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Corrosion Resistance of Functionally Graded Coatings on Plain Steel Rebars

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Abstract

The experimental results obtained on steel rebars with coatings of Si-based particles are described in this paper. It is well known that adding Si to metals generally increases their corrosion, oxidation, and erosion resistance. In this study, it is chosen to use Si-based coatings because of their proven capacity for corrosion protection in Cl⁻ environments. In addition, this paper presents impedance spectroscopy as an alternate technique in determining the corrosion activity of coated steel rebars. Impedance spectroscopy is an electrochemical measurement technique, which measures the response of a system to an applied alternating signal. A major benefit of the technique is its ability to monitor both the bulk and interfacial responses. This research was conducted to characterize the impedance response of several coatings on steel rebars, and in so doing, further understanding of the corrosion susceptibility of the systems. The results suggest that impedance spectroscopy may be useful for monitoring corrosion activity on coated rebar.

1. Introduction

Normally, concrete provides good protection against the corrosion of steel reinforcement. It provides both a chemical and physical barrier for the steel. The highly alkaline pore solution creates an ideal passivating environment, forming an adherent oxide film on the steel surface, while the bulk material acts as a cover providing isolation from the environment. The durability, strength, and relatively low cost of the system are the reason for its widespread use. Because of this durability, however, reinforced concrete structures are frequently used in very aggressive environments.

In most cases, the aggressive conditions causing corrosion in these systems result from chloride attack. Chlorides behave as catalysts in the anodic corrosion reaction, aiding the dissolution of the protective passive layer. Attack by chlorides is particularly insidious. The corrosion in these circumstances is a localized, pitting process, causing extremely high dissolution rates.

Because of the inherent problems associated with rebar corrosion resulting from the ingress of Cl⁻ ions into concrete, the use of other methods to protect is very important (Uhlig et al. 1985; Lemoine et al. 1990). The most common method consists of coating the rebar with fusion-bonded epoxy coatings, although twice as expensive as uncoated black bars. Coated rebars have shown some corrosion resistance but tend to fail prematurely, especially in subtropical marine environments such as the Florida Keys (Callaghan 1993). Other disadvantages are that they can be easily scratched during handling and can debond once in use. In some cases galvanized coatings are used. Galvanized bars show good corrosion resistance, but their zinc coating gradually corrodes as a result of its action as a sacrificial anode. When the zinc has been sacrificed, the rebar behaves like black rebar. Thus, in the long term, galvanized bars may have only a limited advantage over simple black bars.

In search for a better solution, researchers have explored the possibility of imparting better corrosion resistance properties to the steel by alloying it with protective elements. It is well known that adding Si to metals and alloys, including steel, generally increases their corrosion, oxidation, and erosion resistance (Sanjurjo et al. 1993). In this study, the experimental results obtained on steel rebars with coatings of Si-based particles are described. We chose to use Si-based coatings because of their proven capacity for corrosion protection in Cl⁻ environments. Some advantages of this approach include simplicity of application, low cost, strong adhesion, and chemical compatibility of the coating with concrete because of its natural oxidation to silicon oxide (SiO₂). Because of this compatibility, we expect high bond strength between the coated rebars and the con-

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concrete matrix. Therefore, our main objective is to coat rebar with corrosion-resistant Si-based material to significantly lengthen the lifetime of steel-reinforced structures without any detrimental effects on the steels structural properties.

In addition, a secondary objective of this study was to explore impedance spectroscopy (IS) as an alternate technique for determining the corrosion activity of coated steel rebars (Macdonald 1987; Christensen et al. 1994). More precisely, IS was used to monitor and characterize the corrosion susceptibility of the system as a whole, for prediction and prevention of deterioration. The goal of this research was to characterize the impedance response of several coatings on steel rebar, and in so doing, improve our understanding of the corrosion susceptibility of these systems, as they relate to the durability of reinforced concrete structures.

2. Impedance spectroscopy

Impedance spectroscopy is an electrochemical measurement technique, which measures the response of a system to an applied alternating signal (Scuderi et al. 1991; Maccarter et al. 1988; Ford et al. 1998). All materials, to varying degrees, have the ability to pass current. Ohm’s law provides the relationship between the applied voltage, \( V \), and measured current, \( I \), as:

\[
V = IR
\]  

(1)

where \( R \) is the ratio of these two parameters, defined as the resistance of the material. This equation holds for application of dc fields. When an ac field is applied, however, this relationship becomes:

\[
V = I(t) \cdot Z(\omega)
\]  

(2)

where \( V(t) \) is the time-varying voltage, \( I(t) \) is the time-varying current, and \( Z(\omega) \) is the constant of proportionality, defined as the frequency dependent impedance.

The frequency dependent impedance is a complex function, having both real and imaginary components, as the ratio of the voltage and current (time-varying function) has both magnitude and phase angle components (Gu et al. 1992; Brantervik et al. 1991). The real part of the impedance, \( Z_r \), provides information on the resistance of the materials, just like in the case of dc fields. The imaginary component provides us information about the system’s ability not only to pass but also to store charge. This information is not available from dc measurements, and relates to the capacitance or inductance of the material. It is common to plot the impedance in the complex plane as imaginary (\( Z_i \)) versus real (\( Z_r \)) (so-called “Nyquist” plot). The impedance spectra of steel embedded in concrete typically exhibit two distinct features over 10 orders of magnitude in frequency, from 10 mHz to 10 MHz. A high frequency response in the MHz to kHz range, denoted as the HFA (High Frequency Arc), is attributed to the electrical resistance of the cementitious matrix. A low frequency response extending well into the mHz range and below, denoted as the LFA (Low Frequency Arc), is associated with the passive film that forms on the surface of the steel in highly alkaline environments. In special cases, an intermediate frequency arc (IFA) can be observed, but is most often strongly convoluted with the LFA.

Impedance spectroscopy was chosen because it has many advantages as compared with traditional dc techniques. One such benefit is its ability to monitor the entire system, including both the bulk and interfacial responses. Therefore, predictions of corrosion susceptibility are based not only on the state of the interface, but also on the quality of the protective cover. Although the interpretation of impedance data for a given system may be difficult, the technique provides much more information than traditional dc technique, assuming the data is processed and interpreted correctly. An additional challenge in making corrosion measurements in any system is that, even under the best conditions in the field, the corrosion behavior can change from hour to hour due to variation in moisture, temperature, and chloride contents. Therefore, a quick in-situ measurement technique is also desirable. Impedance spectroscopy has these qualities, with a typical measurement taking as little as five minutes (down to 10mHz) or 30 minutes (down to 1mHz).

3. Experimental procedures

3.1 Materials

Dowel steel bars having ¼” diameter were used for investigation. One of the main experimental procedures was to provide a dual coating system for the dowels. The first coating is a thin, continuous metal layer on the steel dowels to mitigate corrosion. The metal layer is thin and metallurgically bonded to the dowel. The reactive layer, when cured in the cement paste, can be denser and stronger than the cured cement paste surrounding it, and can strengthen the concrete bond to the dowels. In this study, five reactive coating materials were used as shown in Fig. 1 and Table 1. These materials are known for a certain reactivity in a highly alkaline environment such as that encountered in fresh cement paste. Thermal spray technology was used to apply the metal and coatings for all the samples.

3.2 Impact test setup

Damage was induced by impact test. The impact test was carried out according to ASTM B 571-97 “Standard Practice for Qualitative Adhesion Testing of Metallic Coatings”. This test is performed to introduce impact damage to only one side of rebar (Fig. 2). By using a pendulum as a falling weight with adjustable height a single flaw is introduced. The pendulum is about 950g. The length between the fulcrum and the impact point is 40 cm and it was dropped from 50 cm. A rippled rebar is used as the impactor. Both the damaged side and the
undamaged side were tested by impedance spectroscopy (IS).

### 3.2 Bending test setup

Bending tests were carried out to simulate the flexure of rebar when lifted by crane. Four point bending was adopted for the tests (Fig. 3). The applied stress (7.9 MPa) was limited to the elastic regime of the rebar when loaded. Both the compressive side and the tensile side were tested by IS.

### 3.3 Test program

The test program was divided into two stages as shown below. In the first stage, the dowels were immersed in simulated pore solution in a plastic tank. Following that, NaCl of 3.5% by total weight of solution was added to the tank. Testing sessions were accomplished every 7 days.

- **Stage I (Simulated concrete condition)**
  - Storage of rebars in simulated pore solution (pH13.5, 4g NaOH/l + 9.8g KOH/l)
  - IS testing @ 7, 14 days

- **Stage II (Simulated corrosive condition)**
  - Storage of rebars in simulated pore solution + chlorides (3.5% NaCl by weight)
  - IS testing @ 7, 14, 28 days

In an effort to standardize testing conditions, each dowel was removed from its storage tank and placed in a testing tank with a copper mesh at the bottom to act as the counter electrode (Fig. 4). Each dowel was placed horizontally in the testing tank such that its lower half was immersed in the pore solution. Care was taken not to excessively damage the coatings by friction between the rubber stoppers and the dowels when removing them from their storage tanks. Both the copper mesh and the dowel were connected to an impedance analyzer and the data (frequency, amplitude, and phase angle) were collected on a PC. These were converted to real and imaginary impedances by standard formula.
3.4 Simulated pore solution

In most cases, unless specified otherwise, simulated pore solutions were made to simulate the pore solution of OPC paste of w/c=0.5 at 100 hours. The main constituents of the pore solution for this system are sodium, potassium, and hydroxide ions. These levels change dramatically during the initial stages of hydration, but remain relatively stable at longer hydration times. For various experiments, synthetic pore solution was used to simulate the highly alkaline environment of cement pastes without disruption from the bulk cement paste microstructure. The ionic composition of these solutions, modeled after Christensen’s work, were 100 mM NaOH, and 175 mM KOH, with a pH of 13.5, similar to that of the aqueous phase of OPC pastes (Ford 1998). Minor constituents, such as sulfur, silicon, calcium, and aluminum ions were ignored for this study because of their low concentration in pore solution at these hydration times (µM). They are, however, more prevalent at early times, and their effect may not be completely negligible.

3.5 Experimental set-up of the frequency response analyzer

Impedance measurements were made with a Frequency Response Analyzer (Solartron Instruments, Hampshire, UK) and the data collection software. Depending on the frequency range used, different electrochemical features of the dowel can be highlighted. In this study, frequency varies from 10mHz to 10kHz and voltage amplitude was 25 mV. Alligator clips and coaxial cables were used to make electrical connection to the specimens, and the cables were kept as short as experimentally possible to reduce immitance effects from the leads (< 10 cm). The number of data plots was 50. Error in individual IS measurements was estimated at ±5%.

4. Results and discussion

4.1 IS and corrosion of a metal

(1) Anticipated impedance response

Figure 5 shows a schematic of the response anticipated for an oxide coating on rebar. All such Nyquist plots in this paper will show the capacitive quadrant, i.e., negative imaginary vs. positive real impedance. In the present work the solution resistance (Rsol in Fig. 5) is negligibly small. Whereas two arcs (one bulk and one oxide/interface) are obtained with rebar in cement/concrete, we only observed a single arc with a barely perceptible offset resistance, corresponding to Rsol in Fig. 6-15. This is unimportant, however, since the primary focus of research was on the oxide coating and its changes with damage, preloading, corrosion, etc. As can be seen in Fig. 6-15, only a portion of the high frequency arc was obtained over the frequencies investigated. Lower frequency data (the dashed portion of the arc in Fig. 5) could be obtained at frequencies below 1 mHz, but such experiments are prohibitively long and unreliable (owing to stability issues). It should also be noted that the response of Fig. 5 is idealized; typical spectra show significant arc depression associated with non-uniform surfaces and properties. Nevertheless, general comparisons are possible between coatings, between treatments (damaged vs. undamaged), etc.

(2) Impedance spectroscopy: coatings vs plain

Figure 6 shows the impedance behavior for an uncoated plain rebar in pore solution vs. the 28-day behavior after addition of the chlorides to the solution. Note that the impedance of the plain (but uncorroded) rebar is significantly smaller than for all the coated rebar specimens in Fig. 7-15. This indicates that all of the coatings employed act in such a manner as to increase the coating/interfacial impedance. The 28-day chloride solution behavior shows how sensitive IS can be to the onset of active corrosion.

4.2 Results of impact tests

In every instance, the coating resistance (Rc, approximately the arc diameter) increased with immersion time in the simulated pore solution (not shown). The Nyquist plots in Fig. 7-11 show the evolution of data for each of the dowels upon immersion in the corrosive NaCl solu-
not all the Nyquist plots are presented here because of the considerable number of measurements done. Frequency values increase from right to left along each arc. The overall electrode resistance, which is a real impedance value on the horizontal axis, would be the diameter of the resulting semicircle if the arc were extrapolated towards the right hand side of the plot.

(1) Result of coating #1 (fused coating, reactive coating of Si powder)

Figure 7 shows the test result for the damaged side of the rebar. A large increase in the impedance was obtained for coated samples #1 after 7 days and 14 days of exposure in corrosive solution. The impedance values are higher with exposure time in the corrosive solution, which suggests additional formation of protective coating. There was a detectable decrease in coating impedance from 14 days to 28 days, however the value remained higher than when initially submerged in the corrosive solution.

(2) Result of Coating #2 (fused coating, reactive coating of Cabosil SiO2)

Both damaged and undamaged sides of the specimen coated with coating #2 failed after 14 and 28 days of immersion in corrosive solution, as indicated by the lower resistance values (Fig. 8). A strong decrease was observed in the resistance values of the damaged side of the specimen with coating #2 after 14 days of immersion in the corrosive solution. Visual observations indicated extensive corrosion with localized pitting areas where rust products formed.

(3) Result of Coating #3 (fused coating, reactive coating of 10% Si powder + 90% slag)

A decrease was observed in the resistance values of both sides of the specimen coated with coating #3 after 28 days of immersion (Fig. 9). The resistance of the damaged side of coating #3 undergoes a dramatic decrease after 28 days of immersion with resistance values being almost equivalent to the bare steel. At the end of 28 days of immersion the corrosion progress is already defined with the resistance values being much lower. From this
figure, it is also observed that the resistance value of the
damaged side of the specimen is much smaller than of
the undamaged side of the specimen. This indicates that
damaged coated rebar is more vulnerable to the corrosive
solution than sound coated rebar.

(4) Result of Coating #4 (fused coating, reactive
coeating of 4% Si powder + 90% slag + 6% Cabosil)
Both damaged and undamaged sides of the specimen
coated with coatings #4 failed after 28 days of immersion
in corrosive solution as indicated by the lower re-
sistance values (Fig. 10). In the spectra taken from both
side of the specimen after 28 days of immersion in cor-
rrosive solution, a decrease in the impedance is very
clear. Visual observations indicated extensive corrosion
with localized pitting areas where rust products formed.

(5) Result of Coating #5 (fused coating, reactive
coeating of 10% Cabosil SiO2 powder + 90% slag)
The damaged side of the specimen coated with coating
#5 measured after 7 days of immersion in the corrosive
solution shows a moderate increase of coating resistance
(Fig. 11). The slight change after 28 days of immersion
may not statistically significant. The results from the
undamaged side of the rebar (not shown) were virtually
identical.

(6) Comparison of coatings #1-#5
Figure 12 shows the rate of impedance change for
coatings #1-#5 with age. The rate of impedance change
was defined as the ratio of the imaginary impedance
value (Zi(t)) with respect to the initial imaginary im-
pedance value (Zi(t=0)) at a frequency of 50 mHz. Note
that coatings #1 and #5 exhibit increases with time. This
indicates that these two coatings employed act in such a
manner as to increase the coating/interfacial impedance.
However, coatings #2, #3 and #4 exhibit decreases in
coating impedance with time, corresponding to the de-
tection of corrosion in the chloride containing solution.

4.3 Results of bending tests
The final three plots (Fig. 13-15) of impedance changes
vs. time in the corrosive solution are for coated rebars
after bending tests. In no case did we observe significant
differences in behavior between the tensile and com-
pressive sides of the rebars, e.g., in Fig. 13 for coating
#1. Otherwise, the trends outlined in Fig. 12 were ob-
served. For example, the rebar with coating #1 exhibited
significant increases in coating resistance with time in the
corrosive solution, in good agreement with the im-
pact results of Fig. 7. This suggests the additional for-
mation of protective coating. On the other hand, the
rebar with coating #2 exhibited significant decreases in
coating resistance with time in the corrosive solution
(Fig. 14), in agreement with the impact results of Fig. 8.
It would appear that active corrosion takes place with this
coating, even in the absence of obvious damage.
Finally, the rebar with coating #5 exhibits moderate

![Fig. 12](image1)
![Fig. 13](image2)
![Fig. 14](image3)
![Fig. 15](image4)
increases in coating resistance with time in the corrosive solution (Fig. 15), in agreement with the impact results in Fig. 11. The overall trends with time (not shown) are quite similar to those shown in Fig. 12.

5. Final considerations

Based upon impedance changes and the absence of visible corrosion products, it appears that coated rebars #1 (Silicon powder) and #5 (Cabosil SiO₂ powder + slag) have the best performance in 3.5% NaCl solution after 28 days. Rebars coated with #2 (Cabosil SiO₂) and #3 (Silicon powder + slag) sustain active corrosion, signaled by significant decreases in coating resistance as registered by impedance spectroscopy. Although impedance spectroscopy could not detect any influence of loading (tensile or compressive) on the behavior of these coatings, there were noticeable drops in coating impedance on the damaged vs. undamaged sides of bars subjected to impact tests. This work suggests that impedance spectroscopy may be useful for monitoring corrosion activity on coated rebar.

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