

Surface Characterization of Reinforcing Steel and the Interaction of Steel with Inhibitors in Pore Solution

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Studies of rebar surfaces following cleaning in various ways and following exposure to corrosive solutions in the presence and absence of inhibitors have been carried out using the surface-sensitive technique: x-ray photoelectron spectroscopy (XPS). After cleaning in hexane, rebar specimens were exposed to simulated pore solution with or without corrosion inhibitors under specified conditions. Subsequent XPS analysis of the rebar specimens indicated that the corrosion inhibitors sodium nitrite, sodium molybdate, sodium dihydrogen phosphate, sodium monofluorophosphate, and sodium tetraborate produced changes in rebar surface chemistry that could be associated with corrosion inhibition. The principal changes were (a) alteration in surface iron content, (b) reduction in the surface hydroxide concentration, and (c) increase in surface oxide oxygen concentration. The results are interpreted to indicate that these inhibitors promote the formation of surface oxides at the expense of hydroxide functionality. Results from the study of sodium tetraborate reveal that this inhibitor produces a coating on the rebar surface.

The deterioration of reinforced concrete structures caused by corrosion of reinforcing steel has long been recognized (1,2). For highway bridges, chloride ions from deicing salts interacting with steel have been implicated in accelerating the degradation of steel and spalling of concrete structures (3). The initiation of chloride-induced corrosion of steel in concrete occurs via localized attack or pitting corrosion (3,4). Treatment of corroded structures with inhibitors offers a practical solution to the corrosion of steel in bridges (5-7). Corrosion inhibitors that have shown promise and are of current interest include calcium or sodium nitrite (8-13), stannous chloride (12), and sodium benzoate (14). As a part of a program to evaluate the effectiveness of inhibitors for the repair of reinforced bridge structures, to identify and test potential new inhibitors, and to investigate the surface chemistry of reinforcing steel (rebar) following aqueous treatment, a surface-sensitive analytical technique, combining especially electron spectroscopy for chemical analysis (ESCA) and x-ray photoelectron spectroscopy (XPS), has been used (15,16). The analyses were carried out to determine the chemical nature of inhibitor constituents on the rebar surface, to evaluate the surface concentration of inhibitor elements, and to correlate the results with corrosion test experiments. It was reasoned

not only that surface analysis measurements could aid in understanding the role and mechanism of corrosion inhibitor action, but also that such measurements would be valuable for determining the effectiveness of inhibitors in short-term screening tests.

EXPERIMENTAL SECTION

Rebar rods were obtained from Roanoke Electric Steel Co., Roanoke, Virginia. The rod composition was formulated to be similar to material used 20 to 30 years ago. Bulk analysis of the rod material provided by the vendor is presented in Table 1. The rebar rods were 1/2 in. in diameter and 6 ft long. Test specimens were prepared by first cutting the bar in half longitudinally and then 1-in. specimens were cut from the split bar. Rebar cleaning experiments were carried out so that throughout the study a common pretreatment designed to remove grease and dirt would be used, and thus a kind of standard surface would be studied. To this end, organic solvents (hydrocarbon, alcohol, and ketone) and an aqueous acid solution were investigated to discover which treatment altered the as-received rebar surface to the smallest extent. Solvents used for tests to select a cleaning solvent included hexane, isopropanol, and acetone. Rods were also cleaned in a 50 weight percent (wt.%) sulfuric acid:distilled water solution for 1 min at room temperature, rinsed three times with distilled water, and dried at 110°C. To facilitate the preparation of samples for surface analysis, a notch was cut in the 1 in. specimens at approximately 3/4 in. from one end of the specimen. After immersion in the inhibitor test solution, the 3/4 in. portion of the treated bar was separated from the 1 in. specimen and analyzed. By using this procedure, the integrity of the treated rebar surface could be maintained, in that no cutting of the samples was required following treatment. The curved, outer portion of the rebar specimen was analyzed.

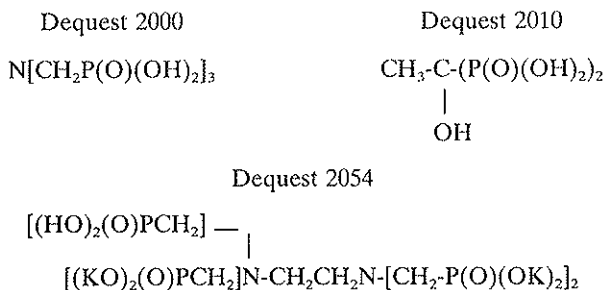
The test solutions were simulated pore solution [KOH (0.600 M); NaOH (0.300 M); saturated with Ca(OH)₂]; pore solution containing NaCl (3.5 wt.%); and pore solution containing NaCl (3.5 wt.%) and inhibitor (0.3 M). The inhibitors studied included sodium nitrite (NaNO₂), sodium molybdate (Na₂MoO₄), sodium dihydrogen phosphate (NaH₂PO₄), sodium monofluorophosphate (Na₂PO₃F), sodium tetraborate (Na₂B₄O₇), and three commercial reagents; Dequest 2000 [aminotri(methylene phosphoric acid), 50 percent active aqueous solution]; Dequest 2010 [1-hydroxyethylidene-1,1-diphosphonic acid, 60 percent active aqueous solution]; and

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TABLE 1 BULK (wt.%) AND SURFACE ANALYSIS (at.%) OF REBAR MATERIAL

Element	wt%	calc. at. %	Rebar Treatment atomic % (measured; XPS)			
			as received	alcohol	hexane	sulfuric acid
C	0.22	1.0	58.4	53.7	56.4	51.9
O	not analyzed		28.7	36.7	31.6	30.3
N	not analyzed		1.41	1.10	1.09	0.96
Fe	97.2	96.5	3.68	3.97	4.64	7.54
P	0.018	0.32	<0.1	<0.1	<0.1	<0.1
S	0.036	0.062	0.85	0.81	0.62	0.58
Si	0.59	1.16	3.26	3.27	2.56	2.04
Na	not analyzed		0.97	<0.1	0.68	0.78
Ca	not analyzed		0.45	0.43	0.59	<0.1
Mn	1.00	1.00	<0.1	<0.1	<0.1	<0.1
Al	0.006	0.01	<0.1	<0.1	<0.1	<0.1
Cu	0.26	0.23	2.06	1.02	1.70	6.01
Zn	not analyzed		0.18	<0.1	0.10	<0.1
Cd	not analyzed		<0.1	<0.1	<0.1	<0.1

Dequest 2054 [hexapotassium hexamethylenediaminetetra(methylene phosphonate), 35 percent active aqueous solution]. The Dequest compounds obtained from Monsanto Chemical Co. had the following compositions:



The test solutions were aerated for at least 1 hr before rebar samples were introduced into the solutions. Exposure time was 8 days. Samples were maintained at 60°C. The exposure procedure was to run five replicate samples at each exposure to provide data for statistical analysis of the results of exposure for individual samples.

Two kinds of experiments were carried out with respect to rebar immersion in pore solutions. In experiments termed "initial inhibition," hexane-cleaned rebar was immersed for 8 days at 60°C in pore solution containing inhibitor (0.300 M) and NaCl (3.5 wt.%). At the end of the exposure, rebar was removed, rinsed with distilled water, and characterized by XPS. For experiments indicated as "delayed inhibition," hexane-cleaned rebar was immersed for 8 days at 60°C in pore solution containing NaCl (3.5 wt.%). At the end of this period the specimens were then immersed for 8 days at 60°C in pore solution containing NaCl (35 wt.%) plus inhibitor (0.300 M). At the end of this exposure time, the rebar samples were removed from solution, washed with distilled water, and the surface chemistry evaluated with XPS. The test temperature of 60°C was selected to accelerate the rate of inhibitor interaction with rebar. XPS results for experiments carried out at room temperature (23°C), indicated that the oxides formed were equivalent to those produced at 60°C.

Surface analysis measurements were carried out using a PHI Perkin-Elmer 5300 photoelectron spectrometer (16). Photoelectrons were generated using Mg K_{α} radiation [$h\nu = 1,253.6$ electron volts (eV)]. Ejected photoelectrons were analyzed using a hemispherical analyzer and the electrons were detected using a position-sensitive detector. In the presentation of elemental analysis results, photoelectron spectral peak areas were measured and subsequently scaled to account for ionization probability and an instrumental sensitivity factor to yield results that were indicative of surface concentration in atomic percent. The precision for the concentration evaluations was determined from measurements on five different rebar specimens and the results are given in the tables in parentheses. The binding energy (BE) scale was calibrated by setting the C 1s hydrocarbon peak BE value at 285.0 eV (17). At least two different measurements on two different rebar samples were made and the average results are given.

RESULTS AND DISCUSSION

The surface analysis results following the treatment of rebar in selected solvents and solutions are presented in Table 1. Hexane cleaning was the treatment selected for the following reasons:

1. The chemical content and the chemical nature of the surface elements on the rebar surface are not altered significantly.
2. Residual solvent on the treated surface is minimal and less than that found following treatment with alcohol, acetone, or other organic solvents.

Following alcohol cleaning, surface concentrations of oxygen increase and surface concentrations of copper and zinc decrease. In addition, the chemical nature of carbon is altered to about 25 atomic percent (at.%) for -COR (for ether, R = alkyl; for alcohol, R = H) functionality, whereas the concentration of this group on as-received rebar is about 10 at.%. For rebar treated with sulfuric acid, significant surface con-

centration changes are noted for the metals. Iron and copper concentrations increase, whereas the surface contents for calcium and zinc decrease below the detection level (<0.1 at. %). Thus, cleaning of rebar with sulfuric acid results in a significant change in surface chemical content. Because the purpose of the present experiments is to simulate as closely as possible long-term exposure to corrosive conditions of rebar used in the construction or repair of bridges, the severe alterations caused by sulfuric acid cleaning are not desirable for this study. The most representative surface is that of rebar that has been cleaned in hexane and dried in an oven.

These studies were made primarily on rebar exposed to corrosion at 60°C. This temperature had been selected for related accelerated corrosion studies (see Dressman et al., a companion paper in this Record). Compared with studies at room temperature, no difference was found between surface oxides formed at 23°C and 60°C. It appears from these findings

that the rate of corrosion changes with temperature but the mechanism does not change.

The surface analysis results following the immersion of rebar in pore solution containing NaCl are compared with the corresponding data presented for hexane-cleaned rebar in Table 2. The principal alterations in surface chemistry as a result of immersion of hexane-cleaned rebar in pore solution containing NaCl are increases in oxygen, iron, silicon, sodium, potassium, and chlorine; and decreases in carbon, nitrogen, and copper. The presence of calcium, potassium, and chlorine on the treated rebar may arise from adsorption of these elements on the oxide surface. Associated with the alteration in the oxygen atomic concentration is a change in the shape of O 1s photopeak. The spectra shown in Figure 1c exhibit features attributed to oxide oxygen (BE \cong 529 eV) as the dominant peak for hexane-cleaned rebar. In the spectra in Figure 1b for rebar immersed in pore solution, contributions by hy-

TABLE 2 SURFACE ANALYSIS RESULTS (IN at. % WITH STANDARD DEVIATIONS IN PARENTHESES) FOR REBAR SPECIMENS FOLLOWING INTERACTION WITH INHIBITORS

Treatment	Element	C	O	N	Fe	Si	Na	Ca	Cl	Inhibitor element
Hexane Cleaned		60.3 (5.3)	28.3 (3.5)	1.83 (0.67)	4.07 (1.04)	1.33 (0.78)	1.67 (0.9)	0.21 (0.2)	---	
8 days chloride-contg. pore sol. 60°		37.4 (2.6)	43.0 (3.2)	0.57 (0.23)	6.43 (0.89)	2.69 (0.15)	3.72 (0.46)	4.24 (0.28)	1.33 (0.08)	---
0.300M NaNO ₂	Initial	49.8	33.2	1.11	5.23	2.08	3.90	1.78	1.10	---
	Inhibition	(8.3)	(4.9)	(0.96)	(2.27)	(0.38)	(1.03)	(1.01)	(0.22)	---
	Delayed Inhibition	57.3 (3.7)	30.7 (2.8)	0.47 (0.12)	5.02 (0.58)	2.39 (1.02)	1.92 (1.11)	1.27 (0.22)	0.44 (0.13)	---
0.300M Na ₂ MoO ₄	Initial	41.6	39.6	1.13	7.29	3.31	4.07	0.81	1.01	Mo 0.46
	Inhibition	(3.7)	(2.2)	(0.21)	(1.08)	(0.56)	(0.83)	(0.27)	(0.09)	(0.15)
	Delayed Inhibition	30.6 (0.74)	45.4 (2.7)	1.92 (0.43)	9.13 (1.92)	5.07 (1.98)	3.83 (0.39)	1.67 (0.83)	1.06 (0.51)	Mo 0.52 (0.07)
0.300M NaH ₂ PO ₄	Initial	35.1	42.3	0.32	5.94	1.67	10.2	0.14	1.81	P 1.54
	Inhibition	(3.84)	(0.41)	(0.40)	(1.42)	(0.36)	(2.6)	(0.03)	(0.55)	(0.44)
	Delayed Inhibition	20.1 (7.4)	48.8 (4.4)	0.22 (0.17)	12.0 (1.3)	2.5 (0.31)	11.5 (3.3)	1.21 (1.6)	1.85 (0.49)	P 2.27 (0.55)
0.300M Na ₂ PO ₃ F	Initial	48.5	32.6	0.38	5.82	2.04	6.60	0.06	1.54	F 0.27
	Inhibition	(9.9)	(5.7)	(0.87)	(3.2)	(0.55)	(2.80)	(0.09)	(1.05)	(0.27)
	Delayed Inhibition	35.5 (4.6)	40.3 (3.9)	0.32 (0.23)	8.39 (0.86)	3.01 (0.78)	6.15 (1.83)	0.50 (0.23)	1.55 (0.05)	F 0.77 (0.18)
0.300M Na ₂ B ₄ O ₇	Initial	61.1	29.4	0.19	<0.1	1.03	3.23	3.15	1.20	P 1.20
	Inhibition	(4.9)	(4.1)	(0.27)		(0.76)	(1.58)	(1.16)	(0.51)	B 5.03
	Delayed Inhibition	39.7 (2.3)	38.8 (4.8)	1.30 (1.13)	0.29 (0.51)	0.73 (0.35)	7.13 (1.82)	1.95 (0.30)	4.77 (2.12)	B 6.14 (1.50)
0.300M Dequest 2000	Initial	18.9	48.9	4.44	5.73	0.55	5.97	0.5	0.08	P 13.2
	Inhibition	(3.9)	(2.8)	(0.33)	(1.97)	(0.35)	(0.68)	(0.33)	(0.12)	(0.9)
	Delayed Inhibition	18.7 (1.4)	45.6 (1.9)	4.39 (0.17)	6.60 (0.42)	0.78 (0.23)	5.75 (1.82)	0.10 (0.18)	0.64 (0.72)	P 13.6 (0.3)
0.300M Dequest 2010	Initial	17.9	50.5	<0.1	14.6	4.56	4.12	0.34	2.20	P 2.72
	Inhibition	(1.4)	(0.7)		(1.5)	(1.21)	(1.35)	(0.11)	(0.81)	(0.45)
	Delayed Inhibition	21.3 (9.9)	48.6 (4.9)	0.27 (0.38)	6.20 (1.51)	2.53 (0.73)	5.70 (1.69)	0.10 (0.10)	1.40 (0.34)	P 2.59 (0.78)
0.300M Dequest 2054	Initial	47.4	33.7	1.50	4.06	1.56	2.28	2.74	0.66	P 3.06
	Inhibition	(2.8)	(3.0)	(0.37)	(1.50)	(0.30)	(0.49)	(1.02)	(0.36)	(0.58)
	Delayed Inhibition	44.3 (8.7)	36.9 (5.0)	1.08 (0.16)	3.80 (0.88)	1.69 (0.88)	2.07 (0.90)	2.07 (0.90)	0.63 (0.22)	P 2.69 (1.08)

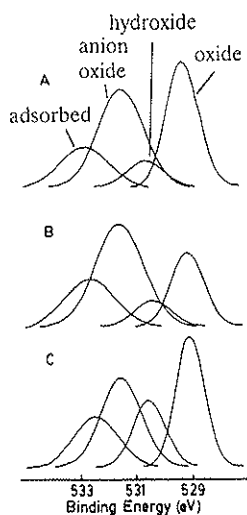


FIGURE 1 Oxygen 1s photoelectron spectra and curve-resolved O 1s spectra for rebar specimens: (a) rebar treated for 8 days at 60°C in chloride-containing pore solution and NaNO₂ (0.300 M); (b) rebar treated for 8 days at 60°C in chloride-containing pore solution; and (c) hexane-treated rebar. (The BE scale has been corrected by reference to a hydrocarbon standard.)

droxide dominate (BE ≈ 530 eV), although the concentration of oxide oxygen remains at a significant level. Additional oxygen photopeaks in the curve-resolved spectrum are attributed to oxygen in silicon-containing species and in adsorbed water.

In the discussion of the analysis for rebar treated in the inhibitor solutions, results obtained for hexane-cleaned rebar and rebar immersed in chloride-containing pore solution are compared. Following that, the results for material from initial and delayed inhibition experiments are compared.

Sodium Nitrite

The surface analysis results following the treatment of rebar with sodium nitrite in pore solution containing chloride are presented in Table 2. The findings for the initial inhibition experiments indicate an increased surface content only for carbon. The surface concentrations of oxygen and calcium decrease, whereas the surface contents of nitrogen, iron, silicon, and sodium remain essentially unchanged.

Of particular interest are the results for nitrogen. The percent nitrogen and the N 1s BE of 399.0 eV for treated rebar are similar (within experimental error) to the results found for rebar treated in pore solution containing chloride. That a nitrogen-containing species with a binding energy not characteristic of nitrite (N 1s BE in sodium nitrite = 404.1 eV)

is detected indicates that nitrite is not chemisorbed on the rebar surface.

Alterations in the oxygen photopeak indicate that a chemical change has taken place on the rebar surface as a result of immersion in nitrite-containing pore solution. Thus, any nitrogen-containing reaction product must be released into solution, or it is the adsorbed nitrogen exhibiting a binding energy at 399.0 eV. The decrease in the oxygen concentration may at first appear surprising in view of the fact that nitrite appears to alter the surface chemistry of rebar. Nevertheless, the change that occurs is an alteration in the distribution of oxygen surface groups.

The oxygen 1s photopeak was curve-resolved (Figure 1a) into contributions from oxide oxygen (BE = 529 to 530 eV); hydroxide oxygen associated with metals (BE = 530 to 531 eV); oxide oxygen for alkali and alkaline earth metal compounds and silicon oxide species (BE = 531 to 532 eV); and adsorbed water (BE = 532 to 533 eV). As a result of the treatment, the OH⁻ oxygen (BE = 530 eV) decreases, whereas the relative percent for the transition metal oxide oxygen (BE = 529 eV) increases for the nitrite-treated sample (see Table 3). Oxygen associated with other functionalities remains unchanged. These findings can be interpreted to suggest that the probable role of nitrite in the inhibition process is to increase oxide surface concentration. Because sodium nitrite is an effective corrosion inhibitor (8, 9), the surface analysis results suggest that one of the characteristics of useful inhibitors would be to increase the surface concentration of metal oxide functionality, especially iron oxide content (see also Dressman et al., a companion paper in this Record).

The results for delayed inhibition samples indicate little or no change (within the error limits) in elemental composition compared to the results for initial inhibition materials. The principal alteration is the increase in the concentration of metal oxide oxygen from 23.6 to 35.5 percent. It is likely that the increase is associated with the formation of additional passive iron oxide at the surface. This interpretation is similar to that presented earlier for other characterization studies (8, 9). In screening tests (Dressman et al.), sodium nitrite was an effective corrosion inhibitor.

Sodium Molybdate

The interaction of sodium molybdate with rebar either by initial or delayed inhibition experiments produced an increased surface concentration of iron and associated iron oxide. Molybdenum was detected on the rebar surface at a concentration of about 0.5 at.% and a corresponding increase in the oxygen associated with Mo(VI) was noted. A comparison of the Mo 3d_{5/2} binding energy for Na₂MoO₄ (BE = 232.4 eV) with that for molybdenum from the two rebar exposure experiments (BE = 232.2 and 232.3 eV for initial and delayed inhibition experiments, respectively) indicates that molybdenum as molybdate [Mo(VI)] is adsorbed on the rebar surface.

A decrease in calcium and an increase in silicon concentrations were found, compared to the data obtained for rebar exposed only to chloride-containing pore solution. Within experimental error, the concentration of other elements did not change. The increase in iron and oxide oxygen and the detection of molybdenum as Mo(VI) indicate that molybdenum

TABLE 3 CURVE-RESOLVED O 1s RESULTS FOR REBAR AND REBAR IMMERSSED IN PORE SOLUTIONS WITH AND WITHOUT INHIBITOR

Sample Treatment	Metal Oxide BE = 529-530	Metal Hydroxide BE = 530-531	Silicon-oxygen oxy anion-oxygen BE = 531-532	adsorbed-oxygen (water) BE = 532-533
hexane cleaned	31.5	15.2	27.7	25.6
pore solution (8 days)	21.7	7.1	50.2	21.0
pore solution + 3.5% NaCl (8 days)	16.0	3.5	61.7	18.9
pore solution + 3.5% NaCl (8 weeks)	15.0	4.3	56.9	23.8
initial inhibition* (ii) NaNO ₂	23.6	3.6	45.6	27.2
delayed inhibition* (di) NaNO ₂	35.5	9.2	34.1	21.2
ii; Na ₂ MoO ₄	32.9	<2.	37.4	29.8
di; Na ₂ MoO ₄	35.9	<2.	43.6	20.6
ii; NaH ₂ PO ₄	38.8	<2.	42.8	18.4
di; NaH ₂ PO ₄	42.1	<2.	41.6	16.3
ii; Na ₂ P ₂ O ₇	34.5	<2.	46.7	18.8
di; Na ₂ P ₂ O ₇	31.2	<2.	48.8	20.0
ii; Na ₂ B ₄ O ₇	3.1	8.7	59.2	29.0
di; Na ₂ B ₄ O ₇	2.2	2.1	72.7	23.0

Dequest oxygen spectra not curve resolved, only interpreted in a qualitative manner in the text.

affects the rebar surface through an adsorption process such that oxide constituent contributions are increased at the surface. If molybdate acts as an oxidizing agent, the surface analysis results cannot identify the reduced molybdenum product. The molybdenum photopeak was characteristic only of Mo(VI), i.e., no reduced molybdenum species were detected at the surface. Lack of detection of reduced molybdenum could occur if the reduced product is not adsorbed on the rebar surface or if the concentration of reduced molybdenum is too small to contribute significantly to the Mo 3d photoelectron signal. However, screening corrosion tests (Dressman et al.) indicate that molybdate is a relatively poor inhibitor.

Sodium Dihydrogen Phosphate (DHP)

The interaction of sodium DHP with rebar surfaces results in little or no significant change in oxygen, nitrogen, silicon, or iron concentrations, whereas the concentrations of sodium and phosphorous increase dramatically in the initial inhibition experiments. In these experiments, the calcium content is reduced significantly compared to that found for rebar treated in chloride-containing pore solution. A comparison of the initial and delayed inhibition results indicates a significant increase in iron content

Accompanying the change in surface concentrations for oxygen in both initial and delayed exposures is an alteration in the surface distribution of oxygen species. The O 1s photopeak was resolved into three components (see Table 3) that are characteristic of metal oxide (BE = 529 to 530 eV), metal hydroxide and phosphate oxygen (BE = 531 to 532 eV); and

adsorbed oxygen, probably water (BE = 532 to 533 eV). Compared with rebar treated in chloride-containing pore solution, the concentration of oxygen surface species for metal oxide increases following phosphate treatment. The concentration of oxygen attributable to OH⁻ is insignificant (<2 at.%) following phosphate treatment. The dominant contribution to the O 1s photopeak in the range 531 to 532 eV is oxygen bound to phosphorus. The detection of phosphate phosphorus on the treated surface combined with the decrease in hydroxide group content may indicate a surface acid-base reaction as the process promoting rebar surface changes that relate to inhibition. The adsorption of phosphate may also aid in corrosion inhibition by passivating potentially active corrosion sites on the rebar surface. Screening tests (Dressman et al.) indicate that DHP is only a modest corrosion inhibitor.

Sodium Monofluorophosphate (MFP)

Inhibition experiments carried out with MFP permitted comparison of the results with those found for DHP. The results are presented in Table 2. The principal differences are that the oxygen, iron, sodium, and phosphorus concentrations are lower on MFP-treated rebar. The results indicate that MFP interacts with rebar to a lesser extent than DHP does. The oxygen functionality distribution is also consistent with this finding in that metal oxide content and phosphate oxygen concentration are both lower for the rebar surface treated with MFP. The expected 1:1 phosphorus to fluorine atomic ratio for PO₃F²⁻ is not found on the rebar surface. The P/F ratio for the initial inhibition samples is 2.6 and that for the

delayed inhibition samples is 1.6. That this ratio is not unity suggests the loss of fluorine for adsorbed phosphate inhibitor. A potential process to account for this observation is hydrolysis of MFP (partial or complete) at the rebar surface or in solution. Either partial or complete hydrolysis would liberate fluoride and phosphate into solution and might result in subsequent adsorption of fluoride and phosphate. The phosphorus 2p binding energy for phosphorus adsorbed on rebar from MFP is equivalent to that for phosphate (PO_4^{3-}) in phosphate salts. The equivalence of BE values is consistent with the proposed hydrolysis process. Corrosion screening tests (Dressman et al.) demonstrate that MFP is a good corrosion inhibitor.

Sodium Tetraborate

The reaction of sodium tetraborate with rebar produced a unique result. The oxygen photopeak is characteristic of oxide oxygen from borate and the boron 1s BE value is equivalent to that for pure sodium tetraborate. Boron is detected at 5 and 6 percent on initial and delayed inhibition rebar specimens, respectively. No iron was detected (<0.1 at.%) in the measurement of the Fe 2p photoelectron spectra for borate-treated rebar. The fact that iron is not detected at the surface, whereas oxygen and boron photopeaks characteristic of borate are detected, suggests that borate reacts under the chosen experimental conditions to produce a coating on the rebar. The behavior of forming a coating on rebar is unlike the modes of interaction found for other inhibitors studied.

On comparison of initial versus delayed inhibition, the atomic concentrations vary as noted; sodium and chlorine increase, whereas calcium decreases. The increase in sodium is consistent with the increase in borate concentration and may indicate adsorption of sodium on the borate coating. The findings for borate treatment suggest that such a coating could function as a barrier layer on the rebar to inhibit chloride-induced corrosion. Sodium tetraborate exhibits good corrosion inhibition in screening tests (Dressman et al.).

Dequest 2000

Dequest 2000 is a trialkylphosphate amine. There are no significant differences in atomic composition on comparing initial and delayed inhibition results. The important surface composition changes for Dequest-treated rebar compared to rebar treated in chloride-containing pore solution are increases in nitrogen, phosphorus, and sodium, and a decrease in calcium. The P/N surface ratio in these samples is 3:1—a result indicative of the presence of adsorbed Dequest active component—trialkylphosphate amine. The oxygen spectra (Table 3) indicate contributions from iron oxide, but the principal contribution is from the phosphate functional group. The phosphorus atomic composition (13 at.%) indicates significant adsorption on rebar samples.

Dequest 2010

The adsorption of this phosphate material on rebar is noted by the appearance of phosphorus in the spectra for initial and

delayed inhibition samples. The concentrations of the respective individual elements are equivalent when comparing initial and delayed treatments, except for iron and silicon. For these latter elements, the concentration is greater following the initial inhibition treatment. The oxygen photopeak could be resolved (Table 3) to indicate contributions from metal oxide and adsorbed oxygen (probably water). However, the principal contribution is from the phosphate oxygen species. The phosphorus 2p binding energy data are indicative of the adsorption of the phosphorus component without change in chemical nature, i.e., no measurable or detectable change in the oxidation state of phosphorus occurs. On the basis of the percent of surface phosphorus, the adsorption of Dequest 2010 is less favorable by at least a factor of four (on a mole percent basis) compared to the adsorption of Dequest 2000 on rebar specimens.

Dequest 2054

The interaction of this ethylenediaminetetraalkylphosphate with rebar does not produce any significant differences in the surface composition when comparing initial and delayed tests. On the basis of the amount of phosphorus present, the quantity of this material present on rebar is at least less than half that for the active component in Dequest 2010. The oxygen functionality includes contributions principally from iron oxide and phosphate from the inhibitor.

The corrosion inhibition performance (Dressman et al.) of Dequest materials is not superior to that of the simple metal salts discussed earlier. The inhibiting activity of Dequest materials was greater than that for molybdate, but less than that for phosphate.

SUMMARY

The mode of inhibitor interaction with rebar samples can be grouped into three classes on the basis of the surface analysis results:

1. Nitrite interacts, leading to the formation of an iron oxide surface, but the inhibitor itself is not adsorbed as nitrite.
2. Tetraborate interacts to form a coating on the rebar surface rendering substrate iron undetectable by surface sensitive analytical measurements.
3. Other inhibitors interact by adsorption on rebar, leading to enhancement of oxide oxygen surface functionalities. In some instances the oxide functionalities could be associated with iron oxide.

From the surface analysis data alone, no inhibitor is significantly the most effective in the delayed inhibition experiments. The findings are consistent with the known corrosion inhibition behavior of nitrite caused by the formation of an oxide surface layer. The surface analysis results suggest that the formation of iron oxide surface components may indicate a desired reaction for potentially active inhibitors. In addition, another potentially beneficial corrosion inhibition process has been revealed in studies of sodium tetraborate solutions in which a coating is produced on the rebar surface.

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