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Current Progress in Corrosion Inhibition of Reinforcing Steel in Concrete using Migrating Corrosion Inhibitors

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ABSTRACT

Several migrating corrosion inhibitors for reinforced concrete were investigated using ASTM G109 and Modified G109. XPS depth profiling showed a 90-100 nm amine-rich layer and chloride ions on the steel rebar surfaces indicating that the modified corrosion inhibitor molecules had suppressed chloride ion interaction and protected the steel rebar passivation layer. There is no indication of corrosion after 400 days of testing. The inhibitor treated samples showed improved resistance polarization (Rp was in the 50 kohm to 60 kohm range, corrosion potentials ranged between -64 mV and -103 mV) and potentiostatic tests showed a significantly lowered corrosion rate. These findings led to investigating the adsorption mechanism where comprehensive testing established a Langmuir adsorption isotherm and verified that chemisorption was responsible for the strong bonding between the inhibitor monolayer and the steel surface.

Keywords: reinforced concrete, migrating corrosion inhibitors, steel corrosion, XPS, adsorption mechanism

INTRODUCTION

The US infrastructure is heavily reliant upon construction materials that are vulnerable to corrosion. Conventional materials like reinforced concrete, prestressed concrete and steel that are used in bridges, highways and building foundations. Reinforcing steel embedded in concrete, however, shows a high amount of resistance to corrosion. Concrete is a highly alkaline material with a pH near 12 that

provides a protective oxide layer for steel when embedded. Under corrosive conditions where oxygen and moisture can ingress through the pores of the concrete to reach the rebar surface, the alkalinity can change and cause the passive layer to breakdown. Carbonation of the concrete, where carbon dioxide reacts with calcium hydroxide or other cement hydrates, and ingress of chlorides are major causes of steel rebar corrosion in concrete. In the case of reinforced concrete samples placed in contact with a 3% NaCl solution, the stages for rebar corrosion deterioration would begin with chloride penetration into the concrete, then corrosion initiation or passive layer breakdown, more progressed corrosion, micro cracking and eventual spalling. Corrosion is a complex phenomenon with many interactions to consider (structural, physical, chemical and environmental considerations), for steel in rebar, as the passive film degrades by chloride ions or the pH drops due to carbonation, the metallic iron at the anode is oxidized to form ferrous ions. It is this simplified reaction that has to be prevented or at least mitigated. Much effort has been focused on the design of new structures to reduce or eliminate corrosion through increased concrete coverage using reduced permeability concrete, admixtures, migrating corrosion inhibitors and replacing the steel reinforcement with alternative materials.

The commercially available migrating corrosion inhibitors used to surface impregnate the concrete samples in this investigation are based on amino carboxylate chemistry [1]. They are designed to provide both anodic and cathodic protection with transport to the rebar surface in roughly 100 days. Transport begins through the concrete pores and proceeds through the capillary structure by liquid diffusion, high vapor pressure and by following microcracks to the rebar surface. At the rebar surface, the inhibitor forms a monomolecular layer of protection against corrosive species [2]. To better understand how the inhibitor works or by what mechanism it is able to adsorb to the surface, a surface adsorption isotherm has to be determined. Many models for adsorption isotherms have been defined (Temkin, Freundlich, Langmuir and Frumkin) and each explains a different relationship between concentration and inhibitor surface coverage on a metal or alloy surface [3, 4]. By measuring the corrosion current density of the non-inhibited solution (Blank) and inhibited solution (or by measuring polarization resistance), the surface coverage, θ, can be calculated from the following formula:

$$\theta = \frac{Icorr(B) - Icorr(I)}{Icorr(B)} \quad \text{or} \quad \theta = \frac{Rp(I) - Rp(B)}{Rp(I)}$$

Where Icorr (B) and Rp (B) are the corrosion current density and polarization resistance of the Blank solution, respectively, while Icorr (I) and Rp (I) are the corrosion current density and polarization resistance of the inhibited solution. Based on the adsorption isotherm, the adsorption equilibrium constant, K_{ad}, can be calculated; for the Langmuir isotherm: $K_{ad}C = (\frac{\theta}{1-\theta})$. This can then be used to calculate the free standard energy of adsorption, $\Delta G_{ad} = -RT \text{ Ln } (K_{ad})$. By repeating the experiment at different temperatures, the enthalpy of adsorption, ΔH_{ad}, can be calculated from Ln C = $(\Delta H_{ad}^{0}/RT)$ + constant. Chemisorption (chemical adsorption) makes strong covalent bonding between the chemical and the surface, so the ΔG_{ad} is usually much higher than for physisorption (physical adsorption) that involves van der Waals interaction. The criterion for chemisorption varies, it can require as little as -40 kJ/mol energy or as much as -100 kJ/mol energy [4-5]; physisorption requires energy between -5 to -25 kJ/mol [4]. The activation energy (ΔH_a) of corrosion is calculated using an Arrhenius type relationship where [5],

$$Icorr \propto \exp(\frac{-\Delta Ha}{RT})$$

The slope of this graph will represent $-\Delta H_a /R$ where R is the gas constant.

EXPERIMENTAL PROCEDURES

The ASTM G 109-92 test structure provides a less aggressive corrosion environment compared with protocols for samples that were partially immersed in a 3.5% NaCl solution for the entire experiment. In the test method described in G 109, Plexiglas dams hold the 3.0% NaCl solution in contact with the surface of the concrete for two week periods and are then set to dry for 2 weeks with this cycle repeating for the duration of the experiment. As seen in Figure 1, three steel rebar were cast in concrete (density of 142 lbs/cu ft) with 1 inch coverage from the top and bottom rebar; concrete dimensions were 3 inches width x 6 inches height, Plexiglas dams were 3 inches x 3 inches. Two concrete samples were coated with Cortec's MCI 2020M inhibitor (inhibitor 1) and MCI 2022 sealer; roughly 15 mL of inhibitor was absorbed into the concrete for 2 coats. Two concrete samples were coated with MCI 2022 inhibitor (inhibitor 2) and sealer. All inhibitor and sealer were painted on with a brush. The remaining 2 samples were untreated (references). Several days after the inhibitor and sealer were applied, the Plexiglas dams were fixed to the top of the concrete beams with silicone.

The rebar potential, polarization resistance and current density data can provide information as to whether the rebar is in the active or passive corrosion state. Estimates made from these parameters for Tafel constants can be input into LPR analysis or can be used for corrosion rate measurement and cathodic protection criteria. Evaluation of the effectiveness of corrosion inhibitors and the effects of concrete composition is often based on these variables. For a more comprehensive approach to the corrosion process, several tests methods were implemented in this investigation. These studies were conducted using an EG&G Potentiostat/Galvanostat (Model 273A with a 5210 Lock-in amplifier), EG&G M398 Electrochemical Impedance Software and a Gamry PC4/750™ Potentiostat/Galvanostat/ZRA using electrochemical impedance spectroscopy EIS300™ systems. The steel rebar/concrete combination can be treated as a porous solution and was modeled by a modified Randles electrical circuit. EIS tests performed on a circuit containing a capacitor and two resistors indicate that this model is an accurate representation of an actual corroding specimen. EIS testing was done by applying a small amplitude-alternating potential signal of varying frequency to the concrete/rebar system, providing fundamental electrochemical parameters. A standard CuCuSO4 reference electrode was used with a steel rebar counter electrode in a 3-electrode configuration with a steel working electrode.

In previous investigations using XPS depth profiling, it was determined that a 90-100 nm amine rich layer and chloride ions were present at the surface of the steel rebar. The XPS results demonstrated that both inhibitor and corrosive species had migrated in through the concrete capillary system, but the inhibitor had managed to coat the surface and neutralize the corrosive species (chloride ions and carbon dioxide) to protect the steel rebar [2]. This information led to investigating the mechanism by which adsorption occurs. To collect data for adsorption isotherms, flat samples were polished (600 grit sandpaper), placed in a flat cell and tested in solutions containing tap water and 3.5% NaCl with varying inhibitor concentration. The Rp value (determined from the EIS Bode plots) was used to fit the data into an adsorption isotherm model. To correlate the corrosion rate with the inhibitor concentration, a series of

linear polarization resistance (LPR) tests were conducted using Gamry's DC105 software and a blank solution (no inhibitor) with 0.5% NaCl; inhibitor concentration was increased by 200 ppm for each subsequent test. To explore the activation energy and adsorption thermodynamics for the inhibitor, cyclic polarization was conducted in temperatures ranging from 23°C to 63°C.

RESULTS & DISCUSSION

Previous experiments (conducted on commercially available corrosion inhibitors) have shown noticeable differences in the treated and untreated samples around 250 days of constant immersion [2, 6-8]. In Figure 2, corrosion potentials vs time are graphed for comparison; this was a constant immersion test. Inhibitor 1 was applied to the surface, mixed in the mortar and directly applied to the rebar before casting (concrete density: 140 lbs/ft^3). The graph also shows untreated concrete samples and samples surface treated with other inhibitors (concrete density for L=130 lbs/ft^3) [2]. Corrosion potentials for an untreated low density concrete sample measured 150 mV more negative than the other samples. The concrete sample was cracked open to physically verify that the rebar was corroding. Figure 3 shows a comparison of the corrosion potential versus time with little variation over the course of a year. The steel rebar appears to have formed a passive layer around day 150 and remained stable in the range of -40mV to 135 mV. Figure 4 shows Rp values versus time obtained by curve fitting the bode plots (Figure 5). The Rp values measured approximately 10000 ohms at the beginning of testing and increased to a range between 50000 to 60000 ohms by day 400. EIS bode plots for treated and untreated concrete are from initial tests and plots from data collected between day 371 and 400.

The potentiostatic tests (Figure 6) contrast the dramatic reduction in current density with increasing inhibitor concentration. The corrosion current density for the blank solution was 10.5 μA and decreased to 0.45 μA with 2000 ppm inhibitor; at saturation level (about 2000 ppm), the corrosion rate remained steady. From the corrosion current for the given concentrations, different adsorption isotherms were constructed to find the best fit for the data. Models were constructed based on surface adsorption which is a function of the corrosion current and the concentration of the solution. Table 1 contains the data obtained from linear polarization resistance. The EIS results showed that adsorption of inhibitor 1 on to the steel surface fits with the Langmuir adsorption isotherm [3, 4] since Ln C and Ln θ-Ln (1-θ) have a linear relation as is shown in (Figure 7). The extent of surface coverage is expressed as the fractional coverage, θ, or the ratio of adsorption sites occupied over the number of adsorption sites available. The changes in enthalpy of adsorption (ΔH_{ad}) and free standard energy of adsorption (ΔG_{ad}) were obtained with adsorption isotherms and elevated temperature tests [3]. Based on results from cyclic polarization, Ln I_{corr} vs. 1000/T °K was plotted (Figure 8); the slope of each line represents ($-\Delta H_{ad}$ /R). Figure 8 contains the data that was used to calculate the activation energy required to corrode the steel with inhibitor (-46 kj/mol) and without (-30 kj/mol). The value calculated for the inhibitor would indicate that the adsorption mechanism is achieved by chemically bonding to the surface.

CONCLUSIONS

Surface treated concrete samples with migrating corrosion inhibitors have been subjected to the ASTM G 109 corrosion test for more than 400 days to confirm effectiveness. Corrosion potentials ranged between -64 and -103 $mV_{(Cu/CuSO4)}$; polarization resistance values measured between 50 kohm and 60 kohm. Potentiostatic tests showed a significantly reduced corrosion rate for steel rebar in the presence of inhibitor. From the LPR and EIS analysis and adsorption isotherms, it was determined that adsorption of inhibitor molecules to the steel surface most closely fit with Langmuir adsorption and was controlled by a chemisorption mechanism.

ACKNOWLEDGEMENT

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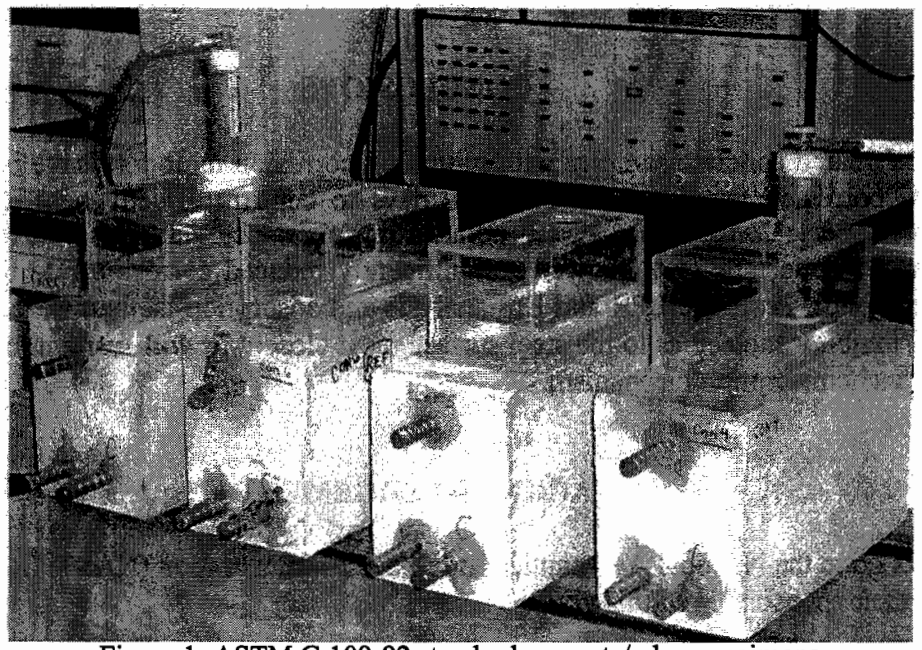

Figure 1: ASTM G 109-92 standard concrete/rebar specimens.

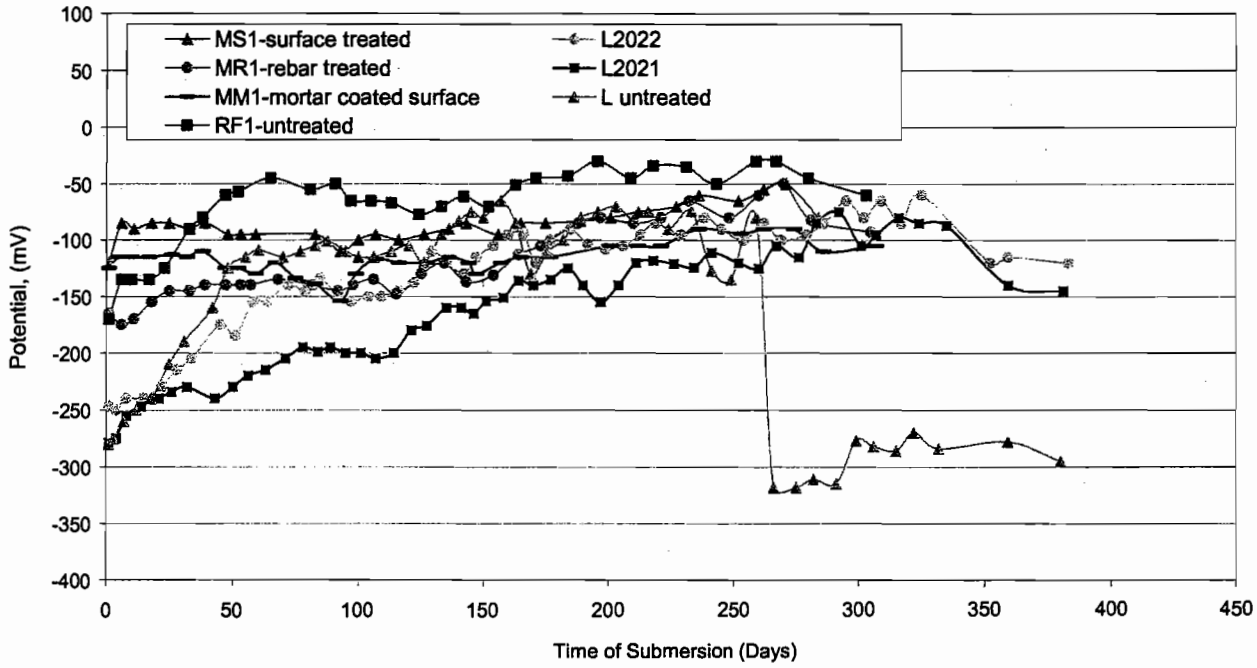

Figure 2: Corrosion Potential vs Time for inhibitors that were applied to the surface, mixed in the mortar and directly applied to the rebar before casting (Concrete density: 140 lbs/ft^3); the graph also compares untreated samples with untreated concrete (L =130 lbs/ft^3) [2].

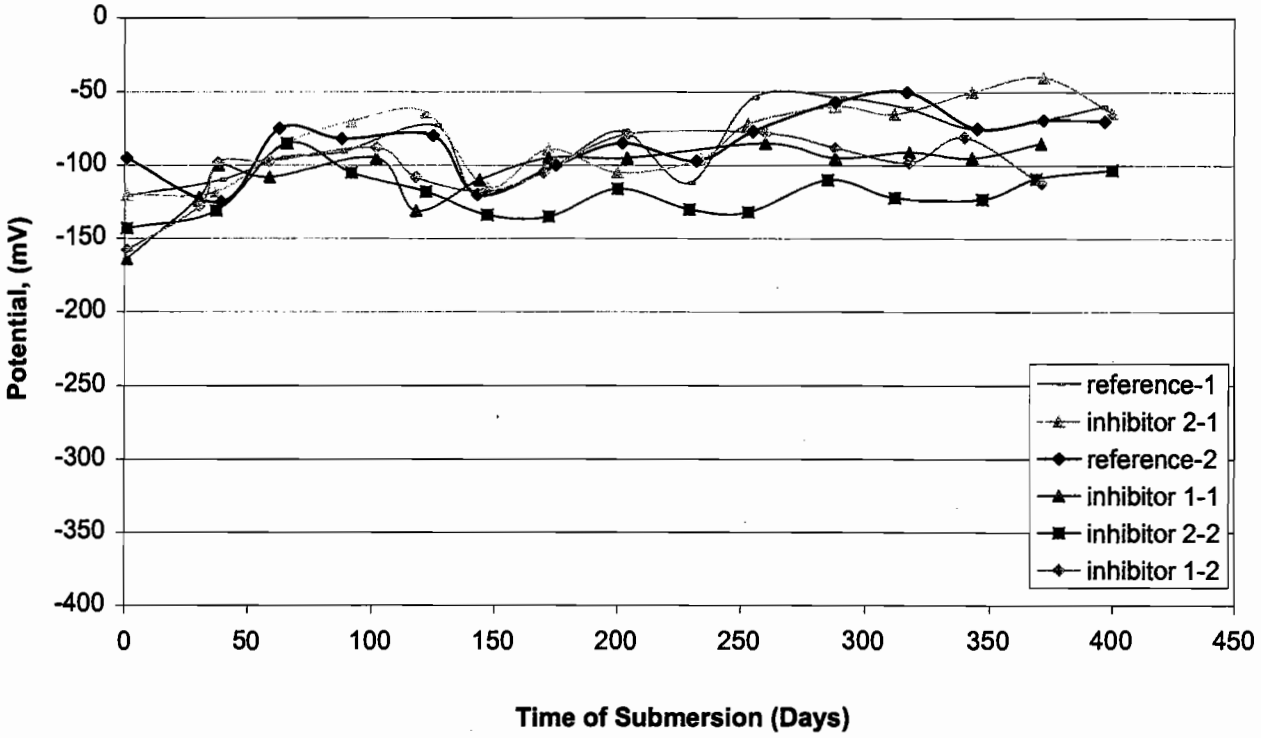

Figure 3: Comparison of corrosion potentials for inhibitor treated and untreated concrete samples per ASTM standard G 109.

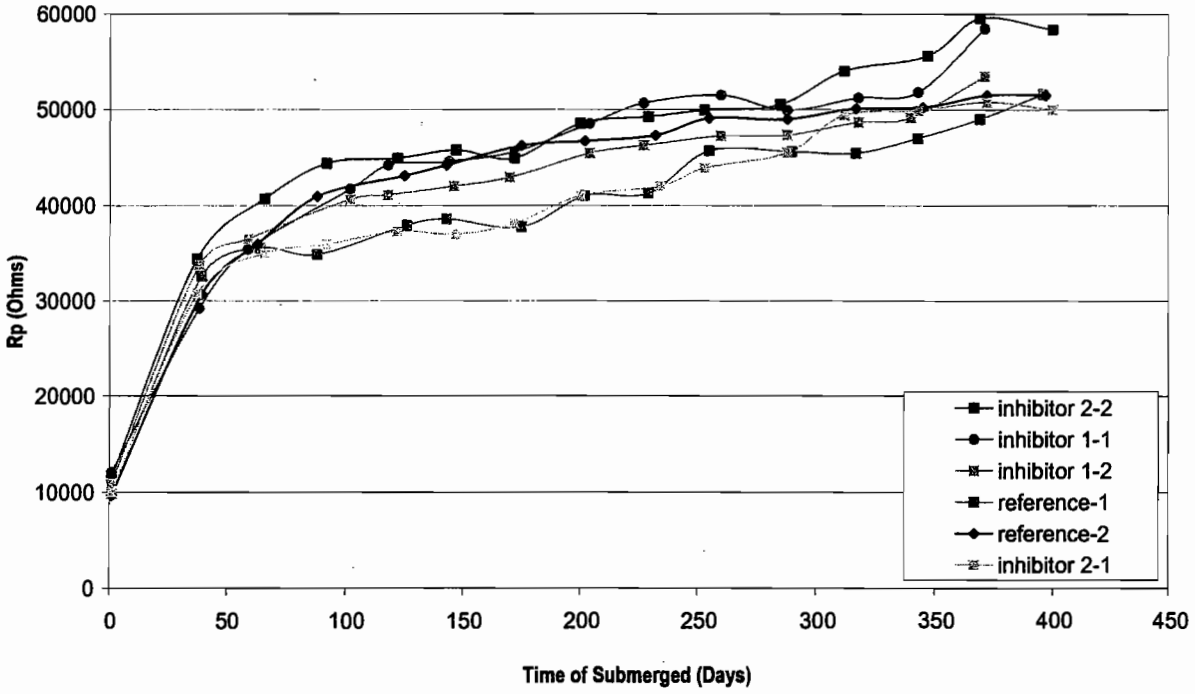

Figure 4: Comparison of polarization resistance (Rp) for treated concrete with untreated concrete per ASTM G 109.

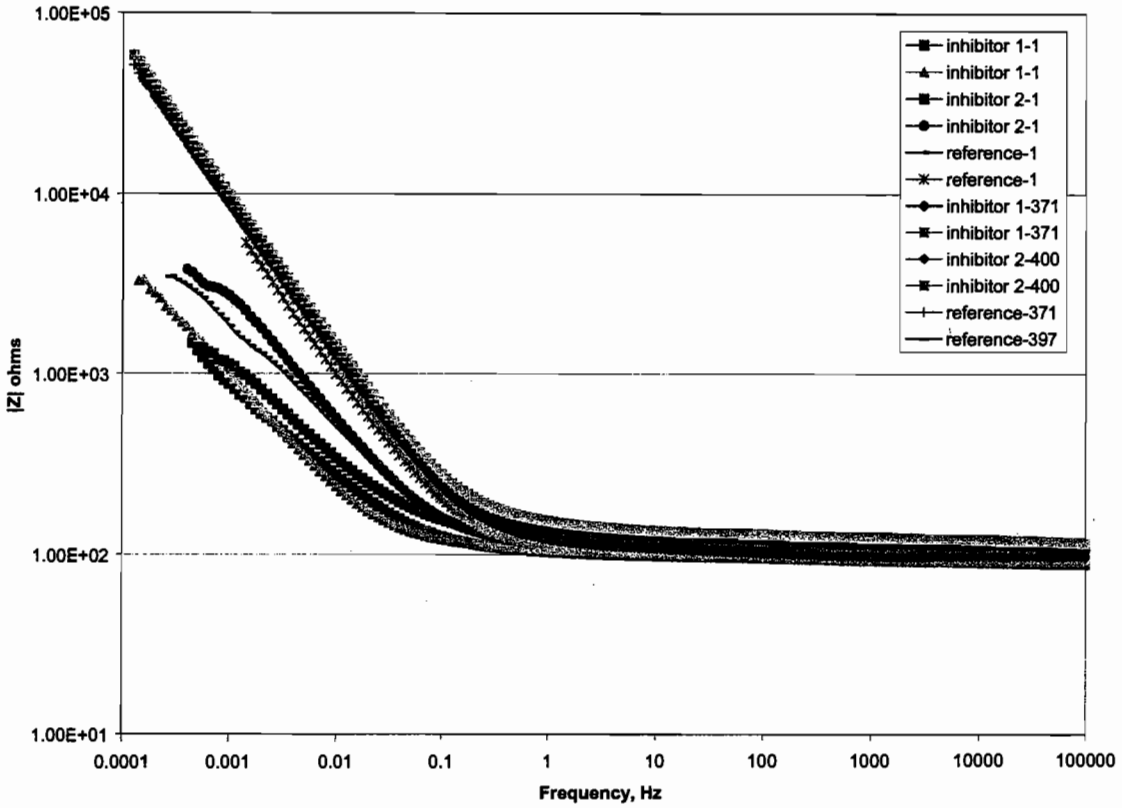

Figure 5: EIS bode plots for treated and untreated concrete from initial tests and plots from data collected between day 371 and 400.

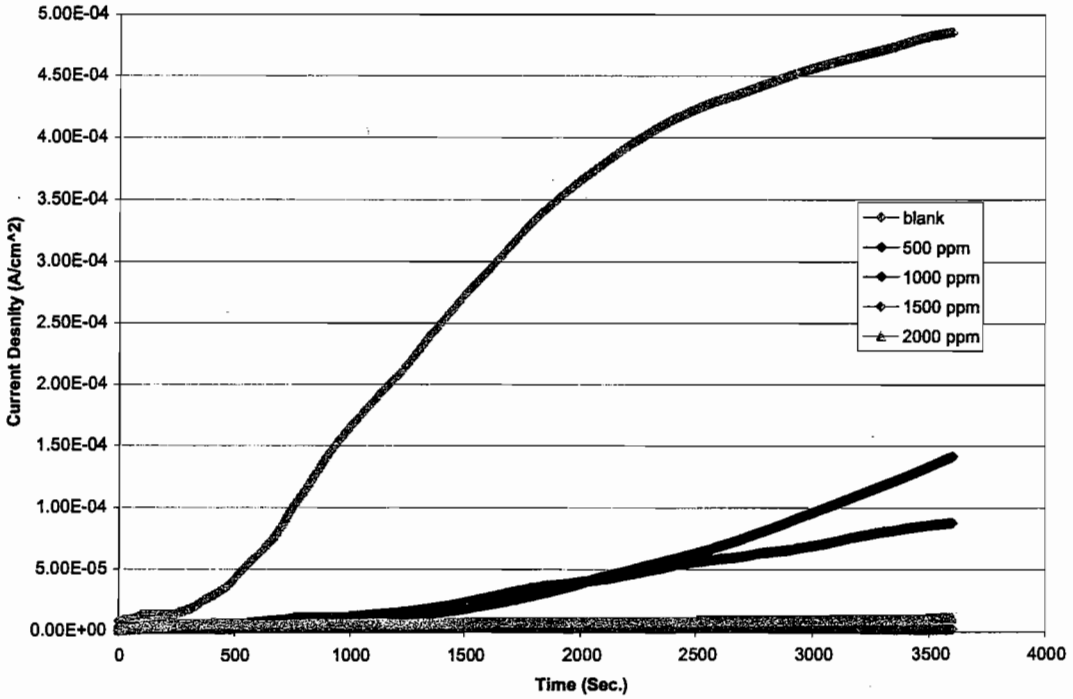

Figure 6: Potentiostatic tests demonstrate a dramatic decrease in current density with higher concentration of inhibitor. Samples were polarized to +20 mV over the open circuit potential.

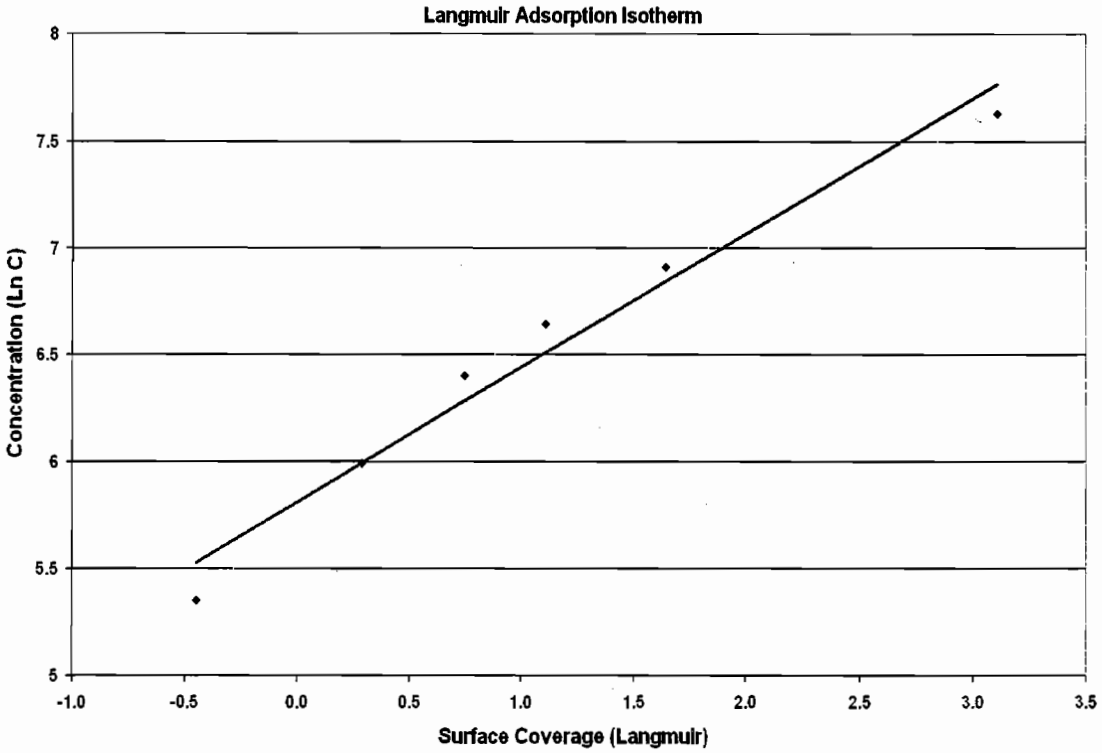

Figure 7: Langmuir adsorption isotherm for different migrating corrosion inhibitor concentrations.

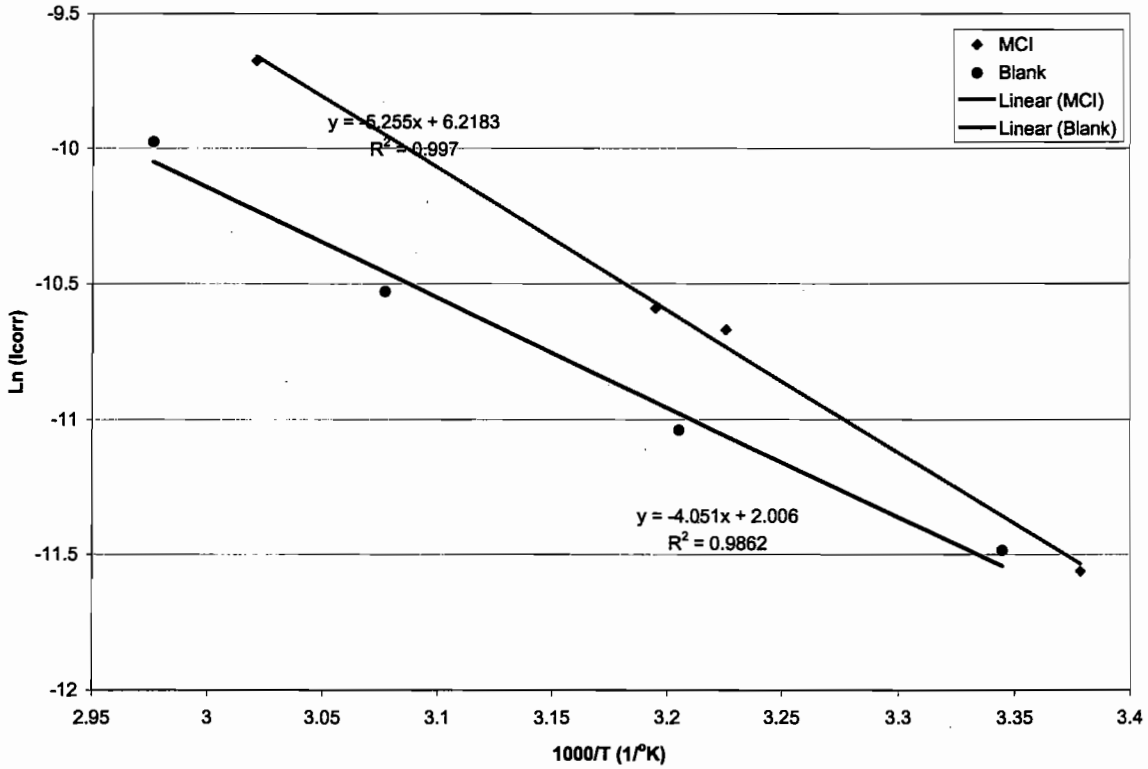

Figure 8: Activation energy calculations for corrosion reactions of steel with and without inhibitor at various temperatures.

Concentration (ppm)	Icorr (μA)	θ	1-θ	Ln θ	Ln (1-θ)	Ln θ-Ln (1-θ)
0	10.5	0	1			
200	6.32	0.398	0.602	-0.921	-0.508	-0.413
400	4.5	0.571	0.429	-0.560	-0.847	0.288
600	3.7	0.648	0.352	-0.434	-1.043	0.609
800	2.6	0.752	0.248	-0.285	-1.396	1.111
1000	1.7	0.838	0.162	-0.177	-1.821	1.644
2000	0.45	0.957	0.043	-0.044	-3.150	3.106

Table 1: LPR test results for given concentrations of inhibitor 1.