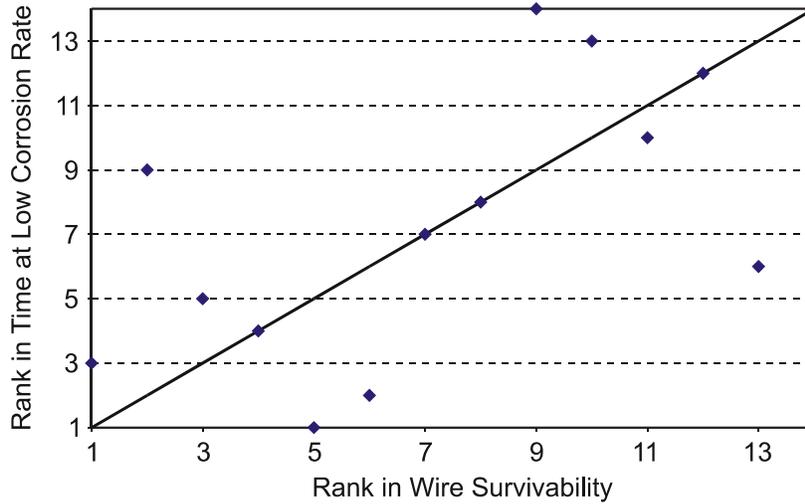
Figure 32. Correlation between wire survivability and time at low corrosion rate. $R^2 = 0.6$.

Figure 33 shows 78 percent correlation between the rankings of compressive strength and permeability for the admixed concrete. High strength correlates with low permeability. Good correlation existed between the two metrics of concrete quality indicating that multiple tests for rudimentary assessment of concrete quality may not be required.
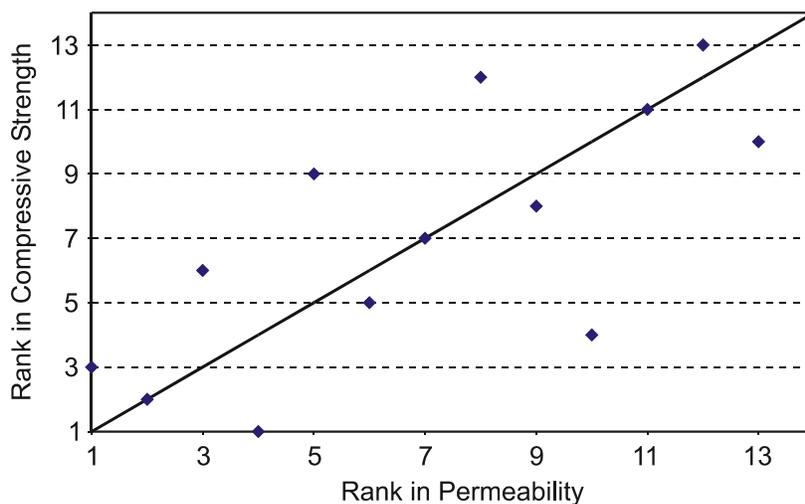
Figure 33. Correlation between permeability and compressive strength in concrete. $R^2 = 0.78$.

Figure 34 demonstrates that no correlation existed between the wire survivability rankings and the compressive strength rankings. Similarly, Figure 35 shows that no correlation existed between the wire survivability and the permeability rankings. These two findings indicate that tests of admixed concrete quality alone cannot predict inhibitor effectiveness in concrete.
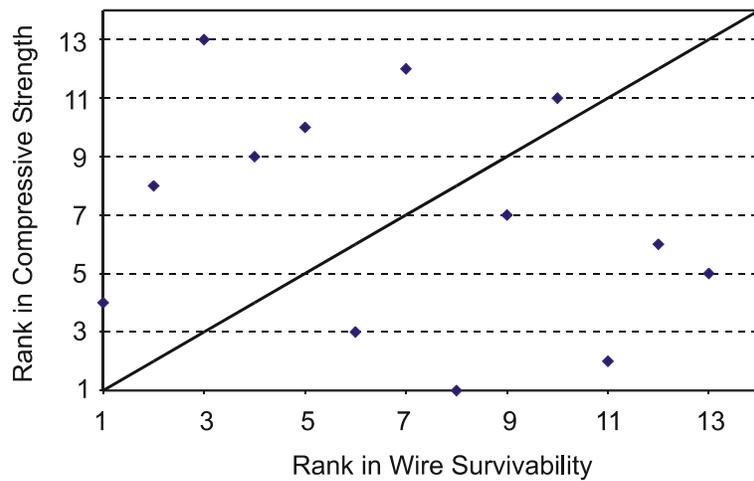
Figure 34. Correlation between wire survivability and compressive strength.
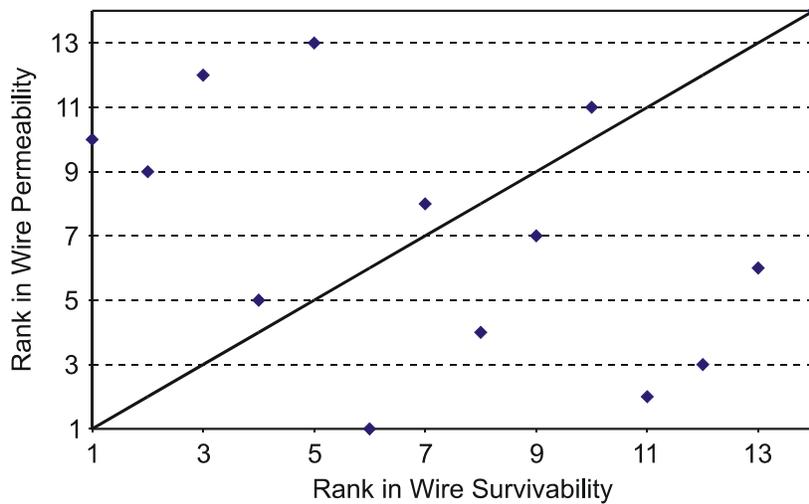
Figure 35. Correlation between wire survivability and permeability.

It is apparent from the results of this study that the selection of an inhibitive admixture for concrete cannot be based on a single test. This section summarizes the results for each inhibitor by comparing the findings of all the tests used in this study. A ranking of the inhibitors from each test metric used in this project and an overall ranking of resistance measurement results and all tests are presented in Table 7.

Table 7. Summary and Ranking of Inhibitor Performance

CHEMICAL COMPOUND	%Active x/n	Rank	% at low corr.rate	Rank	Comp. St. Avg+SD	Rank	Cl Perm. Coulombs	Rank	Rp, Rank 0M NaCl	Rp, Rank .3M NaCl	Rp, Rank .6M NaCl	Overall Score	Overall Rank
AMA(.815)	4/12 33.3	5	710/1200 0.592	2	7112±27 n=3	2	1750 n=1	1	17,000 5	420 9	330 8	46	3 1
AMA(.283)	1/12 8.3	15	271/1212 .224	10	6785±210 n=3	2	3400 n=1	6					12
AMA(2.832)	0/12 0	16	195/1008 0.193	12	NA								16
ATP(.815)	1/11 9.1	12	180/1108 0.162	13	7168±92 n=3	2	2050 n=1	2	7000 7	590 6	850 1	93	12 7
ATP(.283)	1/11 9.1	12	461/1105 0.417	5	6730±178 n=3	7	2200 n=1	3					9
ATP(2.832)	0/7 0	16	33/707 0.047	16	NA								17
BGP(.815)	3/7 42.9	2	238/705 0.334	8	6492±167 n=3	7	4850 n=1	8	18,000 3	800 4	820 2	54	6 3
BGP(.283)	4/9 44.4	1	455/903 0.504	3	6833±65 n=3	2	5150 n=1	9					1
CN(.815)	3/12 25.0	8	440/1212 0.363	8	7750±187 n=3	1	2300 n=1	4	110,000 1	1550 2	550 3	59	8 5
CO	2/15 13.3	11	375/1515 0.248	10	6035±437 n=3	10	6000 n=2	10	2000 9	580 7	495 5	104	10 8
DS(.815)	5/12 41.7	3	527/1200 0.439	5	4131±395 n=3	15	7250 n=1	11	3000 8	770 5	525 4	67	5 6
DS(.283)	3/10 30.0	6	397/1002 0.396	7	5477±50 n=3	14	4750 n=1	8					7
DS(2.832)	1/11 9.1	12	122/1105 0.110	14	NA								15
LN(.815)	3/10 30.0	6	736/999 0.737	1	6130+28 n=3	10	9000 n=1	13	78,000 2	925 3	380 6	55	3 4
NA(.815)	5/12 41.7	3	583/1209 0.482	3	6251±60 n=3	10	3050 n=1	5	17,500 4	430 8	345 7	52	2 2
NA(.283)	2/11 18.9	9	65/1111 0.056	16	6665±30 n=3	7	3500 n=1	7					12
NA(2.832)	1/6 16.7	10	58/606 0.096	14	NA								11
PA(.815)	0/5 0	16	7/194 0.036	16	201±11 n=3	17	9300 n=1	13	8500 6	1840 1		133	17 17

The following explains the terms used in Table 7:

- **Chemical Compound:** Abbreviation signifies compound tested along with the concentration (e.g., LN(.815) signifies lithium nitrate at 0.815 moles/ft^3).

- **% Active, x/n:** For a given series of test blocks that contained a specific inhibitor at a specific concentration, the test wires that remained electrically continuous after 100 weeks, i.e., *active*, were noted and compared to the total number of test wires available at the beginning of the test.

- **Rank (% Active):** The proportion of active wires was ranked numerically from high to low. An analysis of variance (ANOVA) indicated the following statistical ranking with 95 percent confidence: (1=2=3=4=5)>(6=7=8)>(9=10=11)>(12). The rankings were used as is due to the small sample size (n≤15).

- **% at Low Corrosion Rate:** The trend for wire corrosion was to remain low for a period of time and then accelerate before electrical discontinuity. Low corrosion rate is defined as < 0.0002 ohms/week, which is the detection limit of this RCM procedure. The ratio given was determined by : [(number of wires at low corrosion rate) x (the number of weeks per wire)] / [(the total number of wires tested) x (the number of weeks active per wire)].

- **Rank (% at Low Corrosion Rate):** The proportionality test at 95 percent confidence yielded the following differences between the measured proportions: (1)>(2)>(3=4)>(5=6=7)>(8=9)>(10=11)>12>(13)>(14=15)>(16=17=18). This latter ranking was used due to the large sample size.

- **Compressive Strength (average and standard deviation):** This data represent the normalized compressive strength measurements (corrected for air content) for three samples. Note that not all inhibitor concentrations were tested.

- **Rank (Compressive Strength):** Confidence interval testing (p=.05) revealed the following rank differences: (1)>(2=3=4=5=6)>(7=8=9)>(10=11=12=13)>(14)>(15)>(16)>(17). More inhibitor concentrations were tested for compressive strength than are denoted in this table.

- **Chloride Permeability (Coulombs)**: These data represent the coulombs measured in ASTM C1202 for a single sample.

- **Rank (Cl permeability):** These rankings were based on numeric value. No statistics could be performed.

- **Rp, Rank 0M NaCl:** These data represent the polarization resistance (ohms) determined on a single rebar sample in SPS with no sodium chloride. The rank was based on the numeric value determined.

- **Rp, Rank 0.3M NaCl:** These data represent the polarization resistance (ohms) determined on a single rebar sample in SPS with 0.3M NaCl. The rank was based on the numeric value determined.

- **Rp, Rank 0M NaCl:** These data represent the polarization resistance (ohms) determined on a single rebar sample in SPS with 0.6M NaCl. The rank was based on the numeric value determined.

- **Overall Score, Overall Rank:** The corrosion performance of steel in concrete was judged to be the most relevant indicator of the performance of an inhibitive admixture. Thus, the rankings from % Active and % at Low Corrosion Rate were multiplied by 3. The overall score was determined by summing the rankings for those samples that underwent all tests. Two ranks are given. For those samples that were subjected to all tests, an Overall Rank is given in the *bottom right corner*. A Corrosion Rank was determined from the sum of % Active and % at Low Corrosion Rate since these tests were performed on all samples and is of most relevance to this study. This rank is given in the *lower left corner*.

Inhibitors that showed good results in "time-to-open" or "percentage of weeks at low corrosion rate" were regarded as the best inhibitors studied in this project. Since the testing of resistance change in concrete is considered the most reliable indication of inhibitor performance in this project, the ranking from the resistance change results (% active and % at low corr.rate in Table 7) were weighted with a factor of three (chosen arbitrarily) in the computation for the combined ranking of all tests. The other tests, low permeability to chloride, high compressive strength upon addition of inhibitors, and R_p in SPS were also considered important in computing the overall ranking of inhibitors. All of these tests were weighted with a value of one.

Common to all the inhibitors examined at high concentration was the fact that all inhibitor dosages of 2.832 mol/ft^3 performed the worst out of all the dosages for each inhibitor. This result suggested that the addition of 2.832 mol/ft^3 might be an excessive dosage for the concrete to retain its normal setting characteristics and properties.

Results of Testing Aminoethylethanolamine (AMA)

The resistance change measurement results of the aminoethylethanolamine samples support the permeability results in this case. The 0.283 mol/ft^3 dosage performed worse than the control in "percentage of wires active" and in "time at low corrosion rate." On the other hand, the 0.815 mol/ft^3 dosage performed better than the control in both percentage of wires active and in time at low corrosion rate, supporting the fact that the permeability for this inhibitor concentration, as well as that for the lower dosage, was lower than that of the control.

Permeability results from cylinders containing aminoethylethanolamine showed that the 0.283-mol/ft^3 and the 0.815-mol/ft^3 concentrations was associated with significantly lower permeability than that for the control samples. Interestingly, the trend of concentration dependence of permeability on the amount of aminoethylethanolamine did not correlate with resistance change measurement results since the 2.832 mol/ft^3 dosage performed worse than

either the 0.283 mol/ft^3 or the 0.815 mol/ft^3 in resistance measurement results. Unfortunately, since there was no permeability measurement taken for the 2.832 mol/ft^3 dosage, the reason for the failure of this dosage was unclear. It is possible that the large dosage interfered with the concrete setting.

The R$_p$ of aminoethylethanolamine in saturated calcium hydroxide with added chloride was lower than that of the control for both the 0.3 M and 0.6 M chloride dosages. The low R$_p$ further suggests that the key effect of this compound is on concrete permeability. A minimum concentration of aminoethylethanolamine for corrosion protection may be a requirement for this inhibitor since the 0.815 mol/ft^3 dosage performed well in resistance measurement metrics whereas the 0.283 mol/ft^3 dosage performed worse than the control.

The ranking of aminoethylethanolamine at 0.815 mol/ft^3 was 3rd in resistance change data and 1st in overall ranking of the inhibitors, indicating strong promise for this inhibitor at this or similar dosages that should be examined in more depth.

Results of Testing 2-aminothiophenol (ATP)

Permeability testing on 2-aminothiophenol indicated that this compound significantly reduced the permeability of concrete in both concentrations tested. The 0.283-mol/ft^3 and the 0.815-mol/ft^3 dosages produced the second and third lowest permeabilities found in this study. Interestingly, the lower dosage was the only one of the three dosages in the RCM experiment that was equivalent to that of the control. Both the higher dosages, 0.815 mol/ft^3 and 2.832 mol/ft^3, performed much worse than the control in both percentage of active wires and the amount of time the wires spent at low corrosion rates. Considering the low permeability of both the lower dosages of 2-aminothiophenol, the results may indicate an accelerating effect on corrosion when present in concrete. However, the R$_p$ of 2-aminothiophenol in saturated calcium hydroxide with and without added chlorides indicates an increased capability to prevent corrosion with an increased amount of chloride. The strong inhibiting effect of 2-aminothiophenol in chloride solutions is supported by previous research.[16] The inadequacy of the permeability and solution testing results to predict performance in concrete further supports the need for an *in situ* screening test (i.e., admixed into concrete).

Further investigation is required to determine why 2-aminothiophenol does not appear to prevent corrosion in concrete despite good polarization resistance in saturated calcium hydroxide with chloride additions and low permeability to chlorides in concrete. One reason for the poor inhibiting effect in concrete by 2-aminothiophenol may be the extremely low solubility, 0.003 M maximum concentration[61], of this species in water. This extremely low solubility may have allowed the inhibitor to become heterogeneously trapped in the concrete, providing certain areas of the concrete to be a reservoir of replaceable inhibitor and certain areas to be deficient of 2-aminothiophenol. Thus, once the initial concentration of 2-aminothiophenol in pore solution was extinguished by covering the steel, certain areas of the steel were afforded no further protection due to a lack of 2-aminothiophenol in the local chemistry. This lack of inhibition when no inhibitor is present in solution but a film of inhibitor covers the steel is also supported by the literature.[16]

Results of Testing Di-sodium β-glycerophosphate (BGP)

The permeability results showed that di-sodium β-glycerophosphate at concentrations of 0.3 mol/ft^3 and 0.815 mol/ft^3 led to a permeability equivalent to that of the control sample. These permeability test results are interesting because in the RCMs, the 0.283 mol/ft^3 and 0.815 mol/ft^3 dosages performed better in percentage of wires active and in time of wires at low corrosion rate than almost all other inhibitors. Impedance testing of di-sodium β-glycerophosphate in saturated calcium hydroxide with added chlorides produced polarization resistances that were nearly equivalent, 792 ohms-cm^2 and 823 ohms-cm^2, for the 0.3 M and 0.6 M sodium chloride chemistries, respectively. This *constant* corrosion inhibition in the presence of chlorides indicates the potentially excellent corrosion inhibition by di-sodium β-glycerophosphate.

The 0.283 mol/ft^3 dosage of di-sodium β-glycerophosphate results in superior properties for corrosion protection, achieving a ranking of first in resistance change metrics. This dosage ranked first in percentage of active wires after 2 years of testing, ranked third in percentage of weeks at low corrosion rate and had an associated permeability and compressive strength of concrete at least equivalent to those of the control specimens.

This inhibitor also appears to provide inhibition in concrete that is less dependent on concentration since the 0.815 mol/ft^3 dosage also provided excellent inhibition and ranked 6th in resistance change metrics and 3rd in overall ranking. The results of testing in this project suggest that this inhibitor will provide excellent protection of rebar in concrete.

Testing of Calcium Nitrite (CN)

The permeability results of calcium nitrite indicated that the low dosages, 0.283 mol/ft^3 and 0.815 mol/ft^3, were associated with lower permeabilities than that of the control, whereas dosages higher than 0.815 mol/ft^3 were associated with permeabilities that were higher than the control permeability. The significantly lower permeability at 0.815 mol/ft^3 calcium nitrite supported the results of the RCM data where the calcium nitrite performed better than the control specimens. Impedance testing of calcium nitrite in a SPS indicates a strong inhibiting effect in solution that decreases more rapidly than that of the other inhibitors studied as the amount of chloride added is increased. Further resistance change testing of calcium nitrite at higher dosages is required to determine the effects of higher dosages in protecting the steel in concrete with the accompanying rise in chloride permeability of the concrete.

Testing of Di-n-butyl Sulfoxide (DS)

The permeability results for di-n-butyl sulfoxide indicated a strong dependence of the permeability on the amount of inhibitor added. The 0.283 mol/ft^3 dosage was associated with a lower permeability than that of the control, whereas the 0.815 mol/ft^3 dosage was associated with a high permeability when compared with that of the control specimens. Impedance testing indicated that di-n-butyl sulfoxide provides electrochemical inhibition in a SPS. Also,

impedance testing of di-n-butyl sulfoxide indicates a decrease in R_p with an increase in chloride content but a much less severe decrease in comparison with the other inhibitors examined.

The combined results of the permeability and the RCM experiments suggested a strong electrochemical inhibiting effect by di-n-butyl sulfoxide. The 0.815 mol/ft^3 specimens performed well in percentage of wires active and in percentage of weeks at low corrosion rate; the 0.283 mol/ft^3 specimens also performed well in these tests, although to a lesser extent. The reduction in concrete quality from the 0.283 mol/ft^3 dosage to the 0.815 mol/ft^3 suggested that the electrochemical effect of the inhibitor was the determining factor in preventing corrosion at the higher dosage. Though, as with most of the inhibitors examined in this project, there appears to be a limit on concentration where corrosion prevention decreases sharply after a certain high concentration of inhibitor is reached, supported by the 2.832 mol/ft^3 resistance measurement results.

Testing of Lithium Nitrate (LN)

The permeability results for lithium nitrate indicate greatly increased permeability at low dosages, 0.283 mol/ft^3 and 0.815 mol/ft^3. The high permeability to chloride of the 0.815 mol/ft^3 lithium nitrate concrete specimens suggests a significant electrochemical inhibiting effect of the lithium nitrate at this concentration. Since this dosage performed extremely well in both the percentage of weeks at low corrosion rate and percentage of wires active, the inhibiting effect must have been great to counteract the effect of the high permeability of chloride in this concrete. However, the impedance data are ambiguous on the inhibiting effect of lithium nitrate in saturated calcium hydroxide. The R_p of rebar is extremely high before chloride additions and remains high at 0.3 M chloride. But the R_p falls below the control in the 0.6M chloride-containing solution. The obvious corrosion prevention demonstrated in the resistance change measurements (ranked third) and overall ranking of fourth strongly suggest further study of this compound.

Testing of Sodium Metasilicate (NA)

The permeability results for sodium metasilicate indicated a significant decrease in permeability with the addition of sodium metasilicate compared to control specimens. The fact that the permeability for both the 0.283 mol/ft^3 and 0.815 mol/ft^3 dosages was nearly equivalent was interesting. The 0.815 mol/ft^3 resistance measurement specimens were among the best performers in percentage of wires active and in time at low corrosion rate, earning a ranking of second in resistance change and second overall. But the 0.283 mol/ft^3 and 2.832 mol/ft^3 specimens were equivalent to the control in percentage of wires active and performed worse than the control in the time at low corrosion rate. Sodium metasilicate performed poorly when tested in saturated calcium hydroxide exhibiting a better polarization resistance than the control only before the addition of chlorides.

The literature suggests that sodium metasilicate is an anodic inhibitor that forms a thin protective film at anodic sites first. With time and available silicate in solution, the film spreads out over cathodic areas as well.[19] The sodium metasilicate is considered a dangerous inhibitor

that contributes to localized attack when not present in sufficient quantities in solution.[19] This property of the inhibitor may explain the lack of inhibition when tested at a low concentration in a SPS. Also, the poor performance of the lower dosage, 0.283 mol/ft^3, may be explained by the dangerous effect of the inhibitor below a critical concentration.

Testing of Nitrilotrisphosphonic Acid (AMP)(PA)

The permeability tests conducted on phosphonic acid at 0.283 mol/ft^3 and 0.815 mol/ft^3 produced the highest permeability listed on the chart in Figure 30. The phosphonic acid also had the lowest compressive strengths and worst impedance data of all the inhibitors examined. In the measurements taken, the phosphonic acid was the only inhibitor that exhibited two time constants, suggesting a breakdown in passivity. The pH was measured in saturated calcium hydroxide due to a precipitation reaction that could be visually observed upon addition of the phosphonic acid. The pH was found to decrease rapidly from 12.3 to 5 after addition of the phosphonic acid. The effect of the phosphonic acid on the pH is supported in the literature and suggests that phosphonic acid is a viable corrosion inhibitor for steel only in low-to-moderate pH systems.[13] The reaction between phosphonic acid and calcium hydroxide is detrimental to the concrete setting process, the pore solution (reduces the pH), and the cement hydrate. These results explain the resistance change data where the phosphonic acid samples were among the worst tested. For this reason, phosphonic acid should not be considered a potential inhibitor for protection of rebar in concrete.

SUMMARY

Chemical compounds were tested for their effectiveness as steel corrosion inhibitors in high-quality concrete. To facilitate the acquisition of this information:

1. A rapid screening method for quantifying the corrosion-inhibition qualities of inhibitive admixtures in high-quality concrete was developed and employed.

2. Multiple material and corrosion performance characteristics were examined.

3. The relationship between the results of the various methods was examined.

4. An overall inhibitor ranking based collectively on the performed tests conducted was developed.

Inhibitor rankings are provided in Table 7.

Use of Resistance Change Method

The RCM[8-10] along with improvements (prevention of crevice corrosion at block ends and reduction in diffusion distance of chlorides to the steel) allowed a reliable method to quantify corrosion and corrosion mitigation of steel in concrete. Large diameter, low resistance steel rods were attached to the ends of the test wires. This rod/wire system allowed measurement

of the wire resistance in concrete without any crevice corrosion taking place on a wire exit point from the concrete. Skiving of the surface layer of the concrete allowed a reduced cover depth of concrete over the wire to reduce diffusion distance of chloride to the wire while maintaining wire placement in high-quality concrete.

Variations in resistance data resulted from corrosion product buildup on the measurement leads, however trends of continuity status and corrosion rates could be acquired from the resistance data collected. These data allowed the comparative evaluation of various corrosion inhibitors in concrete. Subsequent dissection of concrete RCM specimens proved that corrosion of the embedded wires was scattered along the length of the wire and not focused at the end points. However, more concern for the wire contact points should be implemented in future studies using RCM. A simple protection method for the electrical connections has been devised and should be implemented in subsequent tests.

Evaluation of Material and Corrosion Performance

Several material and corrosion performance characteristics were evaluated to determine the overall efficacy of each compound in prevention of rebar corrosion in concrete. The characteristics examined were:

1. corrosion-inhibition characteristics in high-quality concrete

2. corrosion-inhibition characteristics in SPS

3. effect of admixed inhibitor on chloride permeability of concrete

4. effect of admixed inhibitor on concrete compressive strength.

The RCM provided two types of data measured in 3 or 4 blocks for each different dosage of inhibitor. Initially, the trends in slope of the RCM data with respect to time allowed for qualitative comparison of inhibitor performance. A second type of data that was considered a gold standard for corrosion protection performance consisted of the amount of time to open circuit. The inhibitors and dosages that performed better than calcium nitrite in the RCM are listed by rank:

1. 0.283 mol/ft^3 di-sodium β-glycerophosphate

2. 0.815 mol/ft^3 lithium nitrate

3. 0.815 mol/ft^3 sodium metasilicate

4. 0.815 mol/ft^3 aminoethylethanolamine

5. 0.815 mol/ft^3 di-n-butyl sulfoxide

6. 0.815 mol/ft^3 di-sodium β-glycerophosphate

7. 0.283 mol/ft^3 di-n-butyl sulfoxide.

The results of the EIS of inhibitors in saturated calcium hydroxide provided data on the polarization resistance of the inhibitors in simulated concrete chemistry. The inhibitors were tested on one sample rebar in saturated calcium hydroxide solution, and then after 0.3 M and 0.6 M NaCl additions. The results of testing in SPS did not generally agree with the findings from resistance measurements in concrete except for di-sodium β-glycerophospate and calcium nitrite. The difference between inhibition in solution and in concrete for the majority of the inhibitors suggests that prevention of corrosion in concrete involves *more* than inhibition against chloride attack in a high pH solution containing calcium hydroxide. The amount of mobile inhibitor in cast concrete and the effects of the inhibitor on chloride permeability as assessed by the electrical indication test of concrete are two examples of properties of the inhibitors unable to be judged by testing in SPS. The top four inhibitors tested in SPS at 10 mM each were calcium nitrite, di-sodium β-glycerophosphate, lithium nitrate, and 2-aminothiophenol, respectively.

Concrete cylinders were produced to test the compressive strength and permeability to chloride. Compressive strengths of concrete were carried out on three cylinders per inhibitor dosage and were corrected for air content. Compressive strength provided an excellent measure of the quality of concrete resulting from inhibitor additions. The top four compressive strengths were provided by addition of the following inhibitors and dosages, 0.815 mol/ft^3 calcium nitrite, 0.815 mol/ft^3 2-aminothiophenol, 0.815 mol/ft^3 aminoethylethanolamine, and 0.283 mol/ft^3 di-sodium β-glycerophosphate, respectively.

Permeability was measured using a rapid chloride screening test and allowed some delineation of inhibitor effect provided by reduction of permeability versus chemical inhibition. The four lowest permeability to chloride were provided by the following inhibitors and dosages, 0.815 mol/ft^3 aminoethylethanolamine, 0.815 mol/ft^3 2-aminothiophenol, 0.283 mol/ft^3 2-aminothiophenol, and 0.815 mol/ft^3 calcium nitrite, respectively.

Relationship Between Results of Various Methods

The performance of an inhibitor in concrete is a function of numerous inter-related factors that do not appear to be predicted from any single laboratory test. Correlation graphs between the ranks of inhibitors tested in concrete for corrosion and concrete quality are found in Figures 32 through 35. The graphs illustrate the lack of correlation between concrete quality and corrosion prevention by the various inhibitors. However, the graphs do demonstrate a good correlation (60%) between the two metrics for the RCM, wire survivability and time at low corrosion rate. Also, the graphs demonstrate a good correlation (78%) between the two metrics of concrete quality, permeability and compressive strength. The results of this project support the need for testing of inhibitors in *high-quality concrete* as a screening method for inhibitor application to concrete structures.

Inhibitors with Potential to Replace Calcium Nitrite

A ranking of the inhibitors from each test metric used in this project and an overall ranking are presented in Table 7. Inhibitors that showed good results in time-to-open or percentage of weeks at low corrosion rate were regarded as the best inhibitors studied in this project. Since the testing of resistance change in concrete is considered the most reliable indication of good inhibitors in this project, the ranking from the resistance change results were weighted with a factor of three in the computation for the combined ranking of all tests. The other tests, low permeability to chloride, high compressive strength upon addition of inhibitors, and polarization resistance in SPS were also considered important in computing the overall ranking of inhibitors and all of these tests were weighted with a value of 1.

The inhibitors that performed as well as or better than the calcium nitrite in the overall ranking of inhibitors are considered a good alternative inhibiting admixture to calcium nitrite. These inhibitors and concentrations that performed better than calcium nitrite in overall ranking are listed by overall rank:

1. 0.815 mol/ft^3 aminoethylethanolamine

2. 0.815 mol/ft³ sodium metasilicate

3. 0.815 mol/ft^3 di-sodium β-glycerophosphate

4. 0.815 mol/ft^3 lithium nitrate.

CONCLUSIONS

- The performance of a corrosion inhibitor in concrete is a function of numerous interrelated factors that are not predicted from any single laboratory test.

- Based on the weighted sum of multiple tests (RCM, compression strength, chloride permeability), several inhibitors perform better than calcium nitrite. The inhibitors and concentrations are listed in overall ranking order:

1. 0.815 mol/ft^3 aminoethylethanolamine

2. 0.815 mol/ft³ sodium metasilicate

3. 0.815 mol/ft^3 di-sodium β-glycerophosphate

4. 0.815 mol/ft^3 lithium nitrate.

RECOMMENDATION

Additional tests should be conducted on concrete mixtures containing slag and fly ash. Multiple concentrations of the four most promising inhibitors should be examined. Further testing may lead to the implementation of a better corrosion-inhibiting admixture, which will increase the service life of bridges.

SUGGESTED FUTURE RESEARCH

Further testing of the inhibitor compounds shown to be effective in this project is needed and should include expanded concentrations of di-sodium β-glycerophosphate (0.15 mol/ft^3, 0.3 mol/ft^3, 0.45 mol/ft^3), calcium nitrite (1.63 mol/ft^3, 2.47 mol/ft^3), and lithium nitrate (1.63 mol/ft^3, 2.47 mol/ft^3). Also needed are repeated dosages of sodium metasilicate (0.283 mol/ft^3, 0.815 mol/ft^3, 2.832 mol/ft^3), 0.815 mol/ft^3 aminoethylethanolamine, and more control blocks. Finally, since VDOT and most other DOTs use slag and fly ash in most or all concrete, further inhibitor testing should be conducted in concretes containing these materials. These additional evaluations should help confirm the results of this project and provide additional information on the concentration dependence of these inhibitors.

Also suggested are modifications to the original block production. A new method for setting reference wires in Plexiglas™ tubes was devised and implemented to reduce the number of reference wires destroyed during production. Rubber O-rings should be attached to the rods to prevent chlorides from migrating down the rods to the sensitive lead attachments. Finally, test wires at additional cover depths should be used to observe the dependence on the penetration depth of chloride.

Future research should include DC polarization testing to determine the nature of the inhibition provided by the various chemicals examined. Confirmation of the anodic nature of the inhibition provided by particular inhibitors could justify the need to determine the critical concentration of these inhibitors to prevent accelerated attack.

Finally, testing in concrete in the field will ultimately determine the effectiveness of the chemical compounds examined in this project in preventing rebar corrosion in high-quality concrete.

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