

A Study of Corrosion Control of Mild Steel using Inhibitors under Atmospheric Conditions

by

Abdul Aziz A. Al-Mathami

A Thesis Presented to the

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DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

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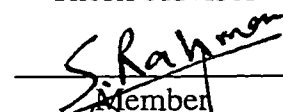
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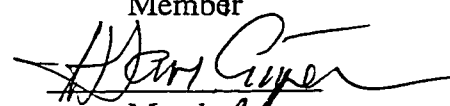
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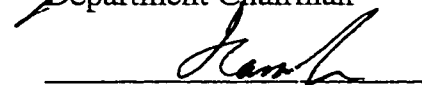
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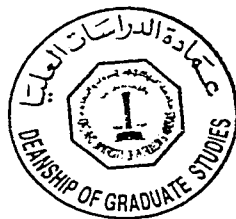
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ABSTRACT

FULL NAME OF STUDENT: ABDUL AZIZ ABDUL RAHMAN AL-MATHAMI
TITLE OF STUDY: A STUDY OF CORROSION CONTROL OF MILD
STEEL USING INHIBITORS UNDER
ATMOSPHERIC CONDITIONS
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The purpose of this study was to search for and evaluate the effectiveness of various inhibitors to slow down or prevent atmospheric corrosion/discoloration of the local mild steel during storage in the Arabian Gulf region. Various inhibitors were reported in the literature that can help in protection against atmospheric corrosion. Among them sodium phosphate, sodium benzoate, sodium nitrite and sodium nitrate were obtained from the local market and first tested on a simulated aqueous solution for the purpose of initial screening. In light of the results obtained, sodium phosphate and sodium benzoate were selected for examination against atmospheric corrosion of steel to be applied at 10 and 100 mM concentrations for 1 day at room temperature. Test specimens were prepared from locally produced reinforcing steel products. Exposure racks were constructed from wood to hold specimens during atmospheric exposure for different periods. Corrosion was evaluated through weight loss determination, electrochemical technique and morphological analysis of corrosion specimens using photograph and scanning electron microscopy (SEM). Atmospheric corrosion inhibition performance of sodium phosphate was better and long lasting than of sodium benzoate. Atmospheric corrosion rates of sodium phosphate treated specimens stayed low even after 6 months of exposure. Atmospheric corrosion inhibition performance of sodium benzoate, on the other hand, was inferior to that of sodium phosphate and, moreover, deteriorated faster with atmospheric exposure time losing its inhibition effectiveness totally at the end of 3 months of atmospheric exposure.

ملخص الرسالة

الاسم : عبد العزيز عبد الرحمن المتحمي

عنوان الرسالة : دراسة حول كبح تآكل الحديد الطل "القابل للطرق أو المطاوع" بواسطة المثبطات في ظروف الجو العادية .

التخصص : هندسة كيميائية

تاريخ التخرج : يناير / ٢٠٠١ م

كان الغرض من هذه الدراسة البحث وتقييم مدى فعالية المثبطات المختلفة لتقليل أو منع تآكل أو تغير لون الحديد المطاوع المنتج محلياً أثناء التخزين في الظروف الجوية لمنطقة الخليج .

هنالك عدة مثبطات مذكورة في المراجع ويمكن لها أن تساعد في حماية الحديد في ظروف الجو العادية ، من ضمنها فوسفات الصوديوم، بترويت الصوديوم، نيترايت الصوديوم ونترات الصوديوم التي أمكن الحصول عليها محلياً . لقد اختبرت هذه المواد أولاً في محاليل مائية بغرض الاختيار الأول وعلى ضوء النتائج المتحصّل عليها تم اختيار فوسفات الصوديوم وبترويت الصوديوم للاختبار في كبح تآكل الحديد في ظروف الجو العادية بعد معالجته بمحاليل منها ذات تركيز من ١٠ إلى ١٠٠ ملي مول . لقد تم تجهيز عينات الاختبار من منتجات حديد التسليح المنتج محلياً . استعملت الأرفق الخشبية لحمل العينات أثناء تعريضها لظروف الجو العادية لفترات زمنية مختلفة ثم تم تحديد مدى التآكل عن طريق تحديد الوزن المفقود ، التقنيات الإلكترونية كيميائية والتحليل المرفولوجية للعينات المتأكلة بطريقة ميكروسبيا الامتصاص الإلكتروني (SEM) . لقد وجد أن كبح تآكل الحديد في الظروف الجوية العادية للعينات المعالجة لفوسفات الصوديوم ظلت منخفضة حتى بعد ستة أشهر من التعرض لظروف الجو العادية أما بالنسبة لبترويت الصوديوم فكانت سرعة الكبح اقل مقارنةً بفوسفات الصوديوم وحدث التغيير بسرعة مع زمن التعرض للجو حتى فقدت فعاليته تماماً بنهاية ثلاثة اشهر من التعرض للجو مباشرة .

CHAPTER 1

INTRODUCTION

Corrosion is the destructive result of chemical reaction between a metal or metal alloy and its environment. Metal atoms in nature are present in chemical compounds (i.e., minerals). Corrosion returns the metal to its combined state in chemical compounds that are similar or even identical to the minerals from which the metals were extracted. Thus, corrosion has been called extractive metallurgy in reverse [Jones, 1995].

Corrosion has been classified in many different ways. One way is to classify it into wet corrosion and dry corrosion [Fontana, 1986]. Wet corrosion occurs when a liquid is present. This usually involves aqueous solutions or electrolytes and accounts for the greatest amount of corrosion. A common example is corrosion of steel by water. Dry corrosion occurs in the absence of a liquid or above the dew point of the environment.

The presence of even small amounts of moisture could change the corrosion picture completely. For example, dry chlorine is practically noncorrosive to ordinary steel, but moist chlorine, or chlorine dissolved in water, is extremely corrosive and attacks most of the common metals and alloys [Fontana, 1986].

Uniform attack is the most common form of corrosion. It is normally characterized by electrochemical reaction that proceeds uniformly over the entire exposed surface or over a large area. The metal becomes thinner and eventually fails. Atmospheric

corrosion is probably the most prevalent example of the uniform corrosion. For example, a sheet iron roof that is exposed to atmosphere will show a uniform rate of rusting over its entire outside surface.

Corrosion by various atmospheres accounts for more failures on a cost and tonnage basis than any other single environment. Atmospheric corrosion is primarily due to moisture and oxygen but is accentuated by contaminants such as sulfur compounds and sodium chloride. Atmospheric corrosion can be reduced by (1) proper materials, including coating, (2) inhibitors [Fontana, 1986].

An inhibitor is a substance that, when added in small concentrations to an environment, decreases the corrosion rate. The scope of this research was to study experimentally different inhibitors that will help in preventing or decreasing the corrosion/discoloration of local mild steel products during storage under atmospheric conditions in Arabian Gulf region (industrial- marine environment).

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

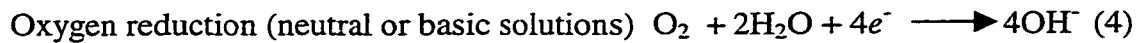
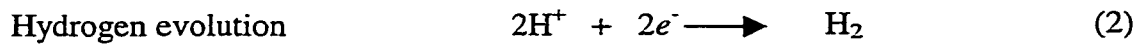
2.1 ATMOSPHERIC CORROSION

Atmospheric corrosion is an electrochemical process that occurs in the presence of a limited amount of electrolyte. The electrolyte is a neutral or slightly acidic solution whose properties are influenced by the chemical composition of the atmosphere and the properties of the corrosion products formed [Barton, 1976]. Like most other forms of corrosion, atmospheric corrosion takes place in cells of anodes and cathodes, operating only when the surface is wet and there is an electrolyte present.

The oxidation of a metal into its ions in a corrosion process is called the anodic reaction. It is indicated by an increase in valence and a production of electrons, and the number of electrons produced equals the valence of the ion. This can be written in the general form:



A decrease in valence charge or the consumption of electrons signifies a reduction or cathodic reaction. There are several different cathodic reactions that are frequently encountered in metallic corrosion. The most common ones are:



Both anodic and cathodic reactions must occur simultaneously and at the same rate on the metal surface [Fontana, 1986].

The composite reaction involving charge transfer or exchange of electrons during corrosion of a metal in an air free hydrochloric acid solution is shown schematically in Figure 1. The metal dissolves by Reaction (1) liberating electrons into the bulk of the metal which migrate to the adjoining surface, where they react with H^+ in the solution to form H_2 by Reaction (2) [Jones, 1995].

Atmospheric corrosion results from the conjoined action of two factors, oxygen and moisture. The absence of either one of these factors means the absence of corrosion attack. Thus atmospheric corrosion is negligible in polar regions and in hot deserts, where moisture does not exist as liquid water [Wranglen, 1985]. Dissolved oxygen is more readily transported through a thin layer of surface water than through bulk water during complete immersion. Thus, corrosion in the splash zone above water is higher than full immersion. Periodic washing by rainwater or tidal fluctuation creates conditions less severe than those of continuous splashing [Jones, 1995].

2.2 PARAMETERS AFFECTING ATMOSPHERIC CORROSION

Parameters that affect atmospheric corrosion are humidity, pollutants and temperature.

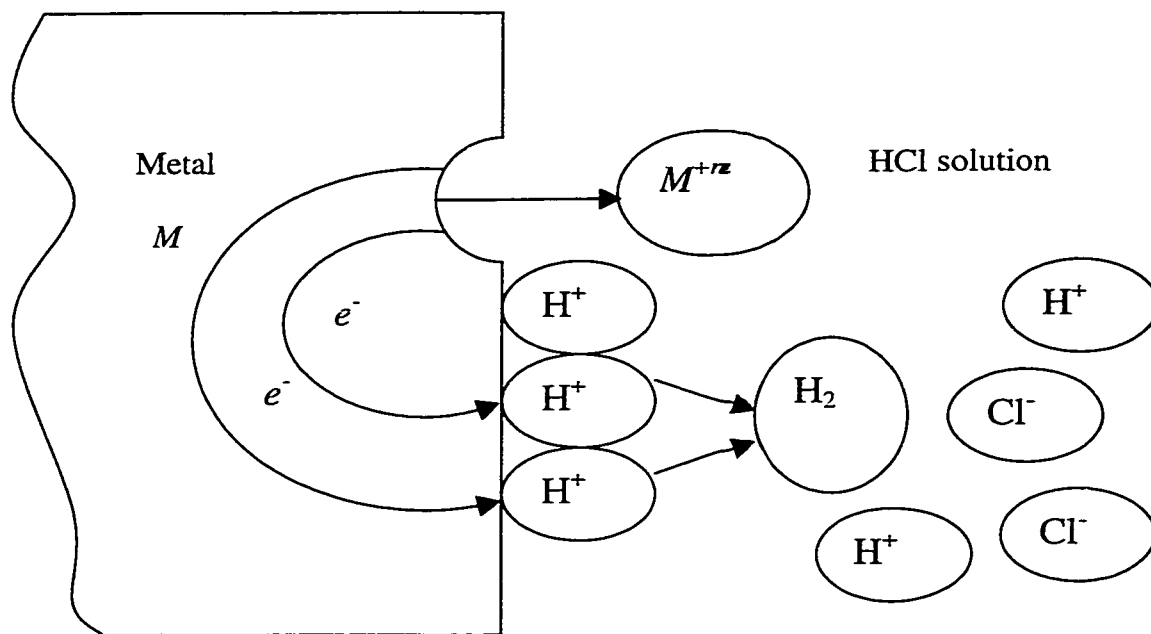


Figure 1. Electrochemical reactions occurring during corrosion of a metal in deaerated hydrochloric acid.

2.2.1 HUMIDITY

Humidity produces a thin layer of condensed water that deposits on the surface to provide the electrolyte needed for electrochemical corrosion. It has been shown that the atmospheric corrosion rate of metals increase rapidly when the relative humidity (RH) rises above a certain threshold value known as the “critical relative humidity” [Brown and Masters, 1982]. Below the critical relative humidity corrosion is negligible. The critical relative humidity was defined as the equilibrium humidity over a saturated solution of a salt present on the metal surface. The salt may be deposited as a contaminant from the atmosphere or it may be a corrosion product. If the humidity in the atmosphere exceeds the critical relative humidity value, the saturated salt solution takes up water until equilibrium is achieved; conversely, the salt solution gives up water to the atmosphere if the humidity is below the critical value [Duncan, 1984]. The critical relative humidity falls, in general, between 50 and 70 % for steel, copper, nickel and zinc.

Ambient RH also affects the adsorption of corrosive species from the atmosphere on metal surface. Adsorption of SO_2 on carbon steel, for instance, increases by about 90 folds as RH increases from 60 to 98% [Johansson and Vannerberg, 1981]. The evaporation rate of electrolyte from the surface is critically dependent on the RH, ambient temperature, temperature difference between the metal surface and its surroundings, and the capacity of corrosion products and contaminants on the metal surface to adsorb and store water.

2.2.2 POLLUTANTS

Pollutants or other atmospheric contaminants increase atmospheric corrosion by enhancing the electrolytic properties and stability of water films that condense on metallic surfaces from the atmosphere. Industrial and marine atmospheres are corrosive environments because; they contain corrosive gas pollutants such as sulfur dioxide (SO₂), hydrogen sulfide (H₂S), chlorine gases, and carry suspended particles of carbon and carbon compounds and salt particles.

Sulfur dioxide, SO₂, is generated by the burning of fuels. SO₂ in the presence of moisture forms sulfuric acid, which is very corrosive. The effect of SO₂ on atmospheric corrosion has been suggested to follow either the acid regeneration cycle or the electrochemical cycle. The acid generation cycle suggests the formation of FeSO₄ from SO₂, Fe, and O₂, then, FeSO₄ is oxidized to rust and free H₂SO₄ which then attacks more iron, giving fresh FeSO₄ and more H₂SO₄, and so on. The electrochemical cycle mechanism suggests that the ferrous sulfate provides an electrolytic path between anodic and cathodic areas. Ferrous sulfate forms by the reaction of H₂SO₄ with iron [Evans, 1976]. Both theories suggest that once ferrous sulfate forms the corrosion continue at an appreciable rate.

Sea-salt is an important atmospheric contaminant that helps in increasing corrosion rate. Oceans and seas are the primary sources of sea-salt in the atmosphere. Wind direction and velocity over the sea affect the accumulation and concentration profile of sea-salt on metal surfaces. Normal sea wind may carry an average of 4.5 to 50 kg (10 –100 lb) of sea-salt per 4.17 cubic km (one cubic mile) of air [Brierly, 1965]. Summitt and Fink (1982) suggested that both salt concentration and corrosion rate

decrease monotonically to about 4 km away from the sea shore with the sharpest decrease occurring within 15 km. Ambler and Bain (1955) evaluated the relation between corrosion and salt. They concluded with the direct relation between salt content and corrosion rate of metals. Pearlstein and Teitell (1970) found that the corrosion rates of steel and non-ferrous metals at seashore are substantially higher than in rain forest and 30 km inland. Caburn (1968) found that steel corrodes more in a marine environment than in an industrial region. Ericson's (1978) results showed that sodium chloride particles on steel surfaces can cause corrosion at relative humidities which are too low for SO₂-induced corrosion to start. Chloride contamination can influence the atmospheric corrosion of steel by decreasing the critical relative humidity for adsorption of moisture from the atmosphere [Mattsson, 1982].

Regarding other atmospheric contaminants, carbon dioxide (CO₂) has appreciable solubility in water (1.45 g per liter of water at 25°C), and the consensus is that it should affect atmospheric corrosion [Weast, 1981-1982].

Hydrogen sulfide (H₂S), that is produced by petrification of organic sulfur compounds, is a minor gas pollutant. H₂S has a significant influence on the corrosion rate of copper and silver, but has little influence on corrosion of iron, cobalt, and nickel [Rice, et al., 1982].

Oxide components of nitrogen are also present in appreciable quantities in atmosphere. The influence of them on metallic corrosion has not been extensively studied [Brown and Masters, 1982; Rice, et al., 1982].

Other particles in the atmosphere, apart from sea salt, can be classified as inert such as silica or adsorbent such as charcoal. The inert, non-adsorbent particles usually

have little effect on the atmospheric corrosion of iron [Brown and Masters, 1982]. However, inert particles can affect corrosion forming differential aeration regions at point of contact [Brown and Masters, 1982; Fyfe, 1976]. The deposition of adsorbent particles from the atmosphere onto metals may accelerate corrosion. Adsorbent particles catalyze the formation of a corrosive acid electrolyte solution [Brown and Masters, 1982; Fyfe, 1976].

The concentration of ammonia in the atmosphere is reported to vary between 10-50 mg/m³ [Brown and Masters, 1982]. Ammonia is readily soluble in water. Ammonium salts tend to reduce the surface tension of water and so help to wet the surface and causes sheet rather than drop-forming condensation on surfaces thus spreading corrosion [Barton, 1976; Rice, et al., 1982].

Chlorine gases, Cl₂ and HCl, are readily soluble in water and form acidic solutions. Chlorine gases reduce the surface pH and yield hygroscopic corrosion products, which can lower the critical relative humidity of the system and thus promote corrosion. Metals such as zinc and copper form stable basic chlorides with chlorine gas and thus reduce chlorine ion (Cl⁻) activity. Iron based alloys, on the other hand, do not bind the Cl⁻ into stable sparingly soluble compound and thus the corrosion activity is not reduced [Rice, et al., 1982].

2.2.3 TEMPERATURE

Temperature has a variable effect on atmospheric corrosion. Ambient atmospheric temperatures keep corrosion rates relatively low but may enhance the condensation of an aqueous surface film to increase corrosion. Exposure to sunlight raises surface

temperature, but does not necessarily accelerate corrosion [Jones, 1995]. Temperature may indirectly affect the atmospheric corrosion; for example, at high relative humidity a rapid small temperature drop causes exceeding of the dew point and so promotes corrosion. On the other hand, a rapid increase in the air temperature reduces the relative humidity below the dew point and thus reduces corrosion.

Moreover, the metal surface temperature, which is dependent on the atmospheric temperature may be influenced by many other factors, including the thermal capacity of the metal structure, its orientation with respect to the sun, intensity of sunlight, wind velocity and direction, and the thermal insulation properties of corrosion products [Fyfe, 1976]. The effects of these parameters with regard to temperature changes may be difficult to predict because of the difficulty in separating the effect of each parameter.

It has been reported that the average temperature in a natural environment may be unimportant for atmospheric corrosion since the corrosion rate, in many instances, is diffusion-controlled [Brown and Masters, 1982].

In summary, a combination of high humidity, high average temperature, and presence of pollutants increase atmospheric corrosion rates. Thus the maximum atmospheric corrosion occurs in marine tropical or semitropical environments. Absence of one or more of these factors may result in low corrosion [Jones, 1995].

2.3 TYPES OF ATMOSPHERES AND THE ARABIAN GULF ATMOSPHERE

There are many types of atmospheres. A common classification based on the climatic conditions of different geographical regions divides them into temperate,

tropical, and arctic. The local atmospheric conditions in any of these areas may be further classified into marine, industrial, urban, and rural climates. The corrosiveness of these types of atmosphere varies considerably. The corrosion rate in an industrial area may be more than one hundred times greater than that in a desert or arctic region [Barton, 1976]. Corrosion of steel on the seacoast is 400 to 500 times greater than in a desert area.

The weather in the Arabian Gulf region is hot and humid providing corrosive environment for metallic structures. In Dhahran and Jubail, the relative humidity is above 50% during most of the year. In summer, air temperature may go up to 50°C. The daily temperature fluctuations can be as high as 20°C during hot seasons, whereas the daily fluctuations of relative humidity may range between 40 to 100% over a 24 hour period.

Petroleum and petrochemical industrial areas and the proximity of the inhabited areas to the shores of the Gulf have caused a dramatic increase in atmospheric corrosion of all metallic structures. The atmospheric corrosion in the Gulf region is aggravated further by high salinity of Gulf water resulting in the high rate of sea-salt deposition (approximately 1.6×10^{-3} kg/m²/y). The chloride and sulfate contents in the atmospheric air of Gulf coast in Dhahran are 63.2×10^{-3} and 33.8×10^{-3} mg/m³ respectively. The salt content is about 500 times greater in Dhahran than that at Long Beach, California, USA, and sulfate content of atmosphere in Dhahran is 100 times that at Long Beach [Allam, et al., 1991]. In addition, sulfur dioxide and organic carbonaceous deposits from burning fuel make the atmosphere in the Gulf region more corrosive.

The conjoint effects of sulfur dioxide and sodium chloride on atmospheric corrosion of steel in the Arabian Gulf were studied [Allam, et al., 1991]. According to this study, atmospheric corrosion starts by the formation of small blisters at discrete

locations on the metal surface. The blister covers are very rich in iron chlorides that formed initially. The formations of iron chlorides indicate that natures of chloride ions are more aggressive than sulfate ions during the initial stages of atmospheric corrosion. During latter stages, as blisters grow, the supply of chloride ions decreases and subsequently the formation of iron chlorides diminishes. In contrast, further formation of iron sulfates at the metal-rust interface during extended exposure indicates that sulfate ions are more corrosive ions during the latter stages of atmospheric corrosion.

2.4 INHIBITION OF ATMOSPHERIC CORROSION

There are numerous inhibitor types and most of the inhibitors have been developed by empirical experimentation. Inhibitors can be classified according to their mechanism and composition as Adsorption-types, Hydrogen-evolution poisons, Scavengers, Oxidizers and Vapor-phase inhibitors. It is important to use enough quantity of inhibitors and check their concentration periodically. When two or more inhibiting substances are added to a corrosive system, the inhibiting effect is sometimes greater than which be achieved by either of two (or more) substances alone. This is called synergistic effect [Fontana, 1986].

The inhibition of atmospheric corrosion can be achieved by organic or inorganic inhibitors. The role of inhibitors can be due to adsorption and phase layers on the metal surface or by the interaction with one of several corrosion products to form a new protective phase rather than by adsorption on the metal surface. The inhibitors such as benzoate and phosphate adsorb on the metal surface and provide a barrier for the entry of aggressive ions like chloride. The inhibitors may also passivate the metal through

stabilization of the passivating oxide film and decreasing its dissolution rate. Inhibitors can also interact with oxide-covered metal surface to form insoluble compounds that plug pores in the oxide film and prevent oxygen reduction reaction at the cathodic sites in neutral solutions [Fontana, 1986].

Inhibitors may be applied at the beginning when a new structure is installed or at any other time the structure is exposed to the atmosphere. Thus the inhibitors are applied on either clean surfaces at the beginning or partially corroded surfaces.

2.5 REVIEW OF PREVIOUS STUDIES

Various inhibitors are reported in the literature that can help in protection against atmospheric corrosion. Among them are Toluylalanine, cyclohexyl amine, dicyclohexylamine nitrite, methylcyclohexylamine, phenylthiourea, sodium benzoate, sebacic acid, sodium nitrite, calcium silicate, sodium phosphate and sodium nitrate.

Saubier, et al. (1994) compared 3-(Toluyyl)-N-(1,1-dimethyl-2-hydroxyethyl)-alanine, known as Toluylalanine (TALA) $C_{15}H_{21}NO_4$, Sebacte (seba) $C_{10}H_{18}O_4$, i-Nonate (i-non) $C_9H_{18}O_2$, m-nitrobenzoate (m-nitro) $C_7H_5NO_4$, i-phthalate (i-phtha) $C_8H_6O_4$, Benzoate (Benz) $C_7H_6NO_2$ and nitrite as inhibitors of corrosion in wet atmosphere. The most effective inhibition was obtained in solution with the passivating TALA.

It has been recently reported that dicyclohexylamine nitrate (DICHAN) provided moderate protection for steel at 65-85% relative humidity [Batsidas and Mora, 1998]. The inhibition of 3-(trimethoxysilyl) propanethiol-1 (TMSPT) was reported to be effective against corrosion of steel in NaCl solutions [Beccaria, et al., 1994]. Some other inhibitors reported to be effective against corrosion are TPI-4 [Trufanova, et al., 1991], $NaNO_2$

water solution [Miglyachenko, 1992], five-membered polynitrogen heterocycles [Tsarenko, et al., 1995], amines such as cyclohexyl amine [Agres and Altsybeeva, 1990], ethanolamine [Andreev, et al., 1997], sulfonates and phosphorous-containing organic compounds [Sementsova, et al., 1998], Imidazole derivatives [Stupnisek-Lisac, et al., 1999] and fatty acid esters [Krauss and Nmai, 1996]. Some commercial coolants are also used as atmospheric corrosion inhibitors [Anderson and Devereux, 1993]. Chromates are effective as atmospheric inhibitors (for aerospace aluminum alloys), however they are identified to be carcinogen and their use therefore is not recommended [Jeffcoate, et al., 1998; Khobaib, et al., 1998]. Non-chromate inhibitor formulations such as borate, molybdate, phosphate and silicate were studied for aluminum aircraft [Khobaib, et al., 1998].

Thiophenol was reported to serve as a good inhibitor (studied at concentrations of 1 mM, 10 mM, 100 mM) for the corrosion of iron and mild steel in acidic solutions [Madhavan, et al., 1998; Bouayed, et al., 1999]. However, thiophenols have not been given much attention as inhibitors because of their obnoxious odour and low solubility in acidic solutions [Madhavan, et al., 1998].

The influence of the concentration of electrolyte anions on the efficiency of acid based inhibitors for steel in the neutral solution was studied using anodic and cathodic polarization at a rotating disk electrode. The N-ethyl-morpholine of a q-benzoyl alcanoic acid and benzoic acid were used as inhibitors. Both inhibitors were found to inhibit the anodic partial reaction. The inhibition effect was more pronounced at low electrolyte concentration [Agarwal and Landolt, 1998].

The corrosion inhibiting performance of a tertiary amine possessing two carboxylic acid groups (N coco-amine-2-propionic acid) was studied on initially clean and pre-corroded mild steel. High levels of efficiency were found of the inhibitor at a concentration level of 10 ppm [Malik, 1999].

The passivity and pitting behavior of A56-70 carbon steel in chromate solutions were studied using electrochemical measurements. Chromate ions play a prominent role in the formation of passive film, but hardly affect the stability of the passive state [Cheng and Luo, 1999].

Corrosion behavior of steel with and without disodium ethylenediamine tetraacetate as inhibitor was studied to see the concentration influence of ferrous sulphate. It was found that corrosion potential decreases in the presence of the FeSO_4 and increase in the presence of the inhibitor. However, the corrosion behavior is not altered much [Gomma, 1999].

The influences of inhibitor concentrations for orthophosphate mixed with polyphosphate were studied on steel. The total concentration of two inhibitors was 15 mg/L. The corrosion rate which was 1.9 mpy at 0% of orthophosphate decreased to 0.3 mpy at 60 % of orthophosphate but then increased up to 1.8 mpy when orthophosphate concentration increased to 100% [Bofardi, 1993].

CHAPTER 3

EXPERIMENTAL

3.1 INHIBITORS

The following four inhibitors which were available in the local market were utilized in this study:

1. Sodium phosphate
2. Sodium nitrite
3. Sodium nitrate
4. Sodium benzoate

The first three of the above inhibitors are inorganic and the last one is organic. First, the inhibitors were examined in a simulated aqueous solution at various application conditions for initial screening. Then, two of the inhibitors, sodium phosphate and sodium benzoate, were selected for examination against atmospheric corrosion.

3.2 TEST SPECIMENS

The test specimens were prepared from locally produced reinforcing steel products. An Energy Dispersive Spectrometry (EDS) analysis was performed on the as-

received steel after polishing and is presented in Table 1. The steel was composed of mostly iron with trace amounts of C, Al, Si, Cl, S, and Mn.

Table 1. Elemental composition of the as received steel (control specimen).

| C, wt% | Al, wt% | Si, wt% | Cl, wt% | Mn, wt% | S, wt% | Fe, wt% |
|--------|---------|---------|---------|---------|--------|---------|
| 0.46 | 0.26 | 0.14 | 0.14 | 0.2 | 0.01 | 98.8 |

Three different groups of specimens were prepared as 5-inch long specimens, 1-inch long specimens and 2 mm thick disk specimens (Figure 2). 5-inch long specimens were used for weight loss determinations, 1-inch long specimens were used for electrochemical measurements and 2 mm thick disk specimens were used in scanning electron microscopy (SEM) study.

5-inch long specimens were used as they are. 1-inch specimens were throttled at one cross sectional side to fit them in the working electrode rod of the electrochemical cell. The 2 mm thick disk specimens were grounded and polished to 600 grit surface finishes. All specimens were washed prior to the study using soap and water, followed by ultrasonic cleaning in acetone and methanol before drying.

3.3 INHIBITOR APPLICATION

Solutions of inhibitors in distilled water were prepared in concentrations ranging from as low as 0.1 mM to as high as 1000 mM utilizing magnetic mixing. Inhibitor application of specimens to be protected was conducted by inserting the specimens in the

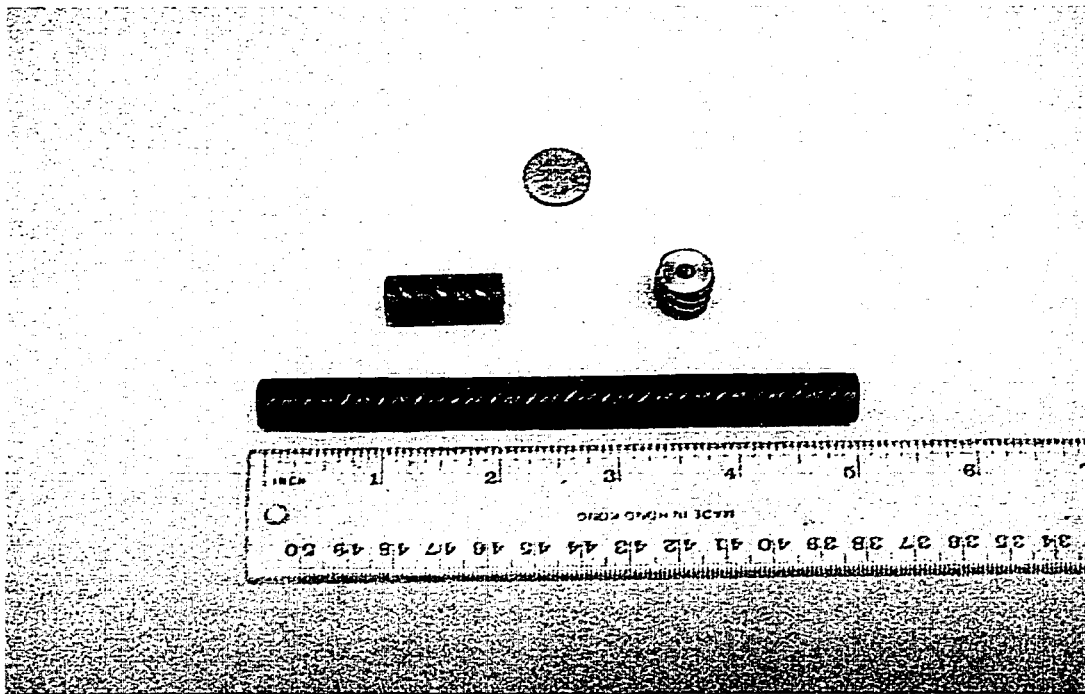


Figure 2. Photograph of the three different types of specimens: SEM analysis specimen (upper), electrochemical test specimens (middle), and weight loss test specimen (lower).

inhibitor solution for a specified period (ranging from 5 minutes to 1 day) either at room temperature or at a higher temperature of 70°C.

3.4 ATMOSPHERIC EXPOSURE

The specimens were exposed to atmosphere in Dhahran (on the roof of the Research Institute of King Fahd University of Petroleum and Minerals) after treating them with the selected inhibitors. A photograph of the exposure racks holding the test specimens is shown in Figure 3 (sketches of exposure racks designed are given in Appendix A). Specimens were exposed for different periods of time, for 5 days, 15 days, 30 days, 90 days, and 180 days, before corrosion measurements. The results were compared to that of unexposed specimens (control samples). The exposure periods and number of specimens for each test are shown in Appendix B.

During exposure, the specimens were visually inspected and any change that occurred in their appearance due to corrosion was recorded photographically.

3.5 INHIBITOR PERFORMANCE ANALYSIS

3.5.1 ATMOSPHERIC CORROSION BY WEIGHT LOSS DETERMINATION

Probably the simplest and most useful technique for corrosion rate determination is the weight loss measurement. The weight losses of the exposed specimens were determined at the end of each exposure period to quantify their corrosion. The procedure given below was followed [ASTM, 1988; NACE, 1976; Allam, et al., 1991].

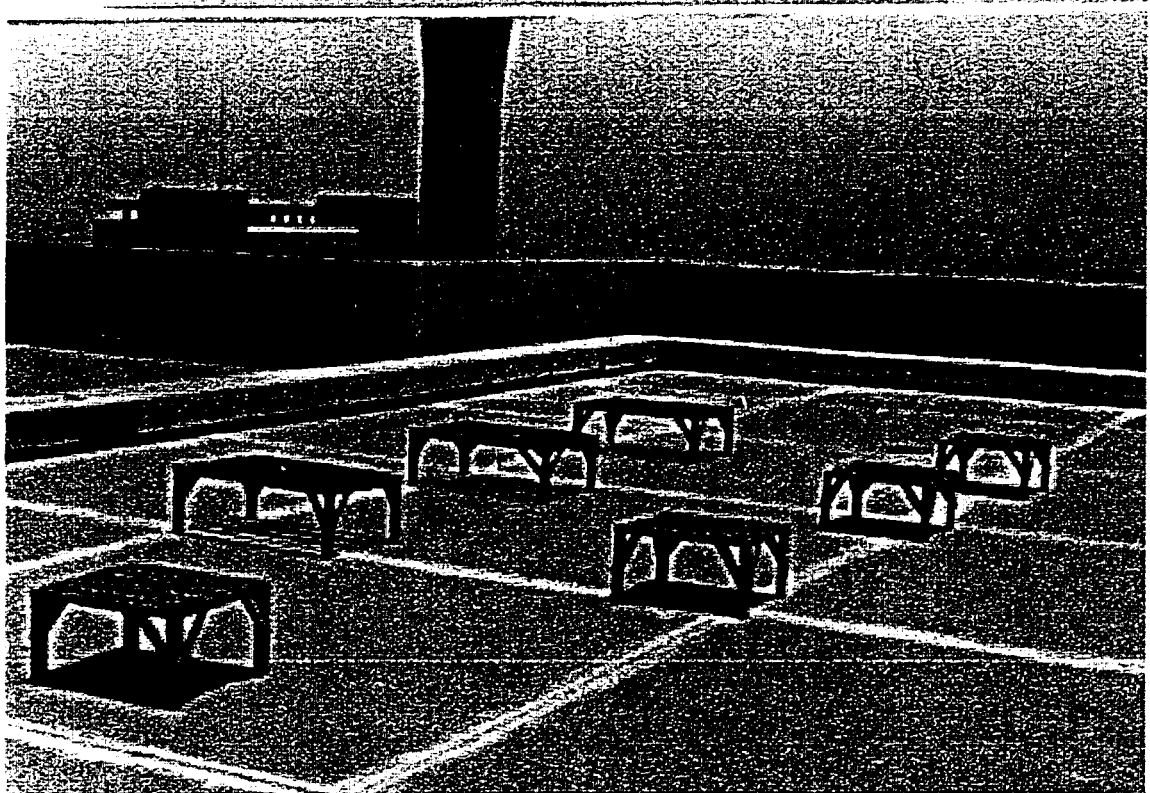


Figure 3. Wooden racks holding the steel specimens for exposure to atmosphere at the roof of the Research Institute building at KFUPM.

- Before any treatment of specimens and exposure:
 1. Specimens were cleaned using acetone and distillate water, and air-dried.
 2. Specimen lengths and diameters were measured to determine the surface areas of specimens.
 3. Initial weights of specimens were determined to the nearest 0.1 mg.

- After atmospheric exposure:
 4. Specimens were cleaned from corrosion products with 10% HCl, washed with acetone and distillate water, and air-dried.
 5. Final weights of specimens were determined to the nearest 0.1 mg.
 6. Weight loss = initial weight – final weight.

The effect of HCl in weight loss determination was also considered as follows:

- Initial weight of unexposed specimen was taken.
- Unexposed specimen was cleaned with 10% HCl, washed and dried.
- Final weight of unexposed specimen was taken.
- Weight loss of this specimen due to acid cleaning is subtracted from the weight loss of each exposed specimen to determine the net weight loss due to atmospheric corrosion.

The corrosion rate by weight loss determination is obtained by the following formula:

$$\text{Corrosion rate (mm/y)} = 87.6 \frac{W}{D A T}$$

Where W is the weight loss in mg, D is the density of sample (7.87 g/cm^3), A is the area of sample in square centimeters, T is exposure time in hours and 87.6 is the conversion factor. Measurements and calculation details of all tests are given in Appendix C.

3.5.2 ELECTROCHEMICAL LABORATORY TESTS UNDER SIMULATED ENVIRONMENT

The effect of inhibitors on the corrosion of steel specimens in a simulated environment was evaluated by electrochemical technique in a standard test cell. The cell was a vessel containing the solution electrolyte and electrodes. The solution electrolyte was distillate water with dissolved salts. The salt solution contained 2% sodium chloride (NaCl) and 1% sodium sulfide (Na_2SO_4) [Allam, et al., 1991]. The steel specimens were the working electrodes (WE) in the electrochemical test cell. A direct current power supply, PS, supplied current (I) to the working electrode through auxiliary electrode (graphite) in the test cell. The auxiliary electrode was made from graphite that is inert to the electrolyte to prevent dissolving of auxiliary electrode. The corrosion current density (I_{corr}) and the polarization resistance (R_p) of the steel specimens were measured with respect to a reference electrode. The reference electrode was saturated calomel electrode (SCE).

A potentiostat (EG&G Model 273A) was connected to the electrochemical cell to give Tafel and polarization curves. A potentiostat is an electronic instrument which can maintain the electrode potential constant at any desired value. It consists of a voltage-error sensor connected to a power supply. When any deviation between the specified and the actual electrode potential occurs, the sensor transmits a signal to the power supply to increase or decrease the applied current as required to correct the error. A block diagram of the potentiostat is given in Figure 4. The three parts that comprise the potentiostat are: i) potential control, ii) control amplifier and iii) current supply. Three electrical leads are connected to three electrodes (working electrode, auxiliary electrode and reference electrode) in the electrolyte solution. The measurement error between the reference and working electrodes in the form of a signal is transmitted to the control amplifier.

The potentiostat is controlled by an external computer. All required data were given to the model through the computer and also the output curves and results were stored in the computer. A photograph of the electrochemical measurement system is shown in Figure 5.

The procedure of corrosion rate determination in the simulated solution by electrochemical technique can be summarized as:

- Preparing the electrochemical the cell:
 1. The cell, reference electrode and graphite electrodes are cleaned with distillate water. The electrodes are put in their position in the cell.
 2. Around 800 ml of simulated aqueous solution is put in the cell.
 3. The specimen to be tested is fitted in the working rod of the cell and put in its position in the cell.

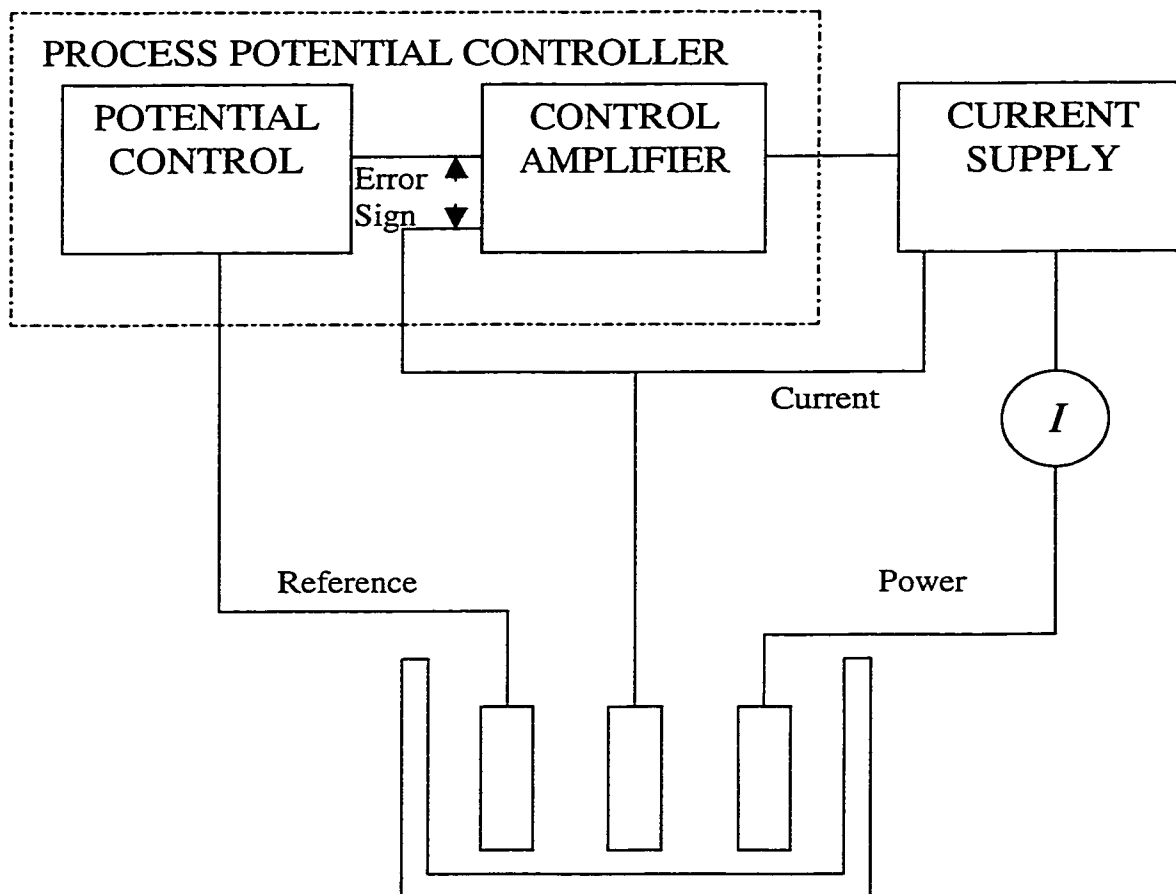


Figure 4. Block diagram of EG&G Model 273 potentiostat.

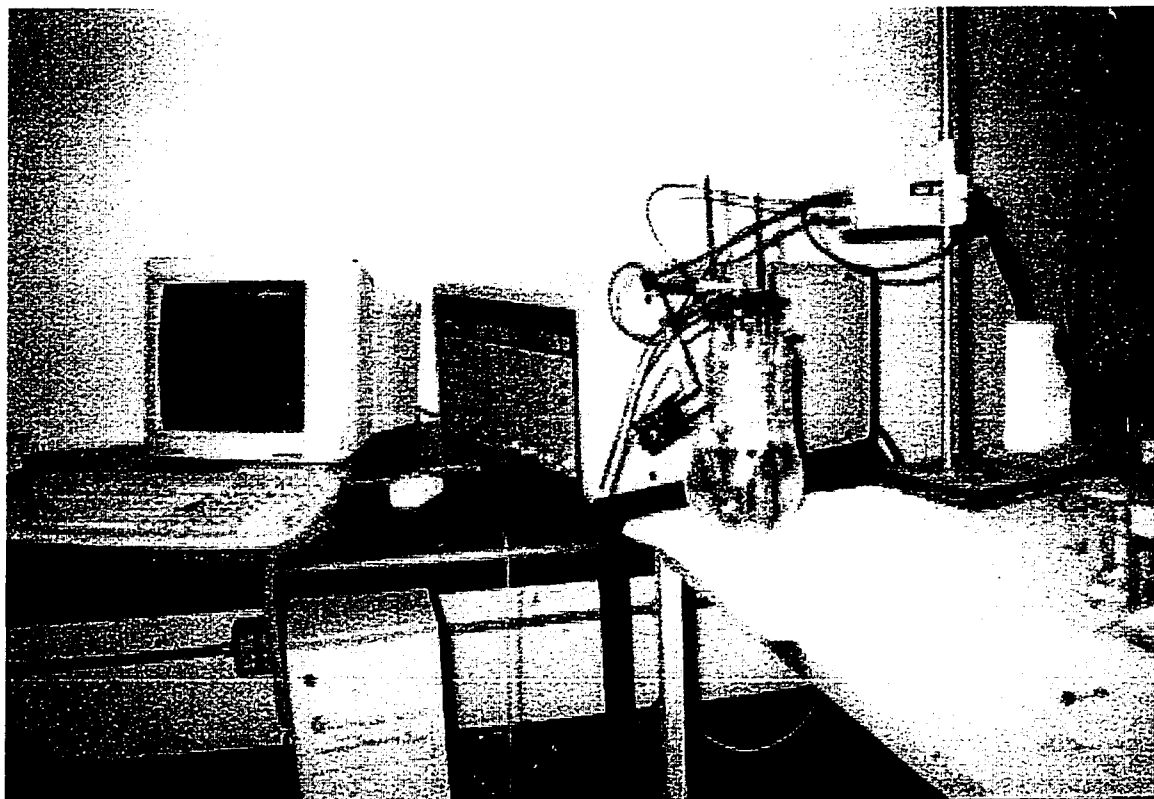


Figure 5. Photograph of the electrochemical cell, potentiostat and computer.

- Running the electrochemical test:
 4. The electrochemical cell is connected to the EG&G Model 273A potentiostat.
 5. The test, tafel or polarization, is chosen and the input data are given to the setup screen of the computer.
 6. Wait about 45 to 60 minutes for E_{corr} (E_{corr} is defined as the open-circuit potential measured just prior to the start of the run) to stabilize. The stability of E_{corr} depended on the inhibitors and concentrations.
 7. The test is run from the setup screen. It takes around one hour for the tafel run and 10 minutes for the polarization run.
 8. Output curves and results (β_{anode} , $\beta_{cathode}$, I_{corr} , R_p , corrosion rate in mpy) are given in the output screen. Calculation procedure of I_{corr} , R_p and corrosion rate in mpy is shown in Appendix D. The results are compiled in Appendix E.

The tafel test was done only once for each inhibitor at 100 mM to obtain tafel constant β_{anode} and $\beta_{cathode}$. β_{anode} and $\beta_{cathode}$ were used in the polarization runs. The input data for tafel and polarization runs are given in Table 2. Sample tafel and polarization curves are given in Figure 6 and 7.

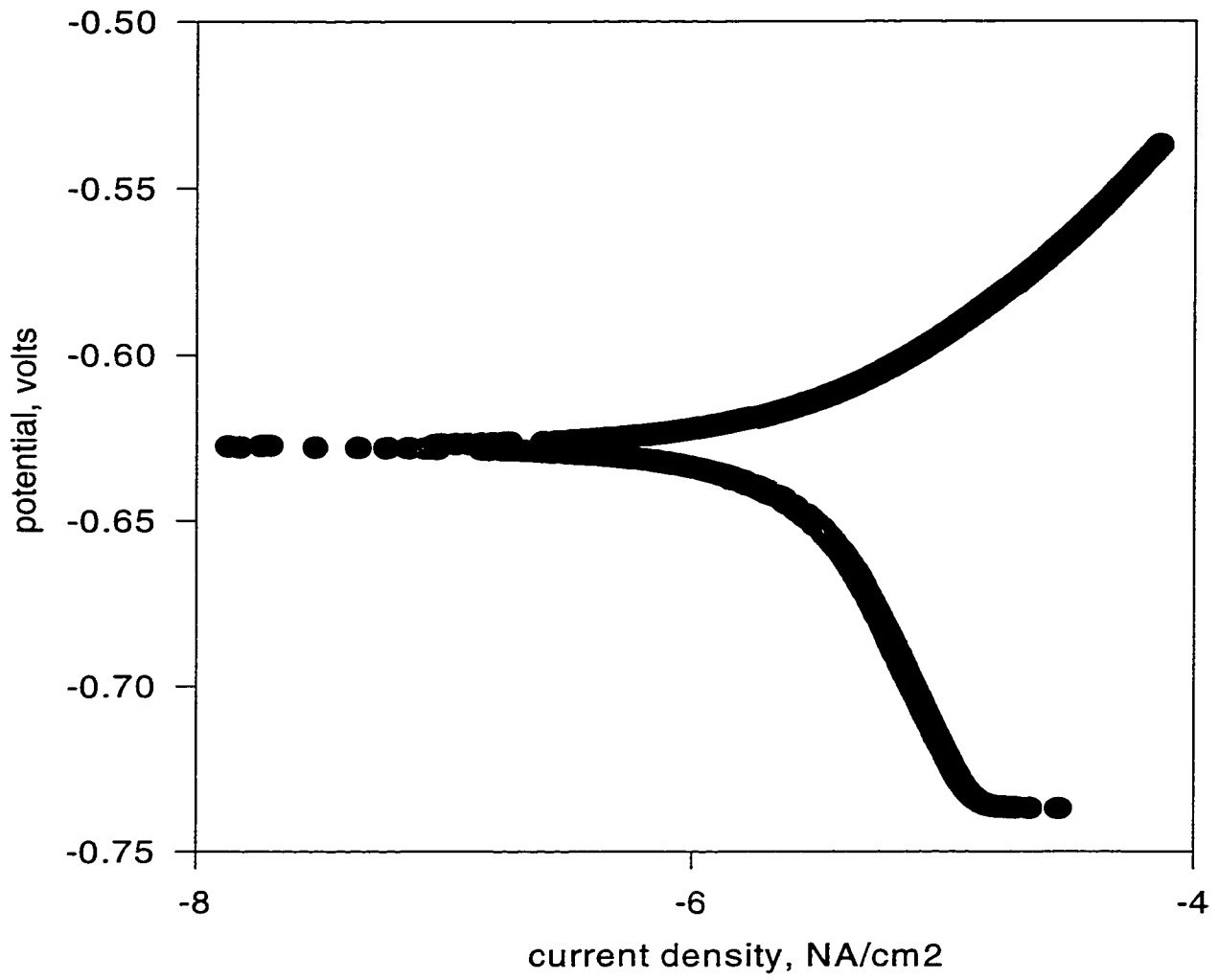


Figure 6. Tafel plot on a specimen treated by sodium phosphate at 100 mM.

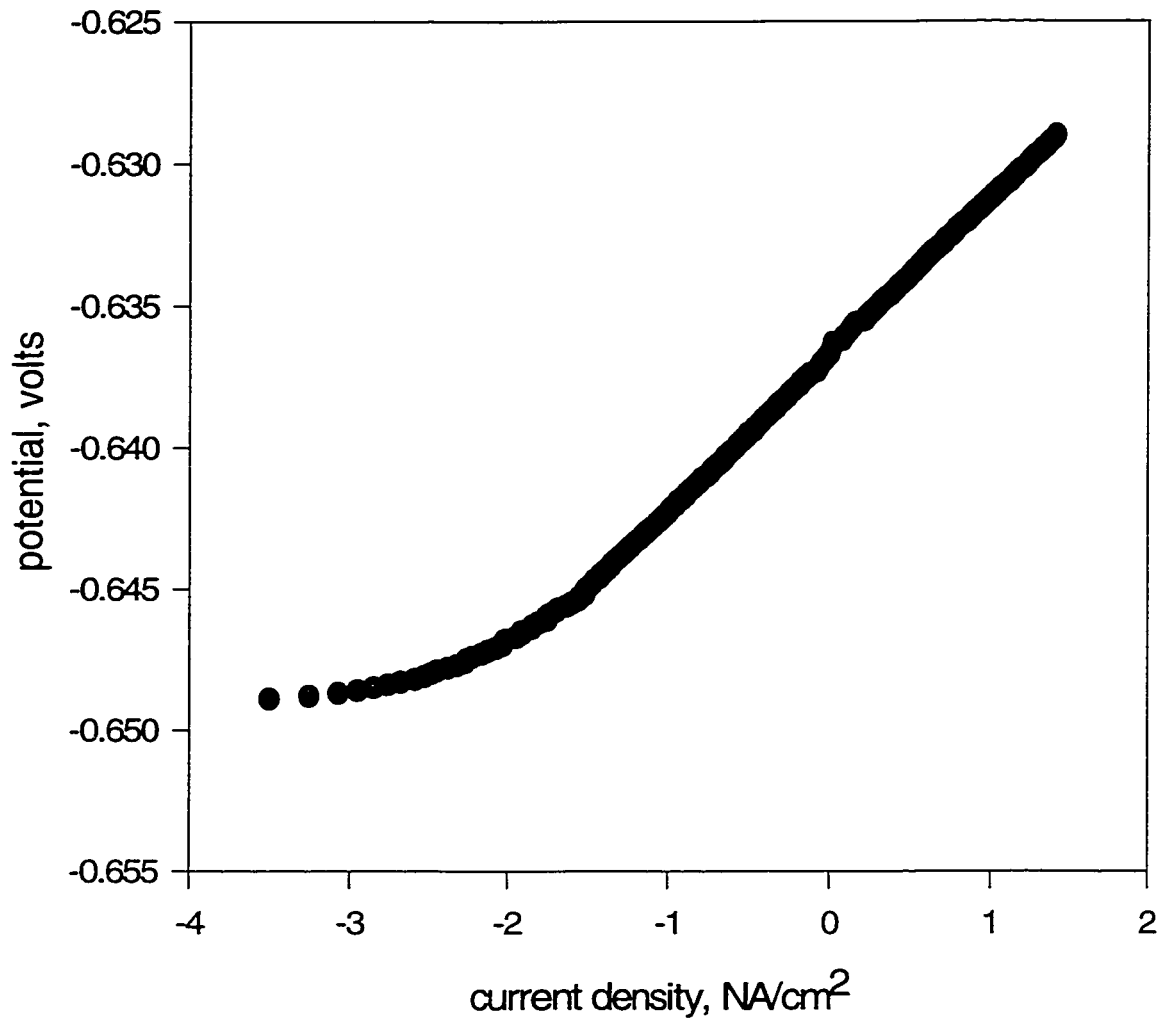


Figure 7. Linear Polarization Resistance (LPR) plot on a specimen treated by sodium phosphate at 100 mM.

Table 2. Input data for tafel and polarization of the electrochemical technique.

| | Input data | |
|-------------------|------------------------|------------------------|
| | Tafel | Polarization |
| Minimum potential | -25 mV | -10 mV |
| Maximum potential | +25 mV | +10 mV |
| Scanning rate | 0.1 mV/s | 0.1 mV/s |
| β_{anode} | - | From the tafel test |
| $\beta_{cathode}$ | - | From the tafel test |
| Sample area | Depends on the sample | Depends on the sample |
| Sample density | 7.87 g/cm ³ | 7.87 g/cm ³ |
| Equivalent weight | 27.89 | 27.89 |

3.6 MORPHOLOGICAL ANALYSIS OF CORROSION SPECIMENS

Morphological changes of the specimens were examined by photography and scanning electron microscopy (SEM). The experimental system used for SEM analysis was JSM-840 Scanning Electron Microscope located at the Research Institute of King Fahd University of Petroleum & Minerals. Compositional analysis of selected surfaces was also done by the EDS (Energy Dispersive Spectrometry) technique available with the SEM system.

RESULTS AND DISCUSSIONS

4.1 SIMULATED LABORATORY TESTS PRIOR TO ATMOSPHERIC CORROSION STUDY

Corrosion inhibition of the inhibitors (sodium phosphate, sodium benzoate, sodium nitrate and sodium nitrite) was first tested in a simulated aqueous solution for the purpose of initial screening of inhibitors and various inhibitor application conditions. Inhibitors were applied on steel specimens as explained in the experimental section and the corrosion rates of the inhibitor applied specimens (with no atmospheric exposure) were determined in the simulated solution of 2% NaCl and 1% Na₂SO₄ through the electrochemical method (as also explained in the previous section). The results obtained are presented below and compiled in Appendix E.

4.1.1 INHIBITOR: SODIUM PHOSPHATE

Corrosion rates of steel specimens treated with 10 mM sodium phosphate at four different application conditions are compared to that of untreated one (control specimen) in Figure 8. Each value is an average of corrosion rates of at least two specimens (three if

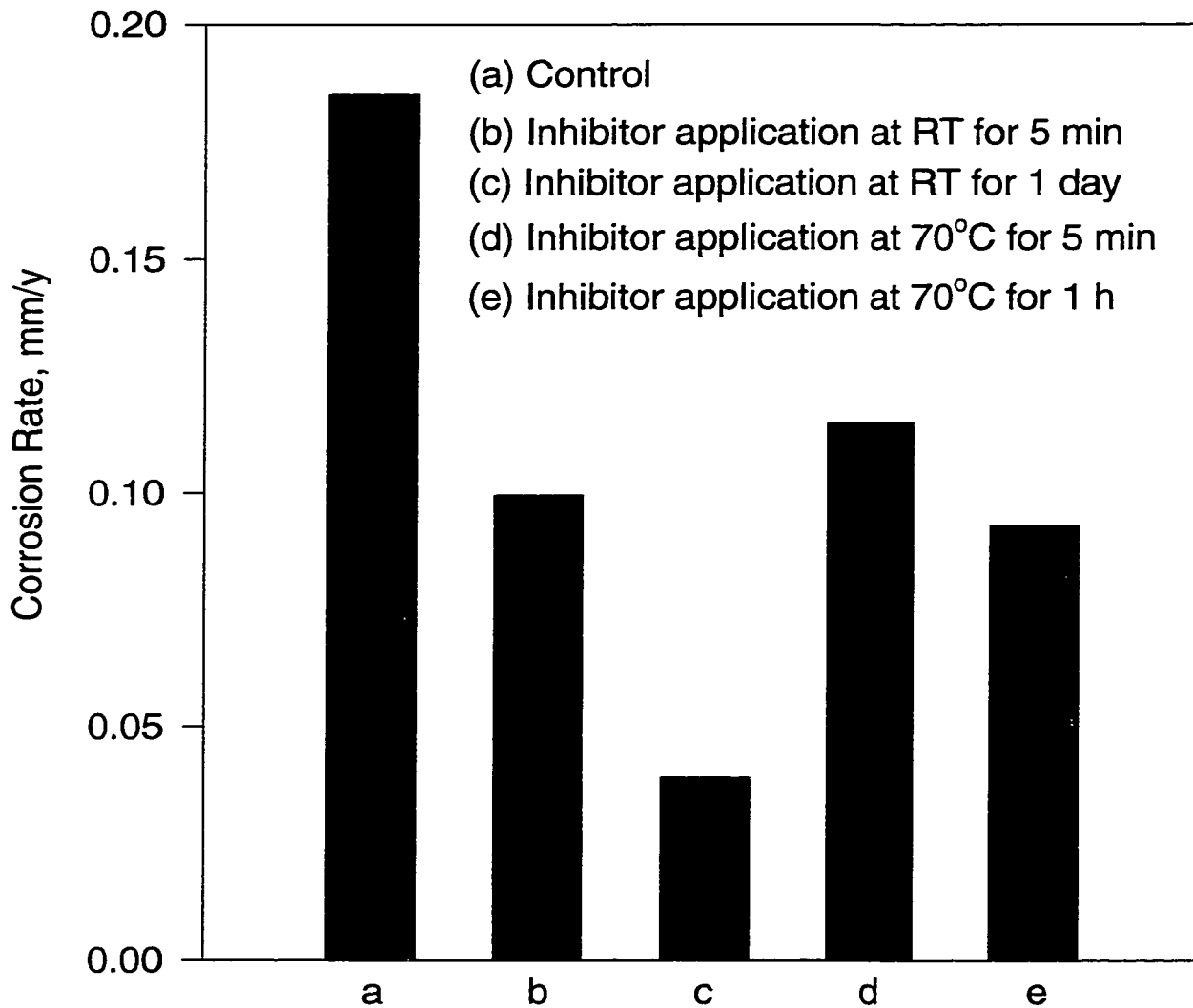


Figure 8. Corrosion rates of unprotected and 10 mM sodium phosphate treated steel specimens at various treatment conditions.

the two rates differ significantly). Untreated steel corrodes at a rate of about 0.185 mm/y. Corrosion rate of steel decreases significantly when treated by 10 mM sodium phosphate. It becomes about 0.099, 0.038, 0.114 and 0.094 mm/y for treatments of 5 minutes at room temperature, 24 hours at room temperature, 5 minutes at 70°C and 1 hour at 70°C, respectively. As seen, inhibitor application at room temperature for a day results in the lowest corrosion rate among the treatment conditions studied.

Figure 9 shows a plot of corrosion rate vs inhibitor concentration for steel treated with sodium phosphate for 1 day at room temperature. Corrosion rate first decreases with increasing inhibitor concentration but then gets very high (higher than that of control specimen) when the concentration of sodium phosphate reaches 1000 mM. A white layer was obvious on the specimens for inhibitor concentrations of 1 mM, 10 mM and 100 mM whereas the surface became dark black with white spots for the inhibitor concentration of 1000 mM.

Corrosion rate vs inhibitor concentration for steel treated with sodium phosphate for 5 minutes at 70°C is plotted in Figure 10. Inhibitor performance at any concentration was not as good as it was for 10 or 100 mM inhibitor application for 1 day at room temperature. An increase in corrosion rate was not observed for the inhibitor concentration of 1000 mM when applied for 5 minutes at 70°C. The extent of white layer forming on the metal surface increased with inhibitor concentration.

4.1.2 INHIBITOR: SODIUM BENZOATE

Figure 11 compared the corrosion rates of steel specimens treated with 10 mM sodium benzoate at three different inhibitor application conditions to that of control

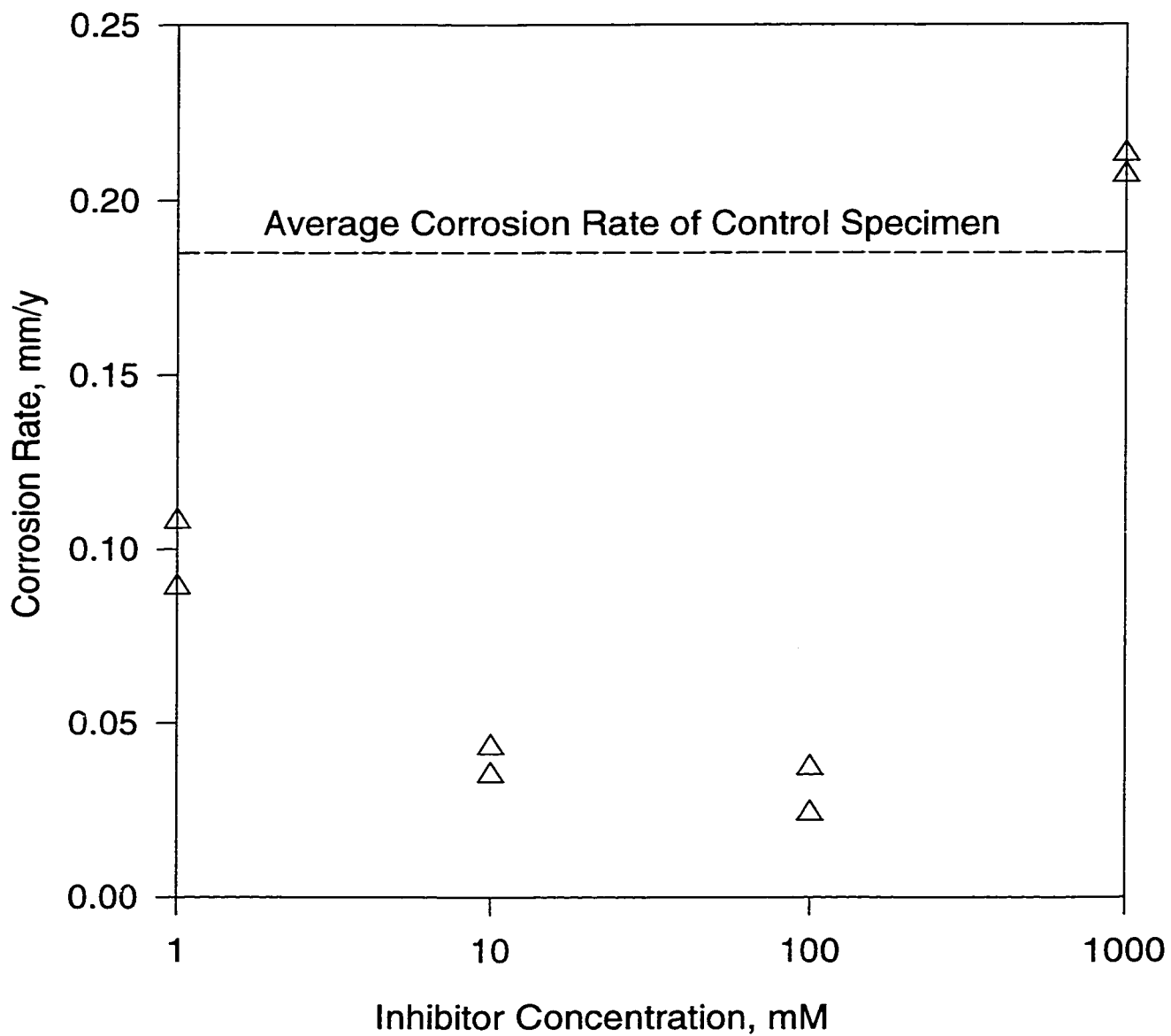


Figure 9. Corrosion rate vs inhibitor concentration for steel treated with sodium phosphate for 1 day at room temperature.

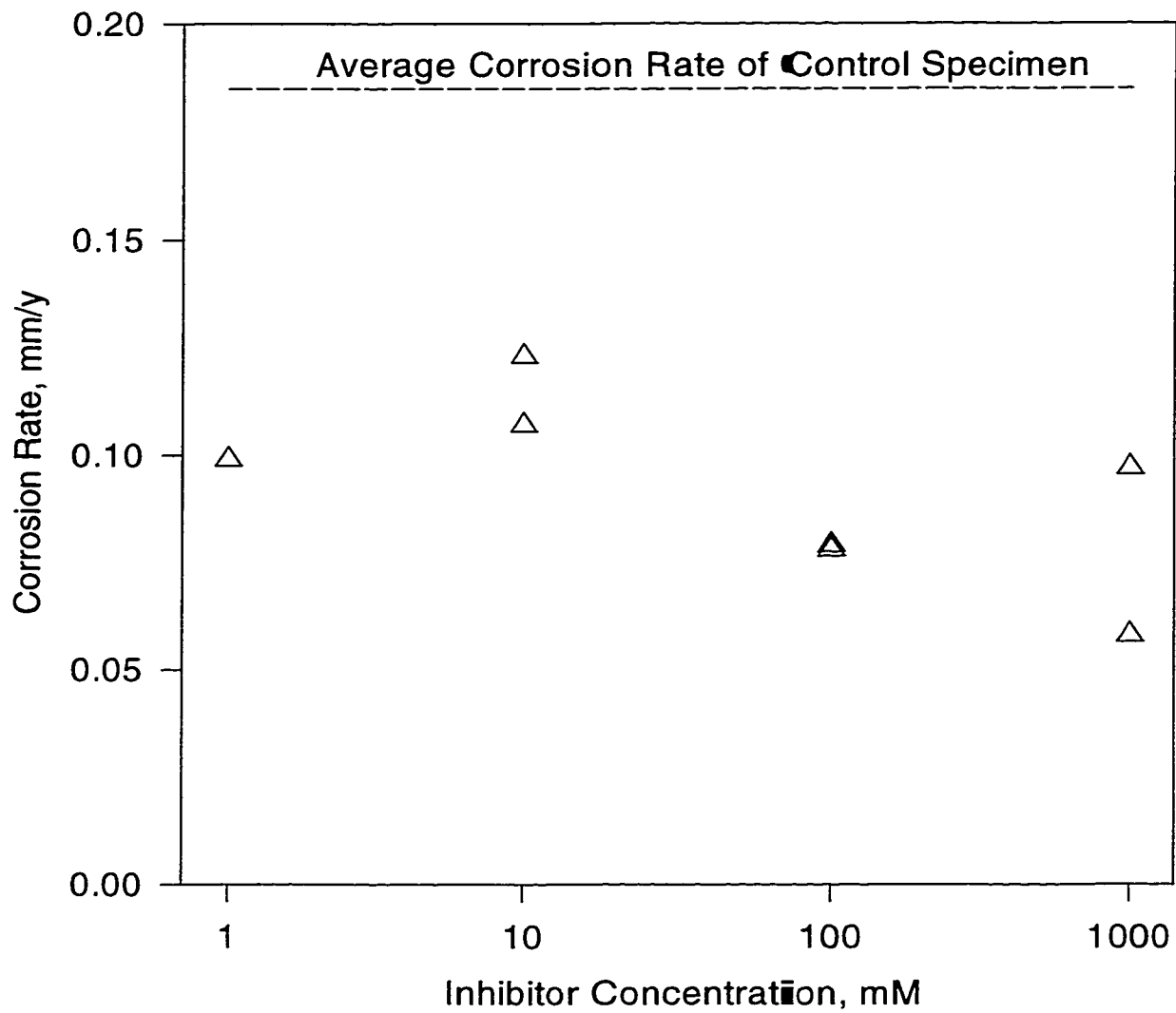


Figure 10. Corrosion rate vs inhibitor concentration for steel treated with sodium phosphate for 5 minutes at 70°C.

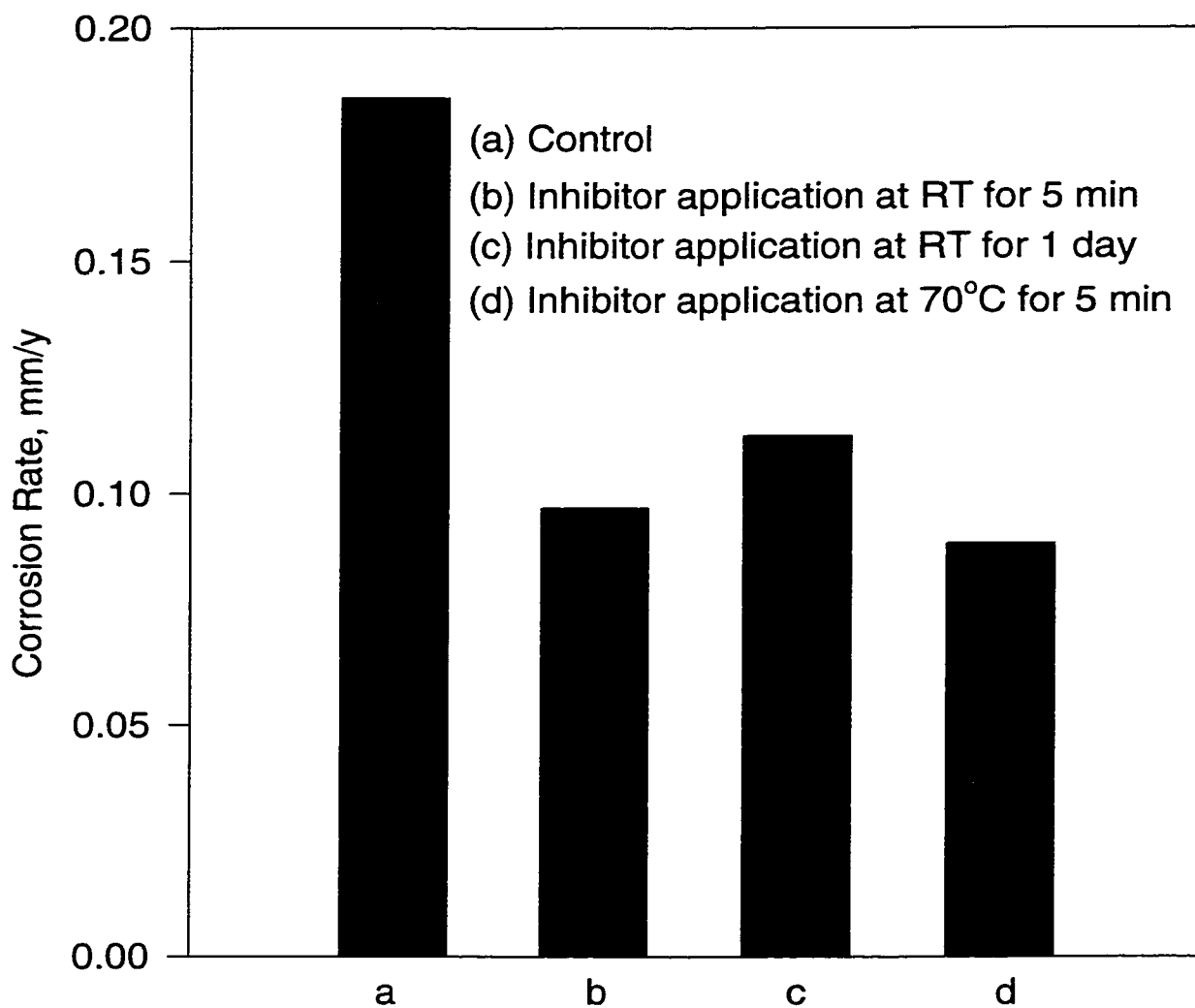


Figure 11. Corrosion rates of unprotected and 10 mM sodium benzoate treated steel specimens at various treatment conditions.

specimen. As seen, corrosion rate of steel decreases in the simulated solution from 0.185 mm/y to values below 0.1 mm/y when treated with 10 mM sodium benzoate. However, the decrease in corrosion rate for any application condition was not as significant as for 10 mM sodium phosphate treatment for 1 day at room temperature (which was 0.04 mm/y).

Corrosion rate in the simulated solution is plotted in Figure 12 against inhibitor concentration for steel treated with sodium benzoate for 1 day at room temperature. Corrosion rate decreases with increasing inhibitor concentration stabilizing above an inhibitor concentration of 10 mM. The specimens treated with 1 mM or lower concentration of sodium benzoate corroded even during inhibitor application (for 24 hours) resulting brown/rust-like spots on the specimens and also a brownish color in the inhibitor solution.

Figure 13 shows a plot of corrosion rate vs inhibitor concentration for steel treated with sodium benzoate for 5 minutes at 70°C. Inhibitor performance was little better than that of room temperature application.

4.1.3 INHIBITOR: SODIUM NITRATE

Corrosion rates of steel specimens treated with 10 mM sodium nitrate at three different application conditions are compared to that of control in Figure 14. Treatment by sodium nitrate also decreased the corrosion rate of steel in the simulated solution. However, they corroded at a little higher rate than those treated by the previous two inhibitors studied.

A plot of corrosion rate vs inhibitor concentration is shown in Figure 15 for steel treated with sodium nitrate for 1 day at room temperature. Change in inhibitor

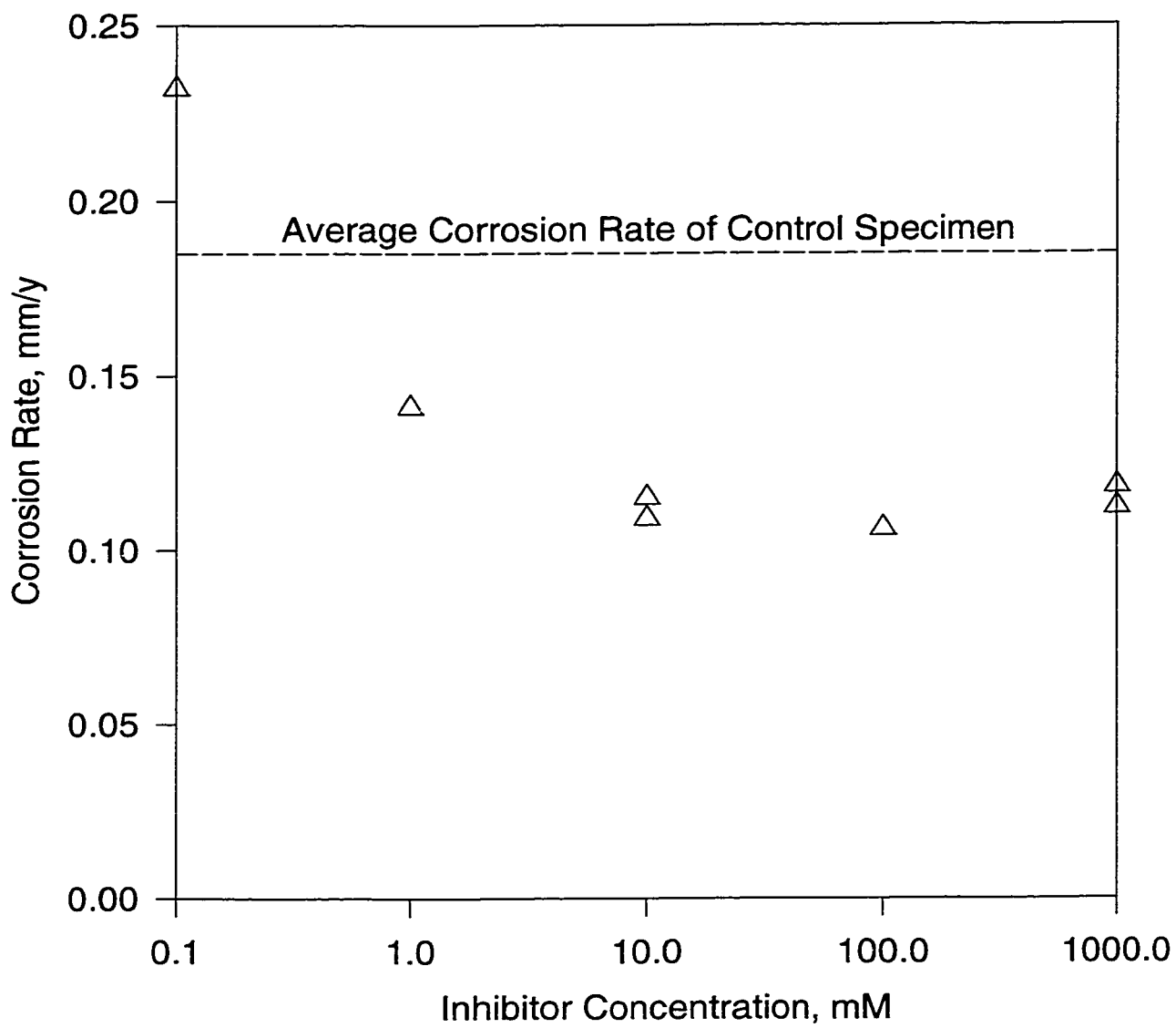


Figure 12. Corrosion rate vs inhibitor concentration for steel treated with sodium benzoate for 1 day at room temperature.

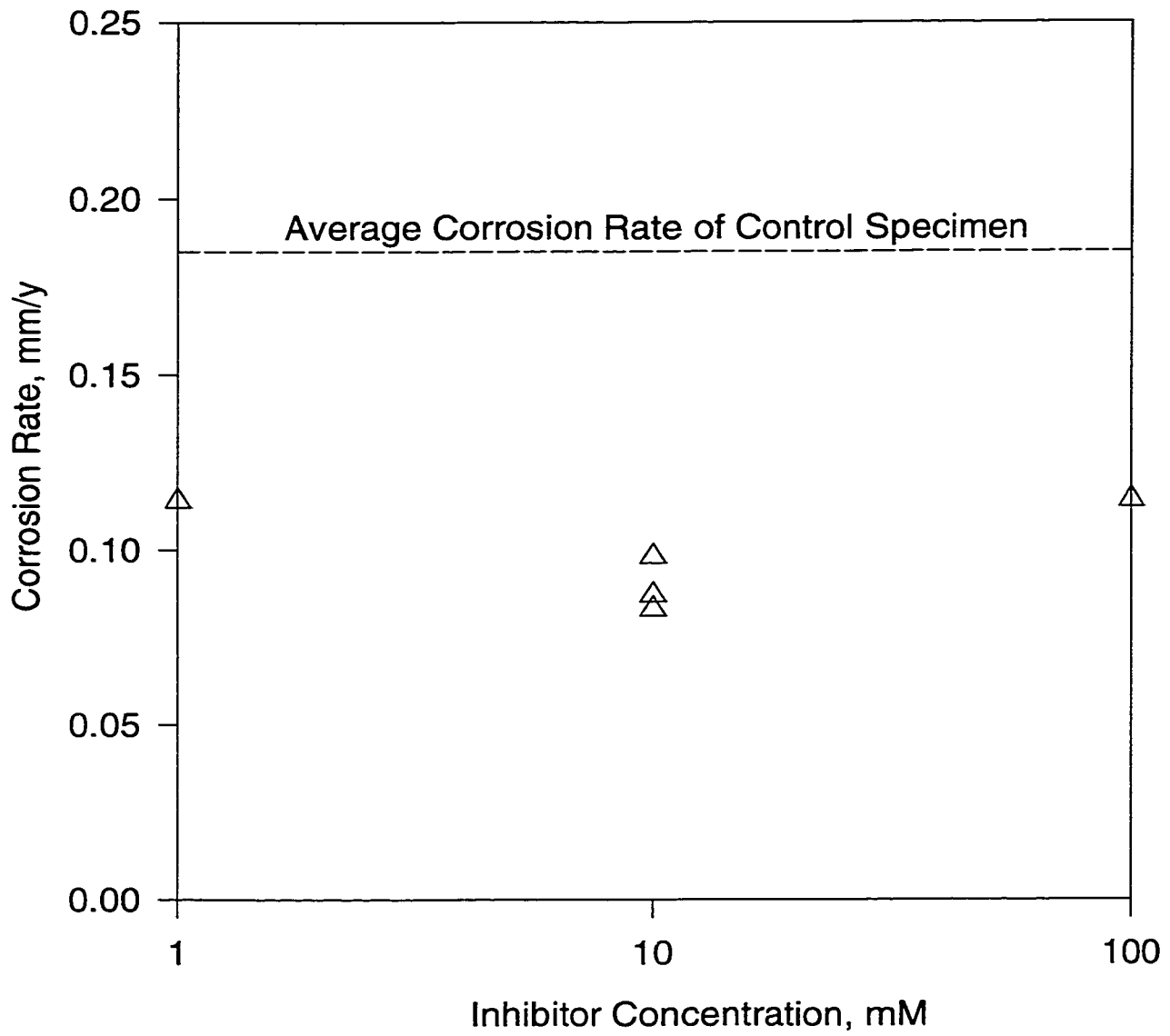


Figure 13. Corrosion rate vs inhibitor concentration for steel treated with sodium benzoate for 5 minutes at 70°C.

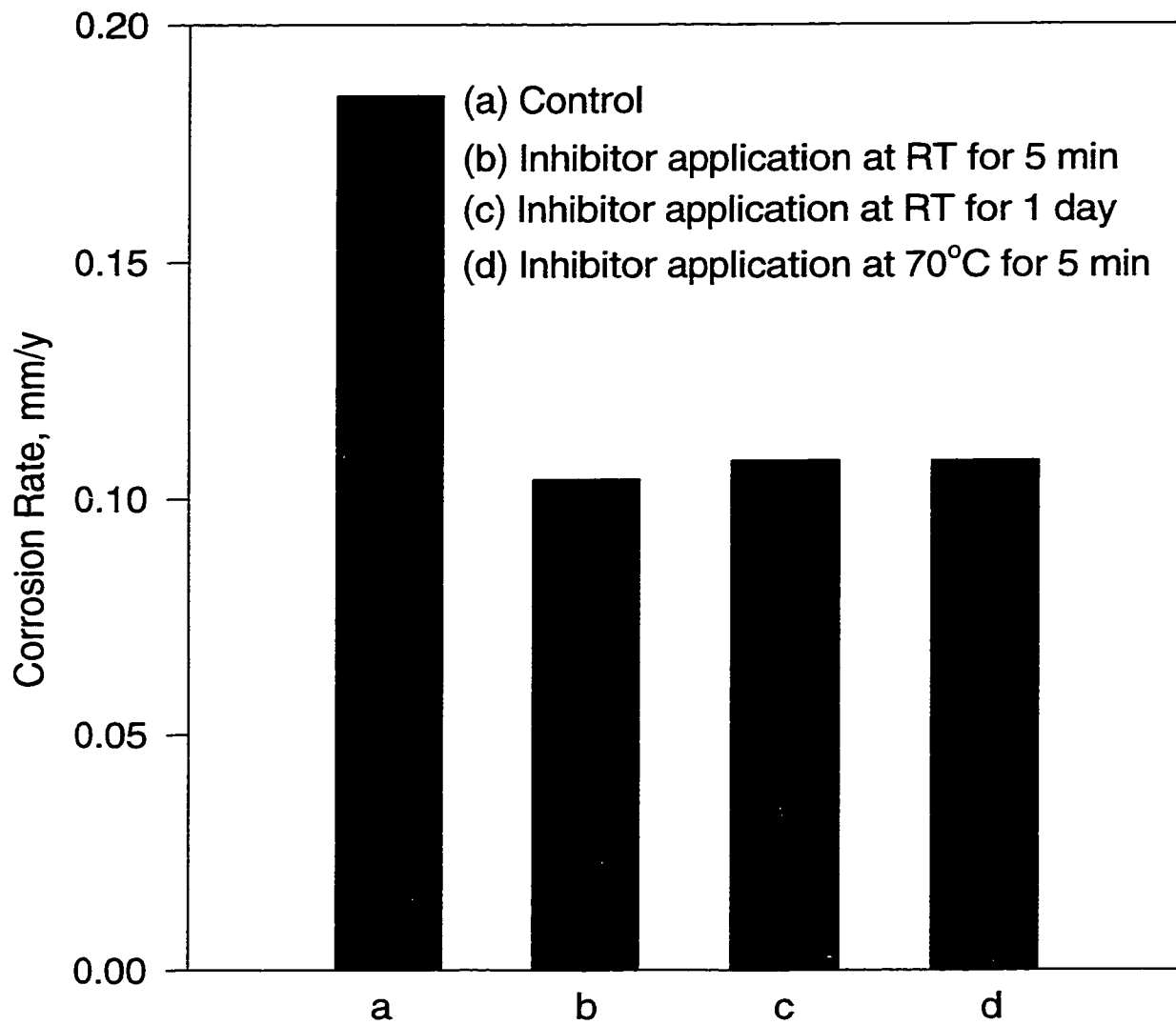


Figure 14. Corrosion rates of unprotected and 10 mM sodium nitrate treated steel specimens at various treatment conditions.

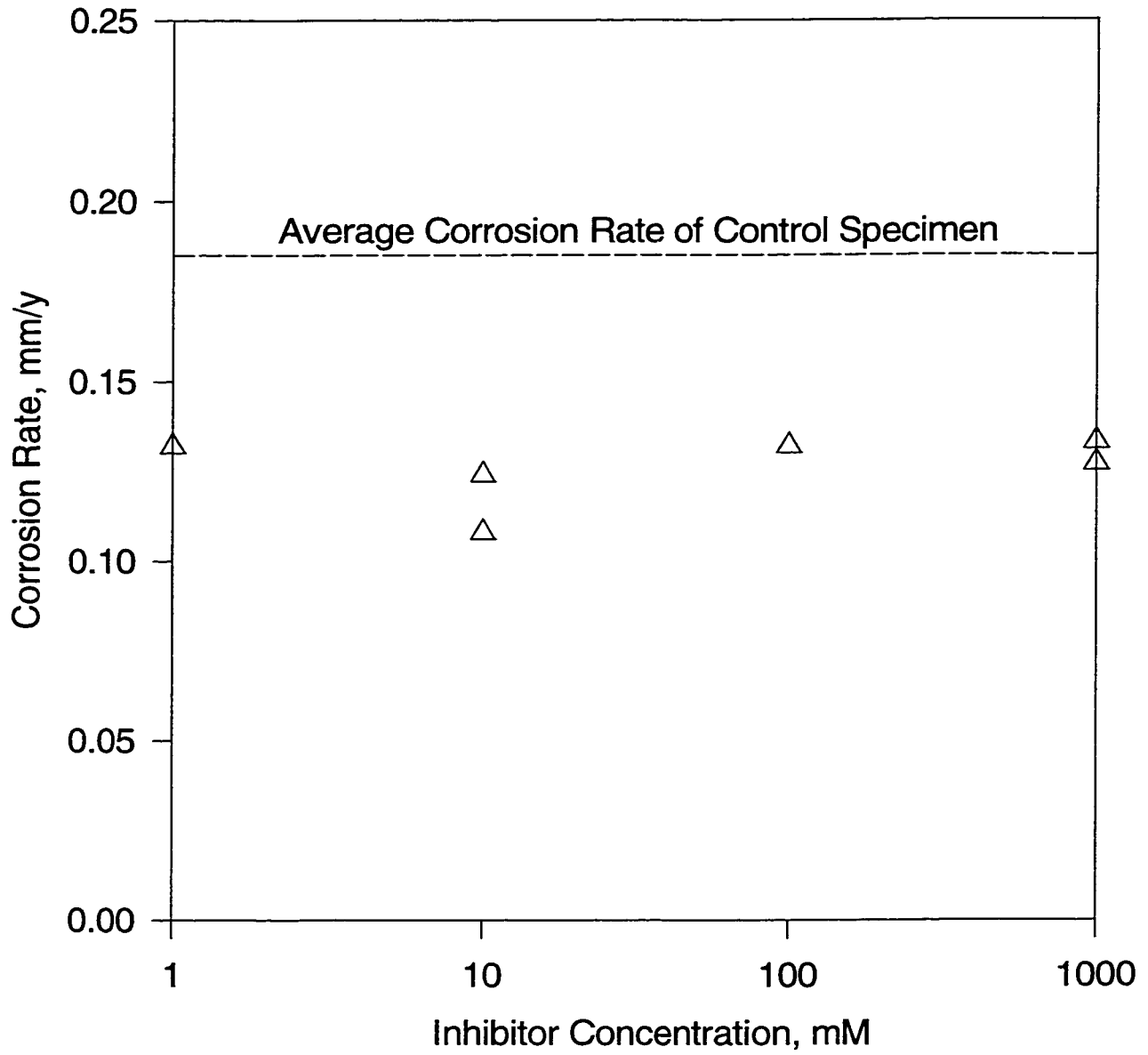


Figure 15. Corrosion rate vs inhibitor concentration for steel treated with sodium nitrate for 1 day at room temperature.

concentration did not have any significant effect on corrosion inhibition for the case of sodium nitrate.

Corrosion rates of steel specimens treated with 10 and 100 mM sodium nitrate for 5 minutes at 70°C are compared to that of untreated steel in Figure 16. An increase of about 50°C did not improve the inhibition performance of sodium nitrate for an inhibitor application duration of 5 minutes.

4.1.4 INHIBITOR: SODIUM NITRITE

Figure 17 compares the corrosion rates of steel specimens treated with 10 mM sodium nitrite at room temperature for 5 minutes and 1 day to that of the control specimen. Inhibition performance of sodium nitrite was not that good at 10 mM especially for 1 day application. It should be noted that the aqueous inhibitor solution becomes a corrosive environment for steel if the inhibitor concentration is not high enough and the steel specimen stays in that solution much longer for 1 day application than just 5-minute application. That is probably the reason for the lower inhibition performance of 1-day treatment with 10 mM sodium nitrite as also indicated in Figure 18 which shows a plot of corrosion rate vs inhibitor concentration for the same treatment condition. Inhibition performance of sodium nitrite at 1 and 10 mM concentration are not as good as at 100 or 1000 mM concentration.

Sodium nitrite was not applied at 70°C because of its flammability and toxicity at higher temperatures.

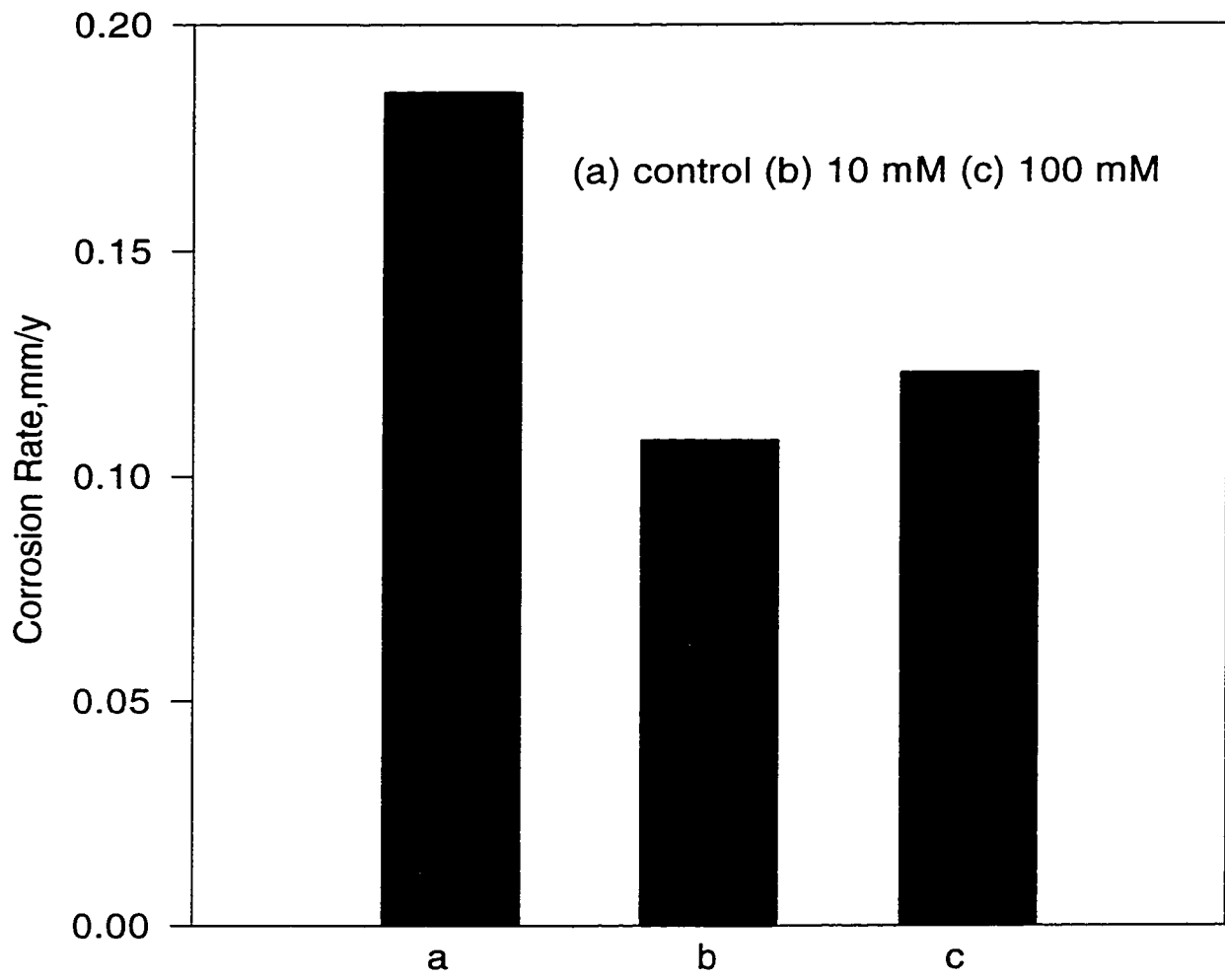


Figure 16. Corrosion rates of unprotected steel and steel treated with 10 and 100 mM sodium nitrate for 5 minutes at 70°C.

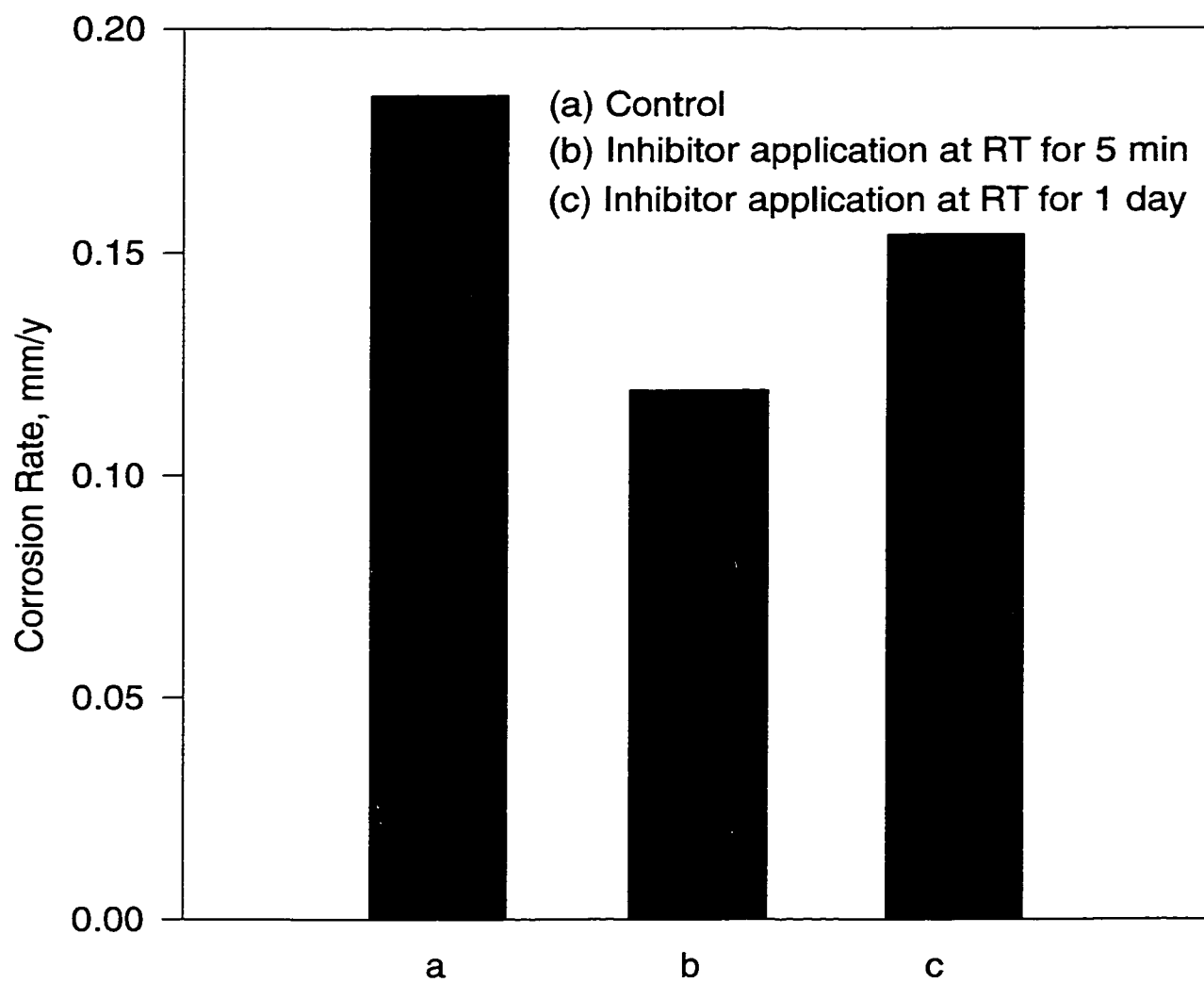


Figure 17. Corrosion rates of unprotected and 10 mM sodium nitrite treated steel specimens at various treatment conditions.

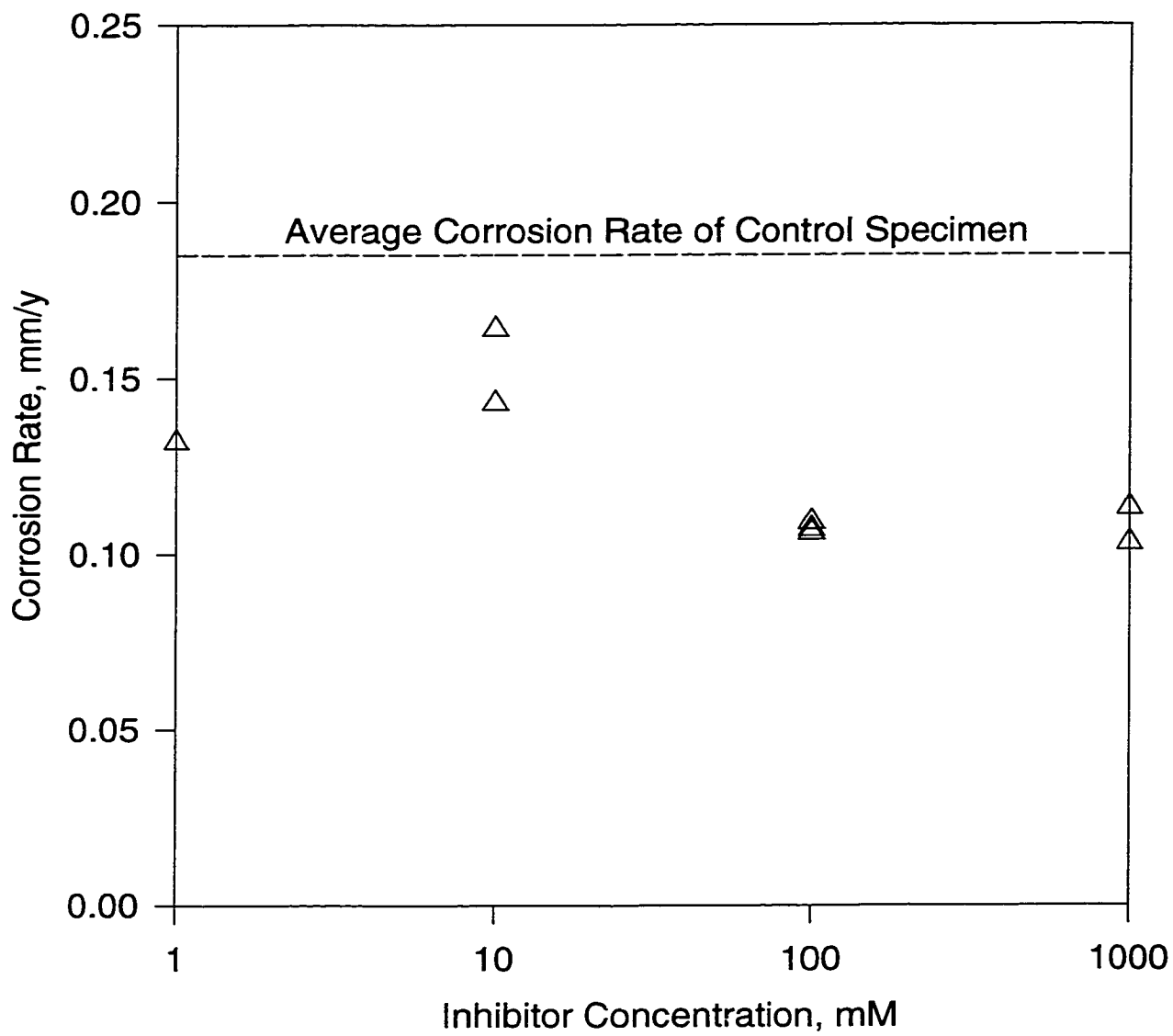


Figure 18. Corrosion rate vs inhibitor concentration for steel treated with sodium nitrite for 1 day at room temperature.

4.1.5 CONCLUDING REMARKS ON THE ABOVE RESULTS

The following remarks can be deduced from the above results:

- Treatment of steel with 10 or 100 mM sodium phosphate for 1 day at room temperature resulted in the best inhibition of corrosion in the simulated aqueous solution of 2% NaCl and 1% Na₂SO₄. Higher (1000 mM) or lower (1 mM) inhibitor concentrations caused an increase in corrosion rate of steel.
- Corrosion inhibition performances of sodium benzoate and sodium nitrite were similar and little better than that of sodium nitrate when enough quantities were used (10, 100 or 1000 mM for sodium benzoate and 100 or 1000 mM for sodium nitrite).
- Application of the inhibitors at a higher temperature (70°C) than room temperature did not have a significant effect on their performance.

In light of the above concluding remarks, sodium phosphate as an inorganic inhibitor and sodium benzoate as an organic inhibitor were selected for examination against atmospheric corrosion of steel to be applied at 10 and 100 mM concentrations for 1 day at room temperature.

4.2 ATMOSPHERIC CORROSION STUDY

Atmospheric corrosion of as received and inhibitor treated steel specimens was studied using electrochemical tests, weight loss measurements and morphological

analysis by photography and scanning electron microscopy (SEM). The results obtained are presented and discussed below.

4.2.1 ELECTROCHEMICAL TESTS

Corrosion rates of unprotected and inhibitor treated steel specimens were determined in the simulated solution of 2% NaCl and 1% Na₂SO₄ by the electrochemical technique before and after exposing them in the atmosphere for specified durations. These measurements obviously do not give the rate of atmospheric corrosion, however they give an indication of the level of corrosion inhibition before and after atmospheric exposure. The results obtained are presented in Figure 19 as corrosion rate relative to that of the untreated steel vs exposure time for untreated, 10 and 100 mM sodium benzoate treated and 10 and 100 mM sodium phosphate treated steel specimens. Each value is an average of three tests. Standard deviations were also included in the plot.

Corrosion rates in the simulated solution before any atmospheric exposure were about 0.135, 0.10, 0.09, 0.06 and 0.035 mm/y for steel as received, steel treated with 10 mM sodium benzoate, steel treated with 100 mM sodium benzoate, steel treated with 10 mM sodium phosphate and steel treated with 100 mM sodium phosphate, respectively, as also presented in the previous section. Corrosion inhibition by sodium phosphate treatment was much more significant than by sodium benzoate treatment. 100 mM inhibitor concentration resulted in a better corrosion protection than 10 mM concentration, in general.

Corrosion rate of all specimens increased significantly with exposure time, probably due to the increase in corrosive atmospheric contamination on the exposed

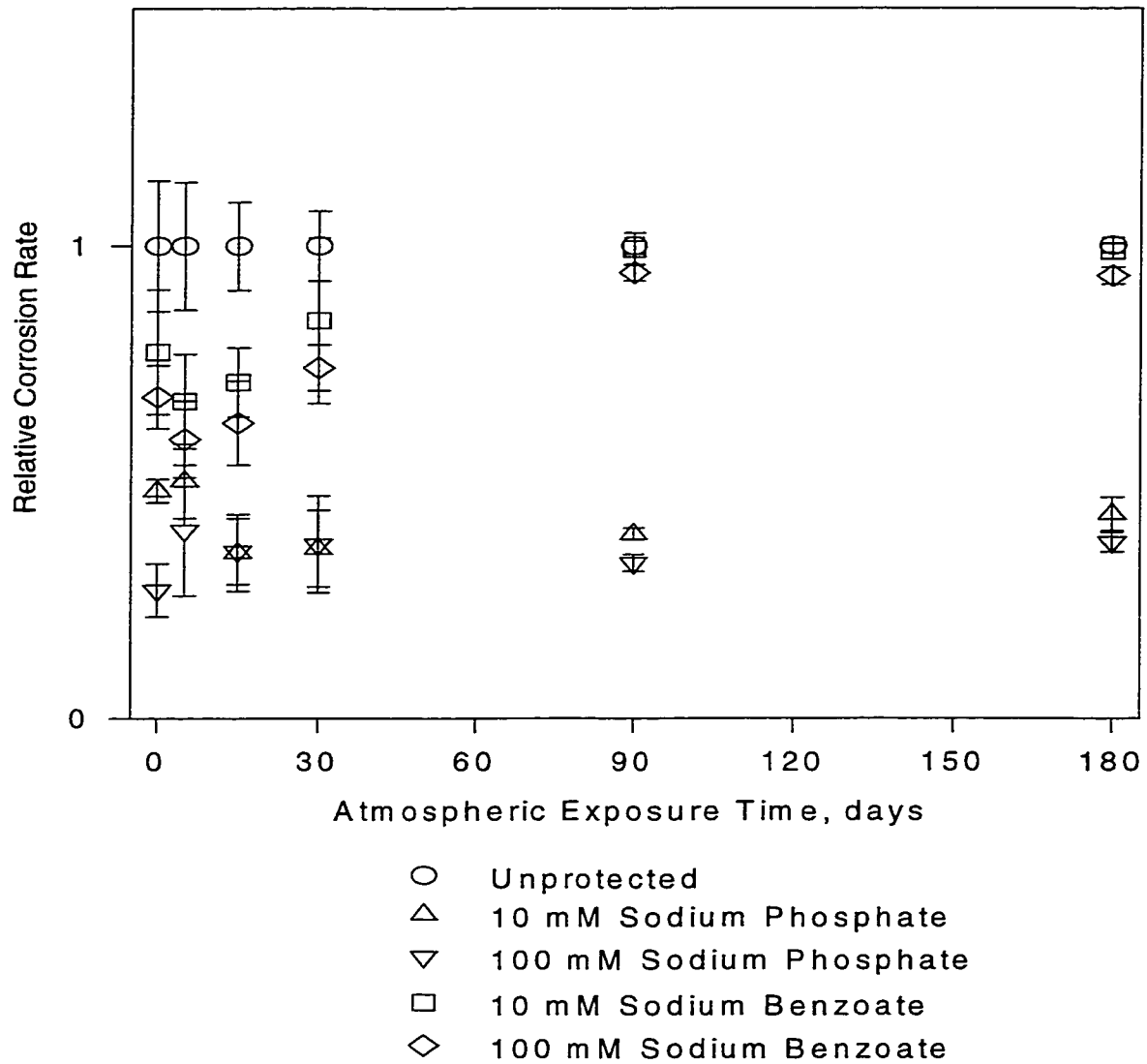


Figure 19. Corrosion rates of untreated and inhibitor treated steel specimens in the simulated solution of 2% NaCl and 1% Na₂SO₄ vs duration of atmospheric exposure.

specimens with time. However, since the corrosion rates of the inhibitor treated specimens relative to that of the untreated ones were of concern and for a more clear presentation, relative corrosion rates were used in the plot. The actual rates can be found in Appendix E.

15 days of atmospheric exposure did not cause deterioration in corrosion inhibition performance of sodium benzoate. However, a deterioration in the corrosion inhibition was observed for 30 or more days of atmospheric exposure. Corrosion rates of untreated and sodium benzoate treated specimens were similar in the simulated solution after 3 or more months of atmospheric exposure.

Sodium phosphate treatment, on the other hand, retained its effectiveness in corrosion inhibition even after 6 months of atmospheric exposure.

4.2.2 STUDY OF ATMOSPHERIC CORROSION

Atmospheric rates of untreated and inhibitor treated steel specimens were determined by weight loss measurements and plotted against exposure duration in Figure 20. The results are also compiled in Appendix C. As seen in Figure 20, after 15 days of exposure, the atmospheric corrosion rates determined are about 0.096, 0.074, 0.06, 0.04 and 0.035 mm/y for untreated steel, steel treated with 10 mM sodium benzoate, steel treated with 100 mM sodium benzoate, steel treated with 10 mM sodium phosphate and steel treated with 100 mM sodium phosphate, respectively.

Atmospheric corrosion rates of the inhibitor treated specimens were lower than that of the unprotected specimens for the case of both inhibitors. However, sodium

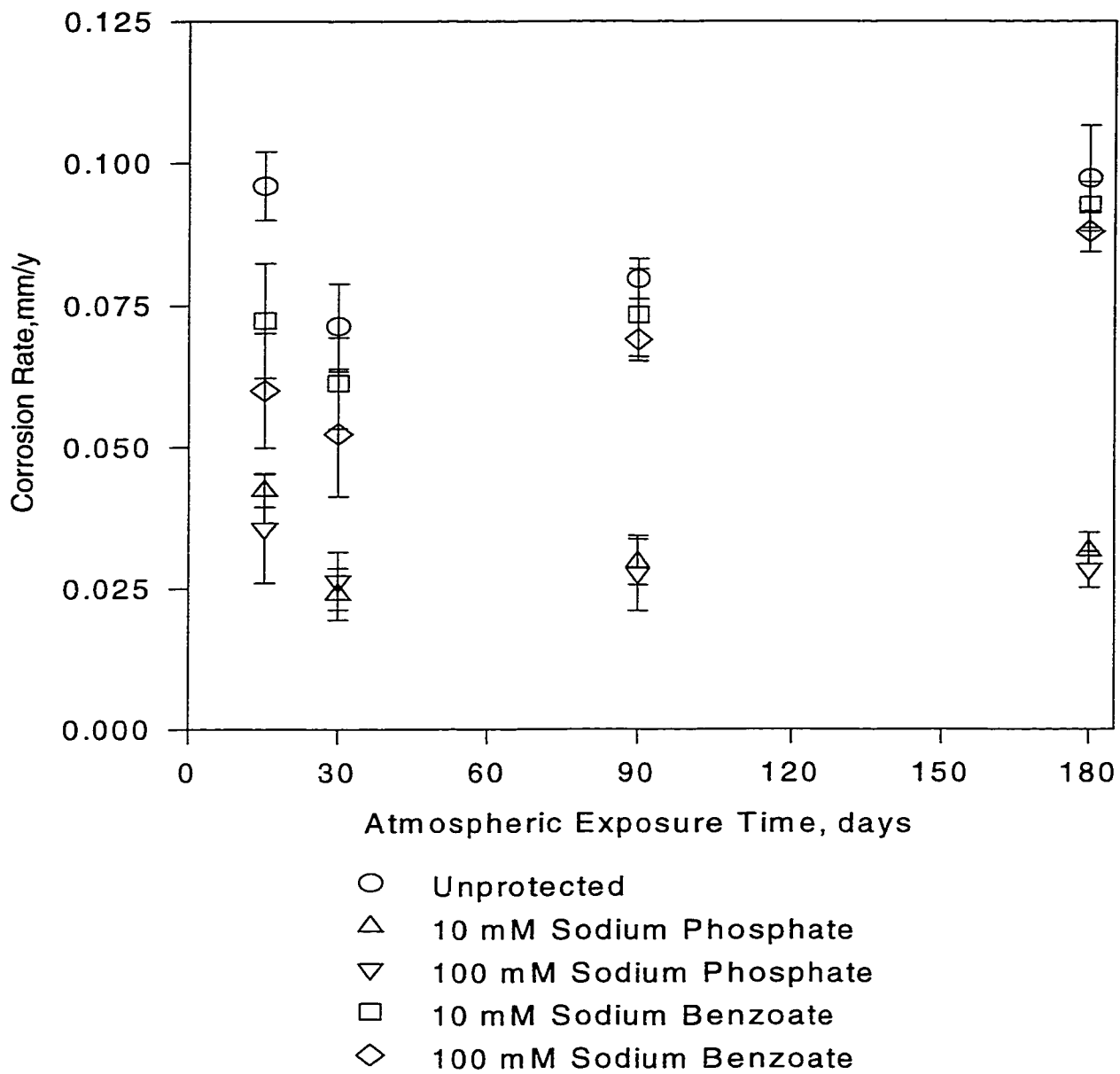


Figure 20. Atmospheric corrosion rate of untreated and inhibitor treated steel vs atmospheric exposure period.

phosphate treatment was more effective in inhibiting atmospheric corrosion than sodium benzoate treatment. 100 mM inhibitor concentration resulted again in better protection against atmospheric corrosion than 10 mM concentration. However, the difference in their effectiveness was not that significant for the case of sodium phosphate.

Atmospheric corrosion rates of sodium phosphate treated specimens stayed low even after 6 months of exposure.

Atmospheric corrosion inhibition performance of sodium benzoate, on the other hand, deteriorated with exposure time. Atmospheric corrosion rates of sodium benzoate treated specimens were close to that of the untreated specimens after 30 or more days of atmospheric exposure.

4.2.3 MORPHOLOGICAL ANALYSIS OF CORROSION SPECIMENS

Steel specimens were observed by photography during their exposure to atmosphere. Figures 21 and 22 show untreated specimens after a month of atmospheric exposure. Significant discoloration on the steel specimens, especially on the polished cross-sectional surface of the steel specimens for electrochemical tests, can be seen. Specimens treated with sodium benzoate or sodium phosphate, on the other hand, did not show such discoloration at the end of their exposure to atmosphere for 30 days (Figures 23, 24, 25, 26, 27, 28, 29, 30). A white coating on the sodium phosphate treated specimens was still present as seen in Figures 27, 28, 29 and 30 and it was more extensive on the specimens treated with 100 mM solution than on those treated with 10 mM solution, as also mentioned earlier.

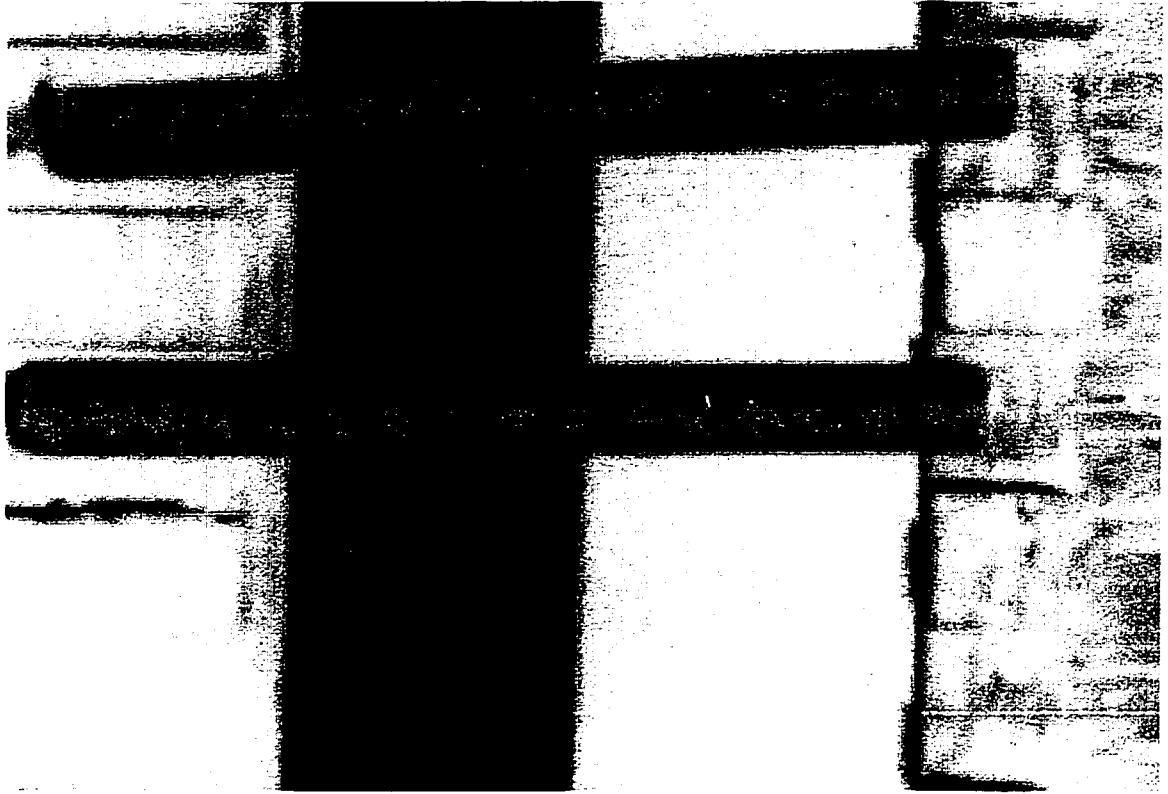


Figure 21. Photograph of untreated weight loss test specimens after a month of atmospheric exposure.



Figure 22. Photograph of untreated electrochemical test specimens after a month of atmospheric exposure.

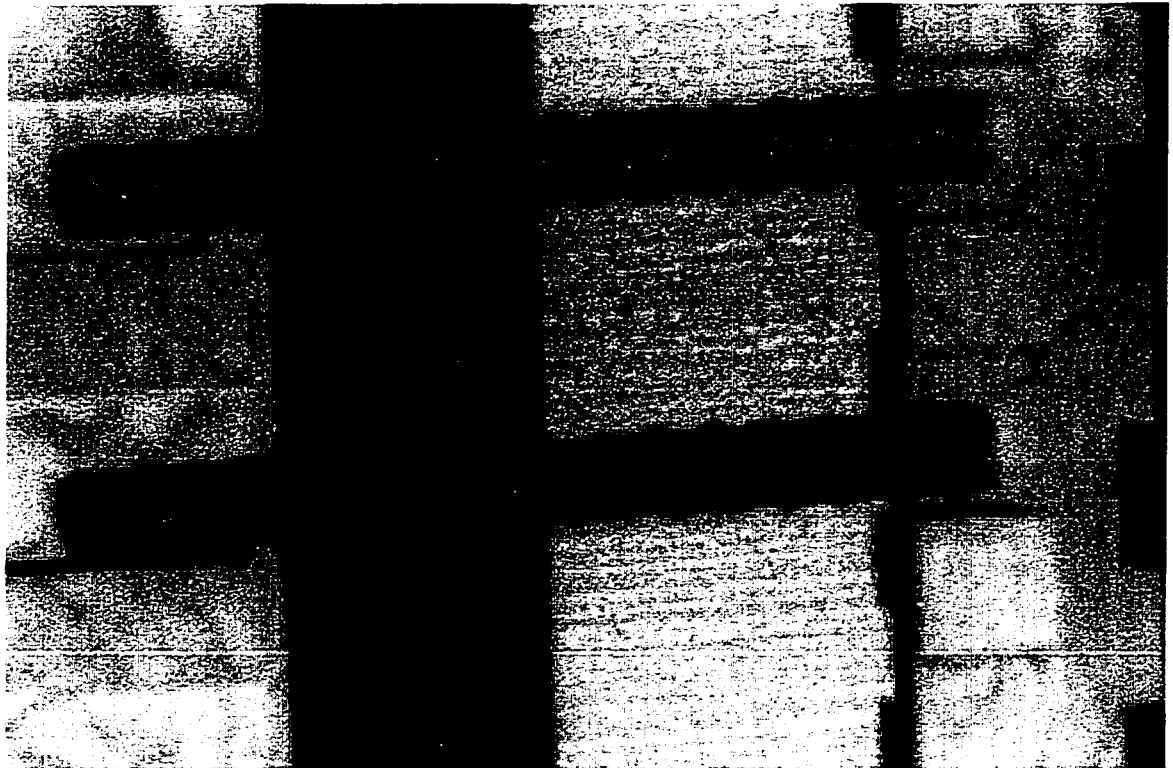


Figure 23. Photograph of weight loss test specimens exposed to atmosphere for one month after treatment with 10 mM sodium benzoate.

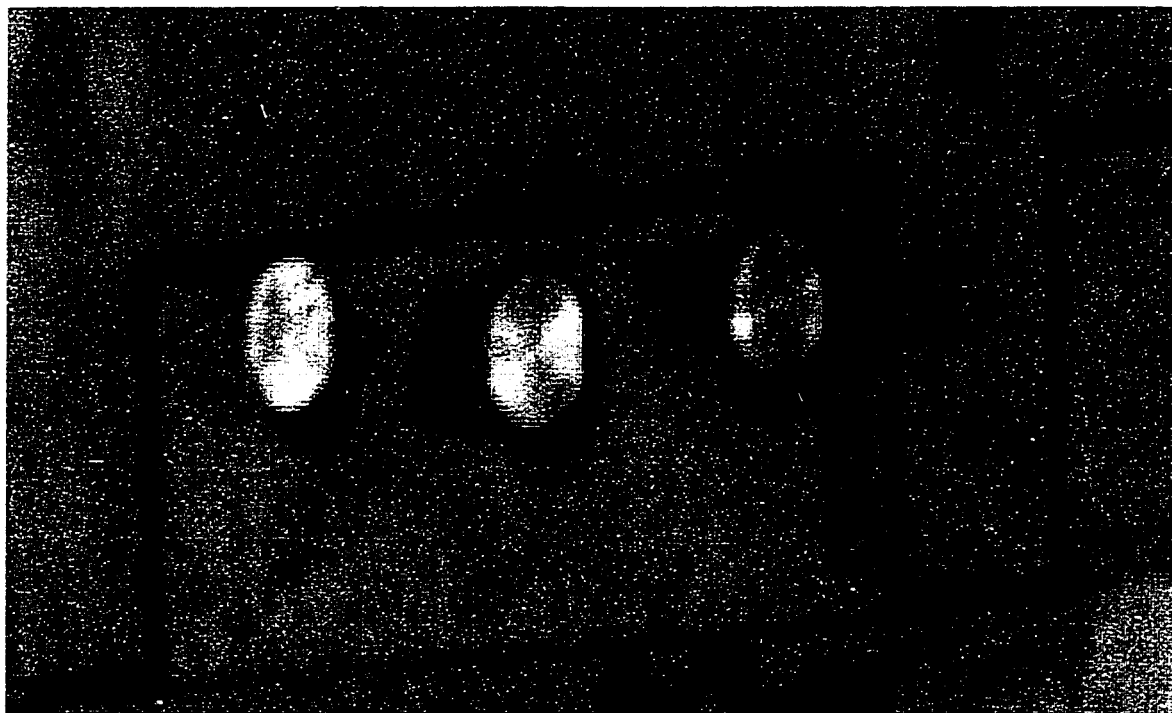


Figure 24. Photograph of electrochemical test specimens exposed to atmosphere for a month after treatment with 10 mM sodium benzoate.

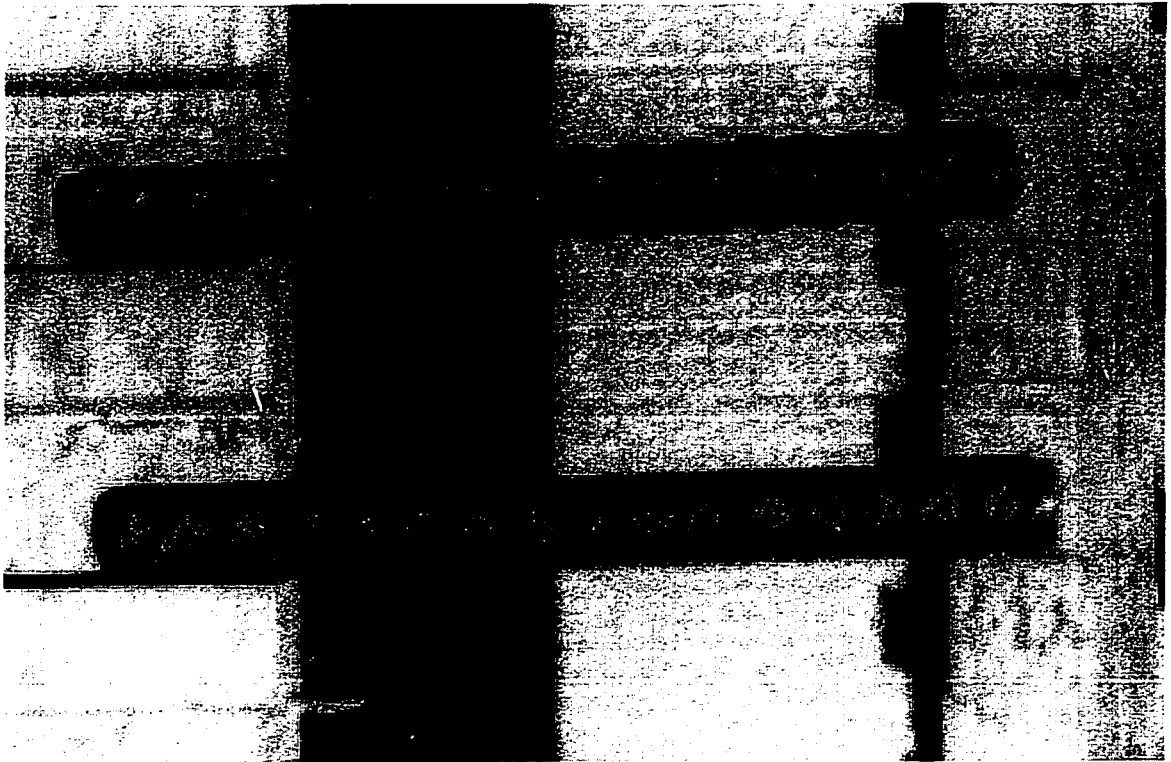


Figure 25. Photograph of weight loss test specimens exposed to atmosphere for a month after treatment with 100 mM sodium benzoate.

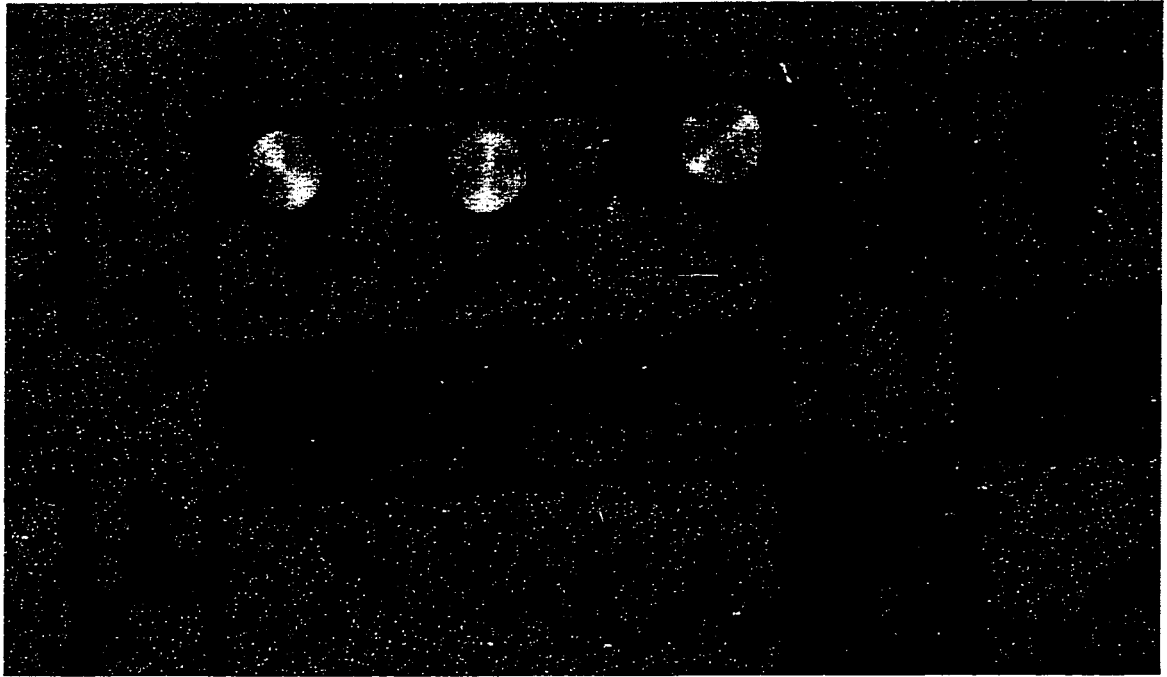


Figure 26. Photograph of electrochemical test specimens exposed to atmosphere for a month after treatment with 100 mM sodium benzoate.

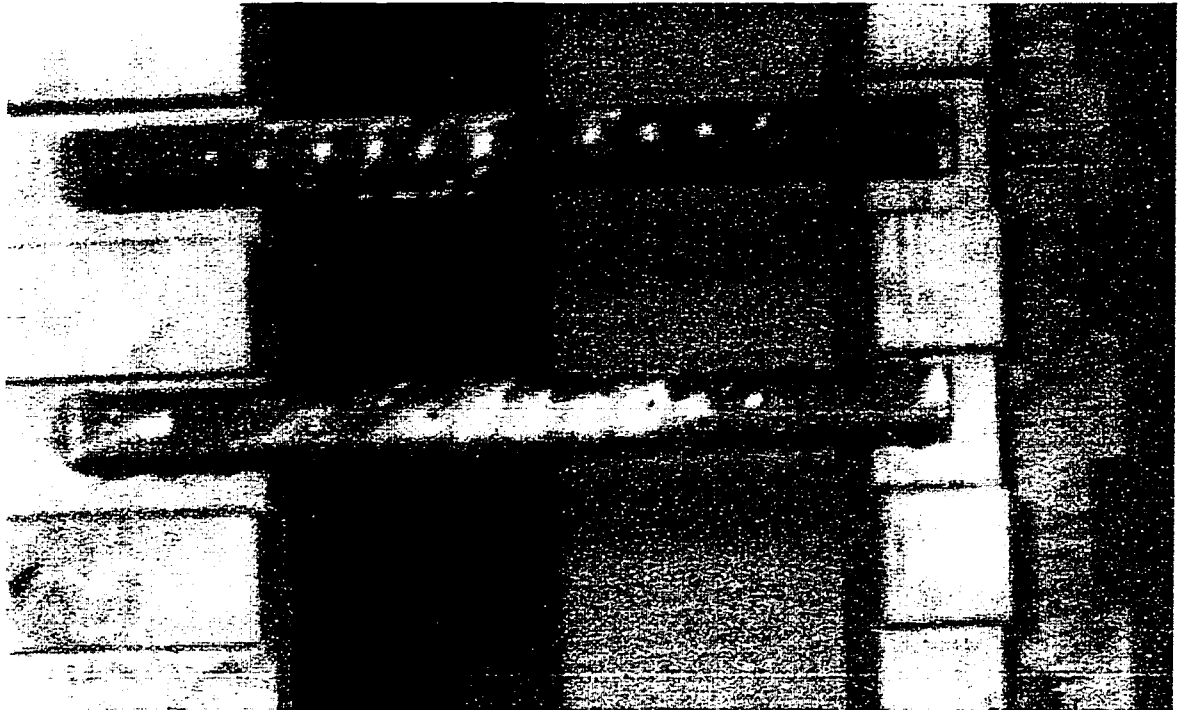


Figure 27. Photograph of weight loss test specimens exposed to atmosphere for a month after treatment with 10 mM sodium phosphate.

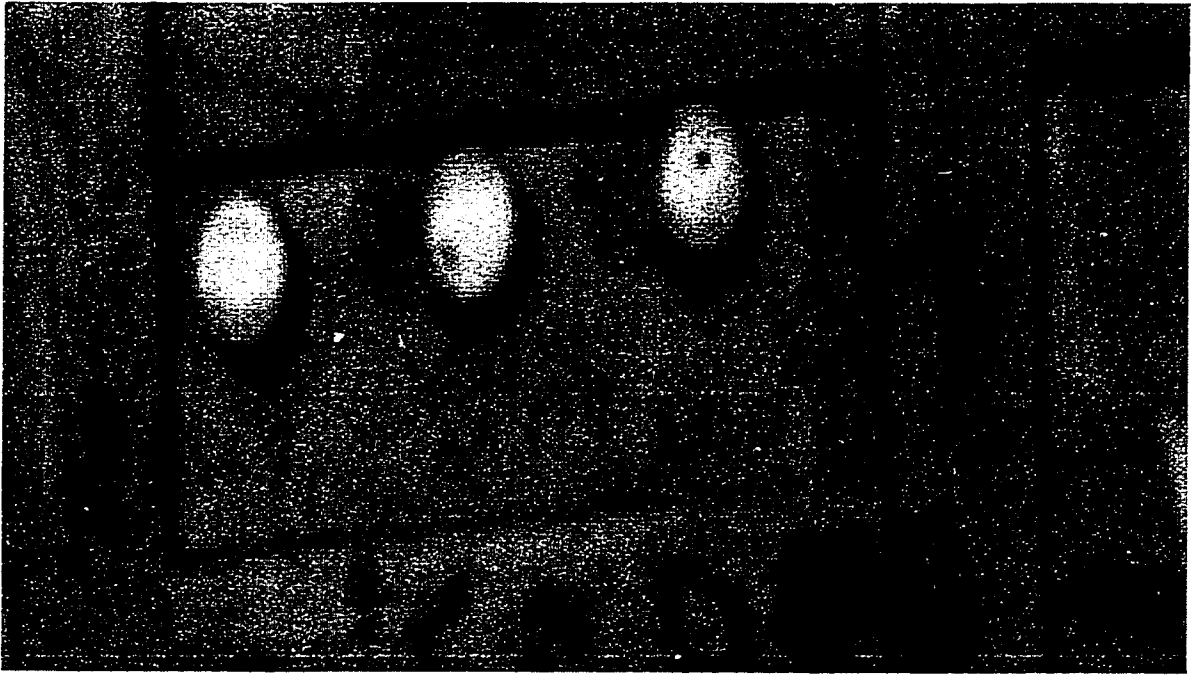


Figure 28. Photograph of electrochemical test specimens exposed to atmosphere for a month after treatment with 10 mM sodium phosphate.

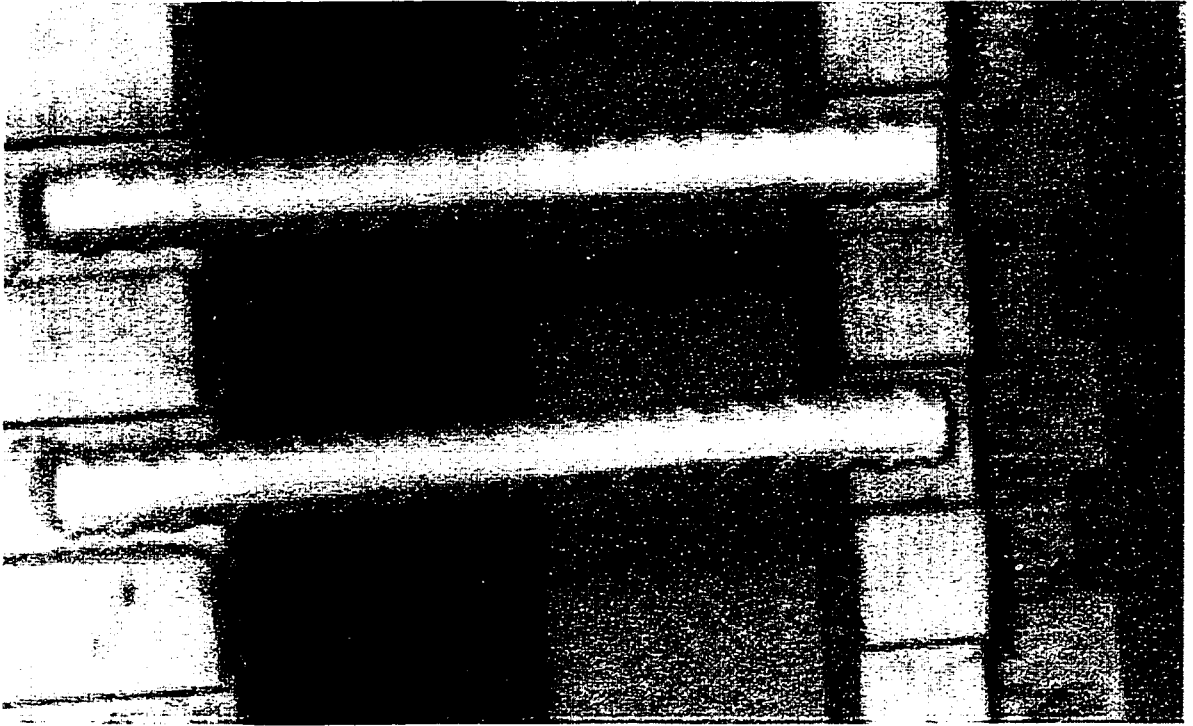


Figure 29. Photograph of weight loss test specimens exposed to atmosphere for a month after treatment with 100 mM sodium phosphate.

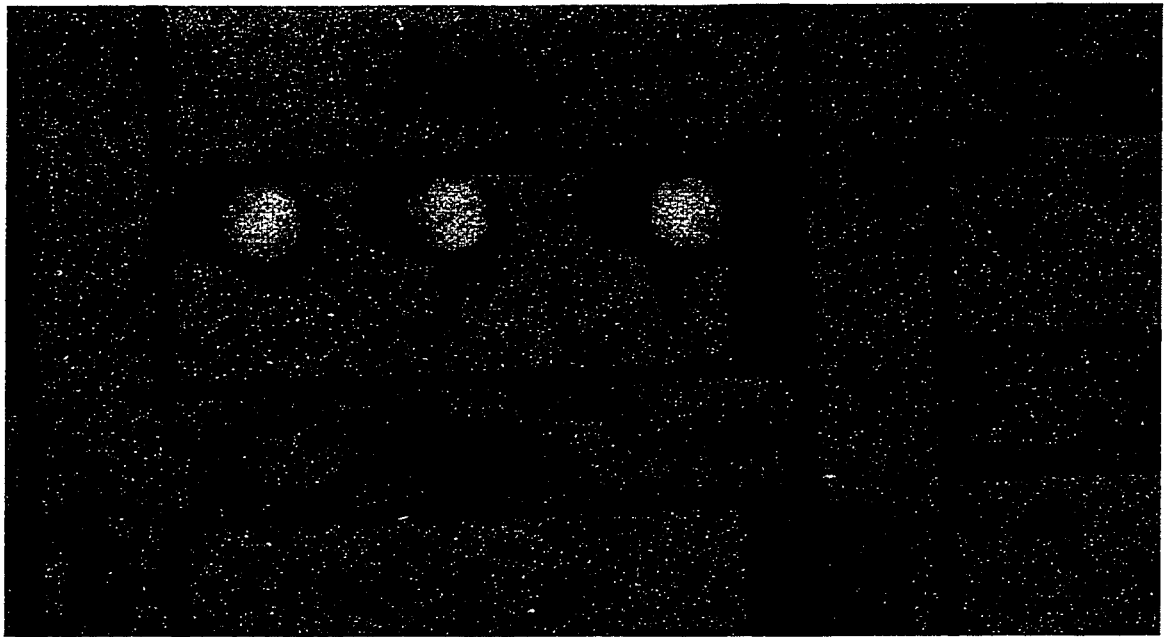


Figure 30. Photograph of electrochemical test specimens exposed to atmosphere for a month after treatment with 100 mM sodium phosphate.

Extent of discoloration on the steel specimens increased with exposure period (Figures 31, 32, 33, 34, 35, 36, 37, 38, 39, 40). 3 months of atmospheric exposure resulted in heavy corrosion on the untreated specimens. Discoloration was also extensive on sodium benzoate treated specimens (Figures 33, 34, 35, and 36). However, as the figures show, corrosion on the sodium benzoate treated specimens was not as significant as the corrosion on the untreated specimens. The discoloration on the sodium phosphate treated specimens was at a lower extent (Figure 37, 38, 39 and 40). White coating was still partially present on the specimens after 3 months of atmospheric exposure, especially on those treated with 100 mM sodium phosphate solution.

The above observations are in good agreement with the previously discussed corrosion rate measurements.

SEM/EDS studies were performed on an as received steel specimen (control) and inhibitor treated and untreated specimens after atmospheric exposure of 5 days. Photographs of the specimens are shown in Figures 41-45.

Figure 46 is an SEM micrograph taken on an as received steel specimen (control) after polishing. EDS analysis of the surface was presented in Table 1. As expected, no significant contamination but lots of polishing scratches were observed on the surface. The surface was composed of mostly iron with trace amounts of C, Al, Si, Cl, S, and Mn.

Figure 47 is an SEM micrograph of the surface of an untreated steel specimen at the end of 5 days of exposure to atmosphere. Table 3 presents the EDS analysis of that surface on three different points, one on the dark spot near the center, one on the bigger white spot at left and one at the center part away from the dark or white spots.

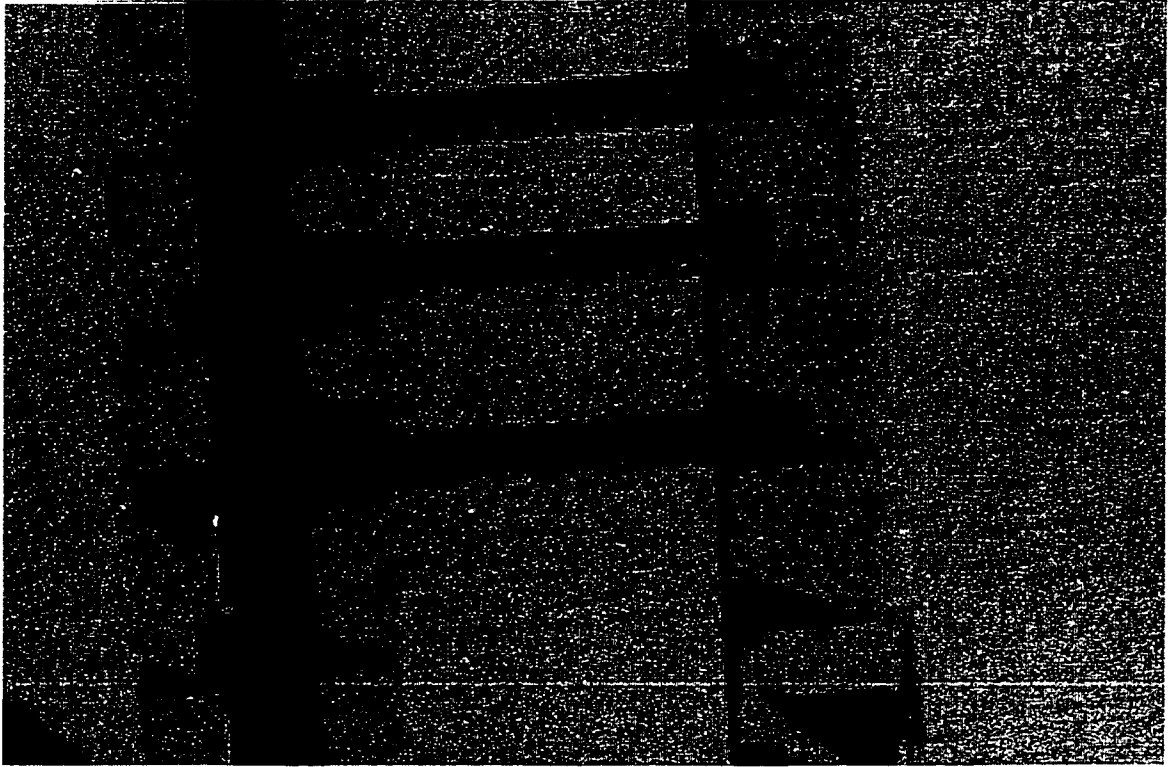


Figure 31. Photograph of untreated weight loss test specimens after 3 months of atmospheric exposure.

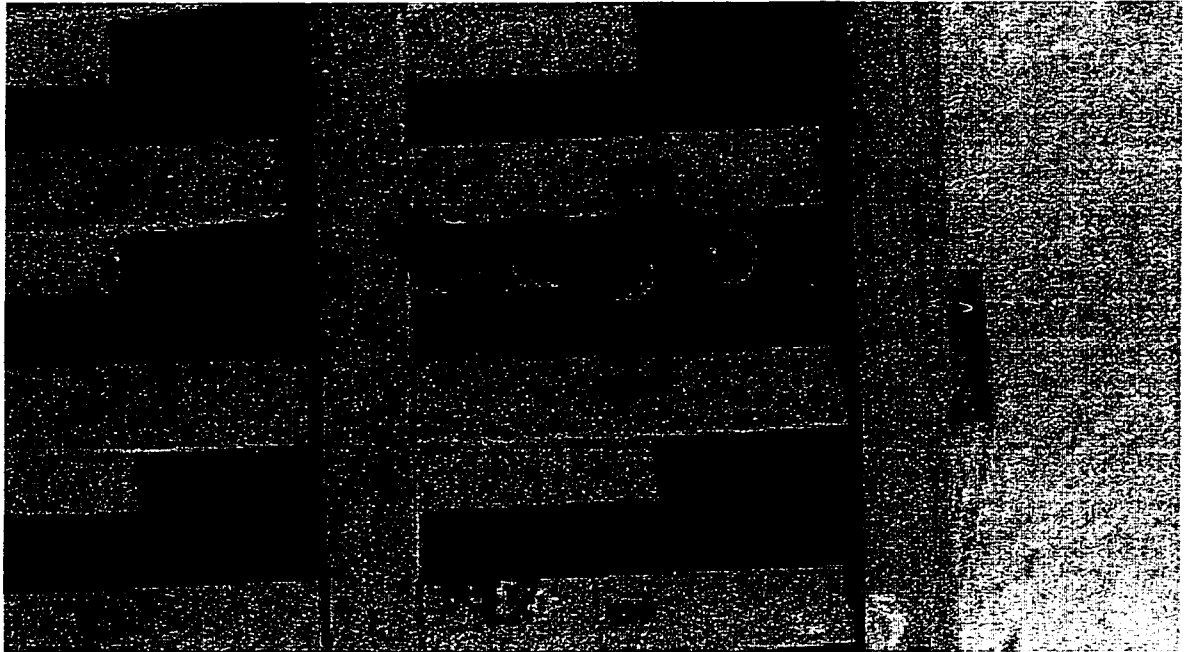


Figure 32. Photograph of untreated electrochemical test specimens after 3 months of atmospheric exposure.



Figure 33. Photograph of weight loss test specimens exposed to atmosphere for 3 months after treatment with 10 mM sodium benzoate.

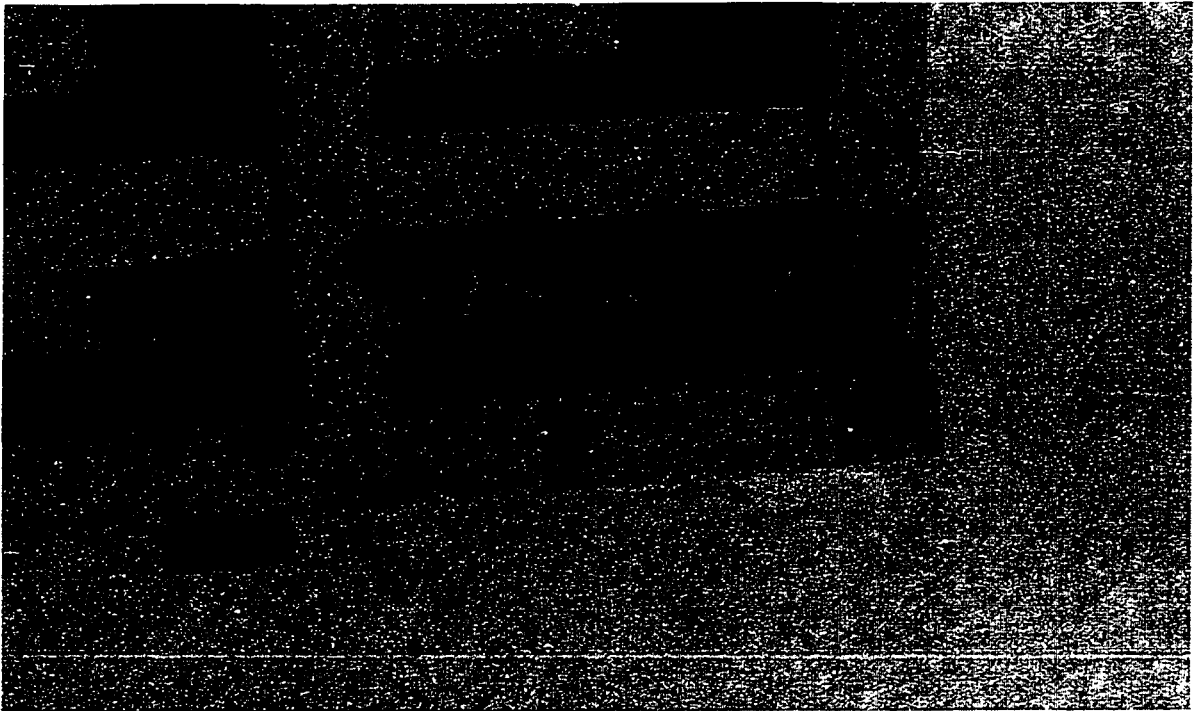


Figure 34. Photograph of electrochemical test specimens exposed to atmosphere for 3 months after treatment with 10 mM sodium benzoate.

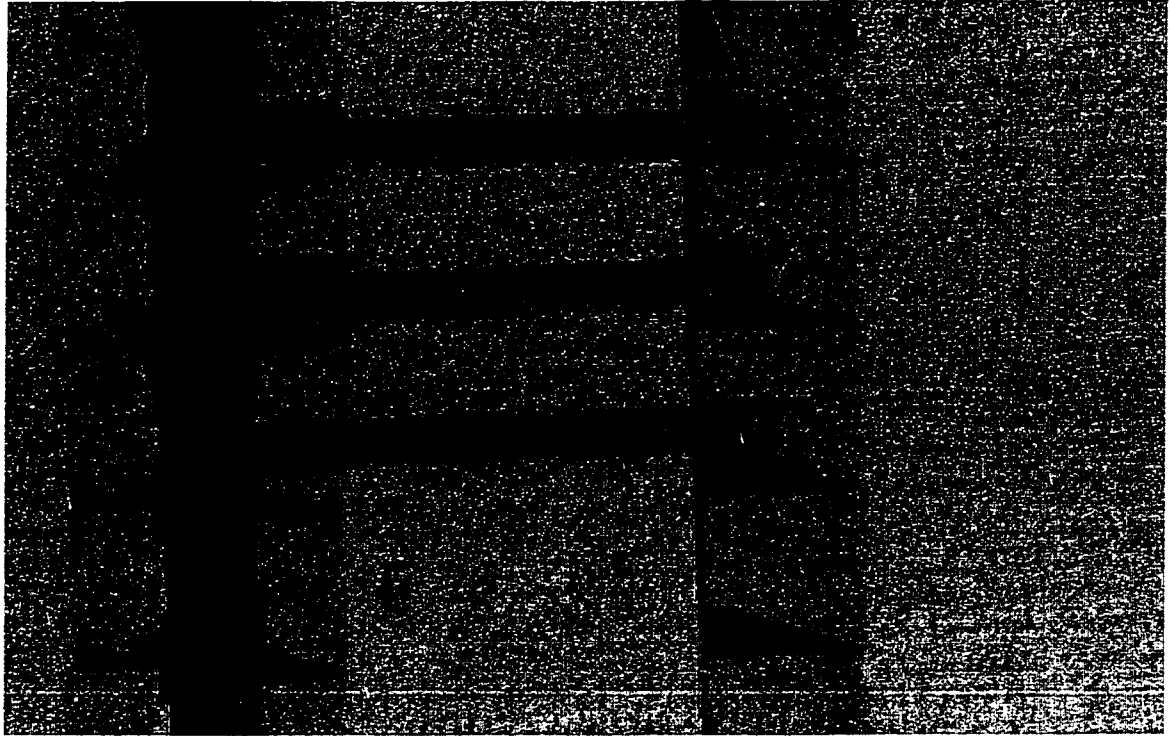


Figure 35. Photograph of weight loss test specimens exposed to atmosphere for 3 months after treatment with 100 mM sodium benzoate.

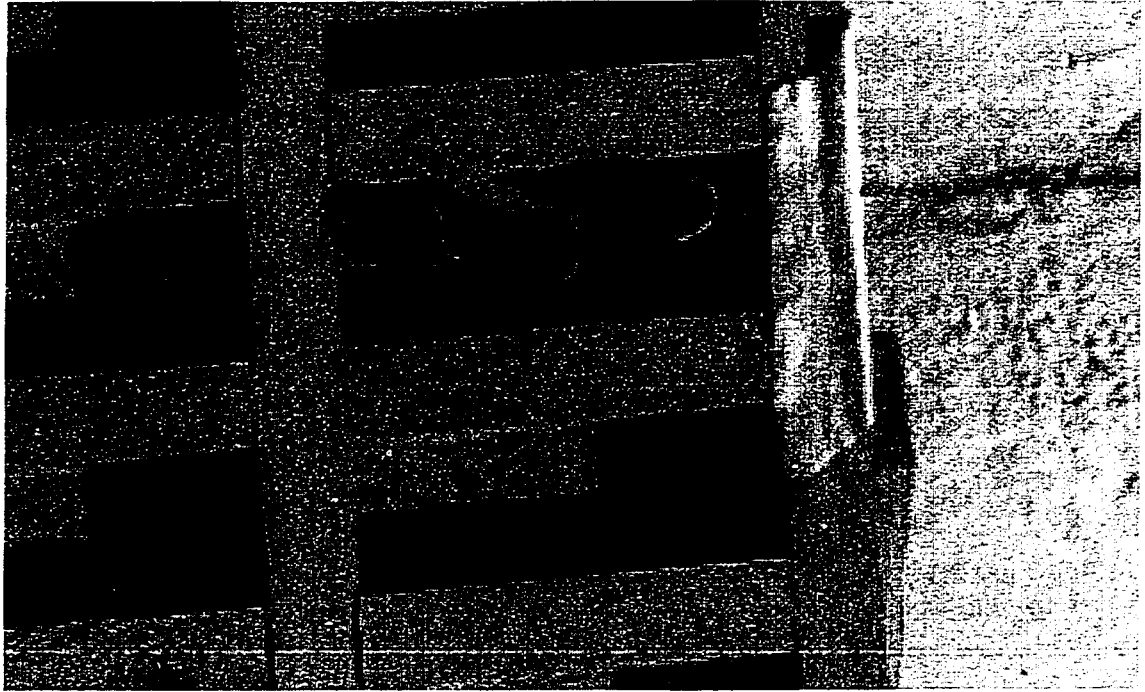


Figure 36. Photograph of electrochemical test specimens exposed to atmosphere for 3 months after treatment with 100 mM sodium benzoate.

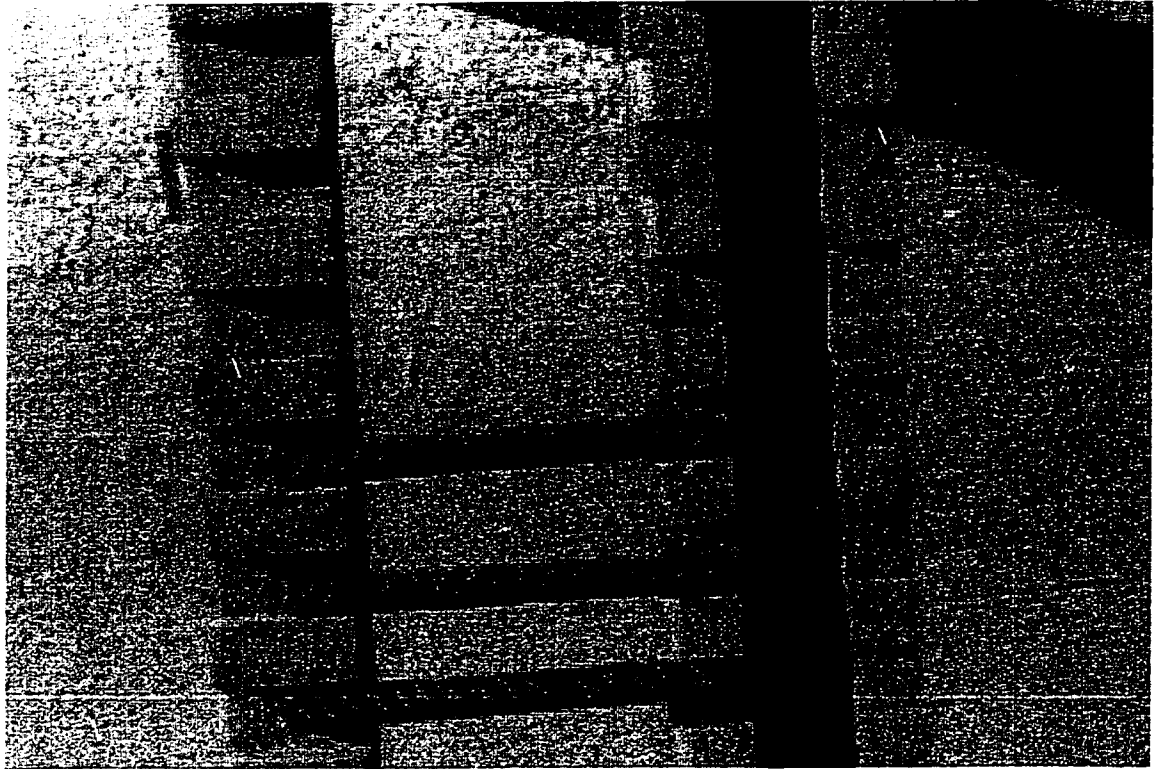


Figure 37. Photograph of weight loss test specimens exposed to atmosphere for 3 months after treatment with 10 mM sodium phosphate.



Figure 38. Photograph of electrochemical test specimens exposed to atmosphere for 3 months after treatment with 10 mM sodium phosphate.

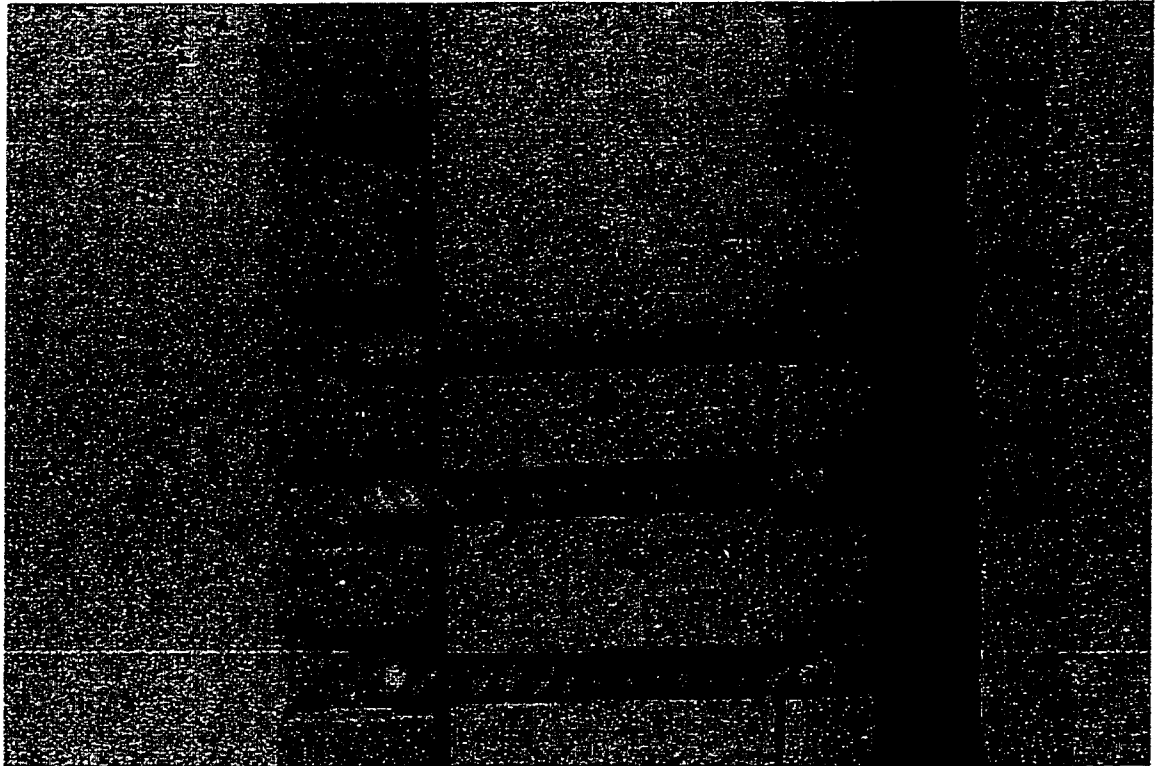


Figure 39. Photograph of weight loss test specimens exposed to atmosphere for 3 months after treatment with 100 mM sodium phosphate.

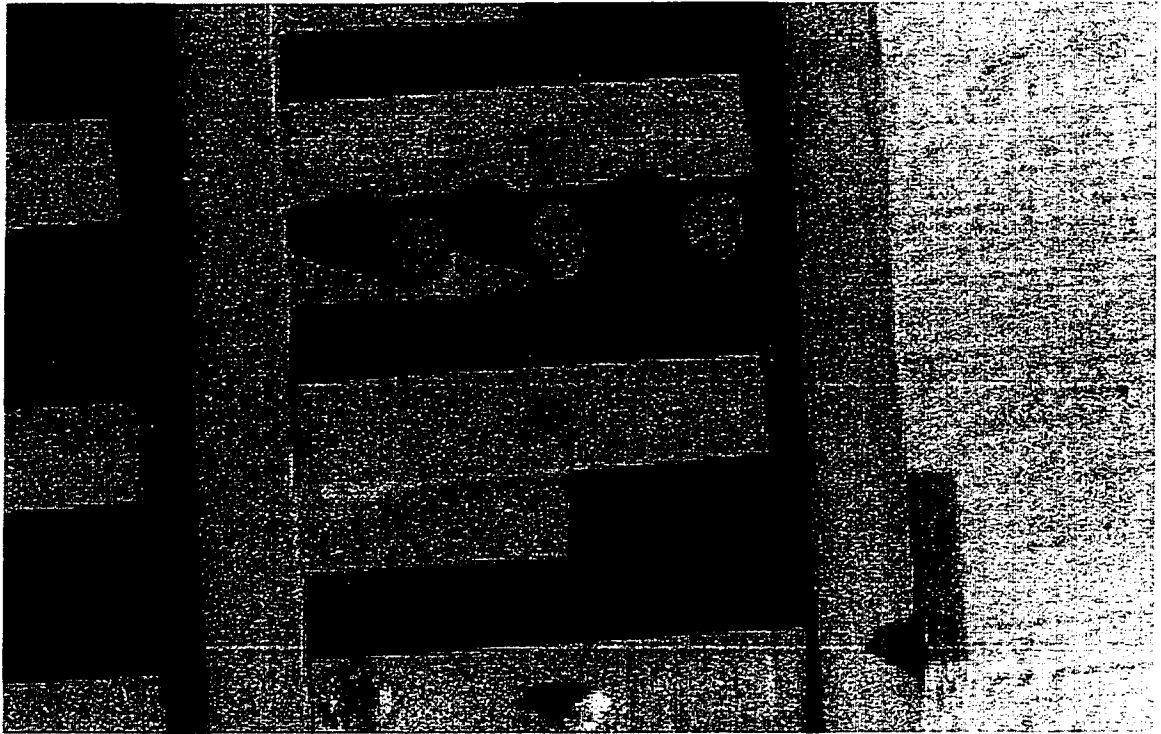


Figure 40. Photograph of electrochemical test specimens exposed to atmosphere for 3 months after treatment with 100 mM sodium phosphate.

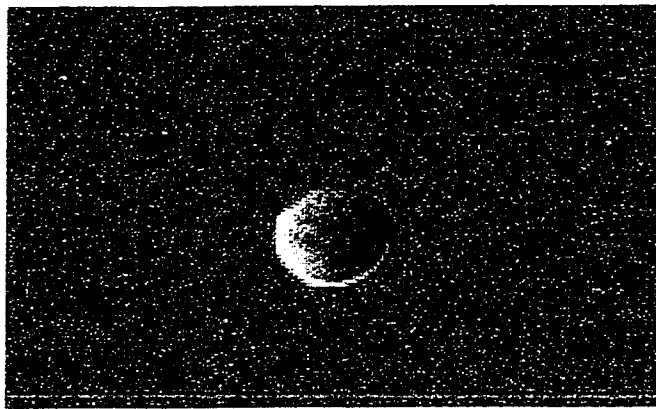


Figure 41. Photograph of the as-received steel specimen after polishing (control) for SEM/EDS analysis.

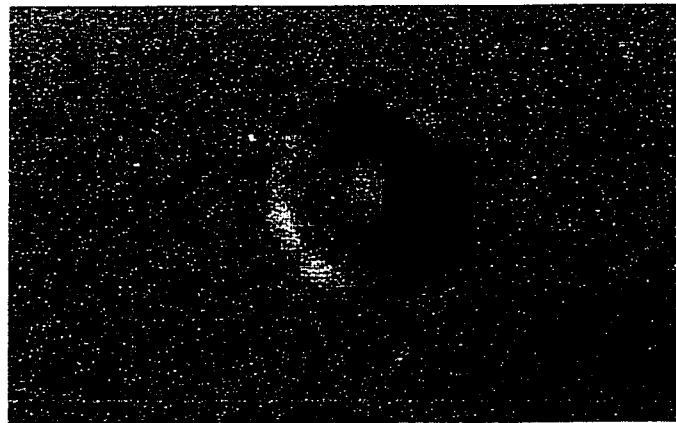


Figure 42. Photograph of an untreated SEM/EDS test specimen after 5 days of atmospheric exposure.

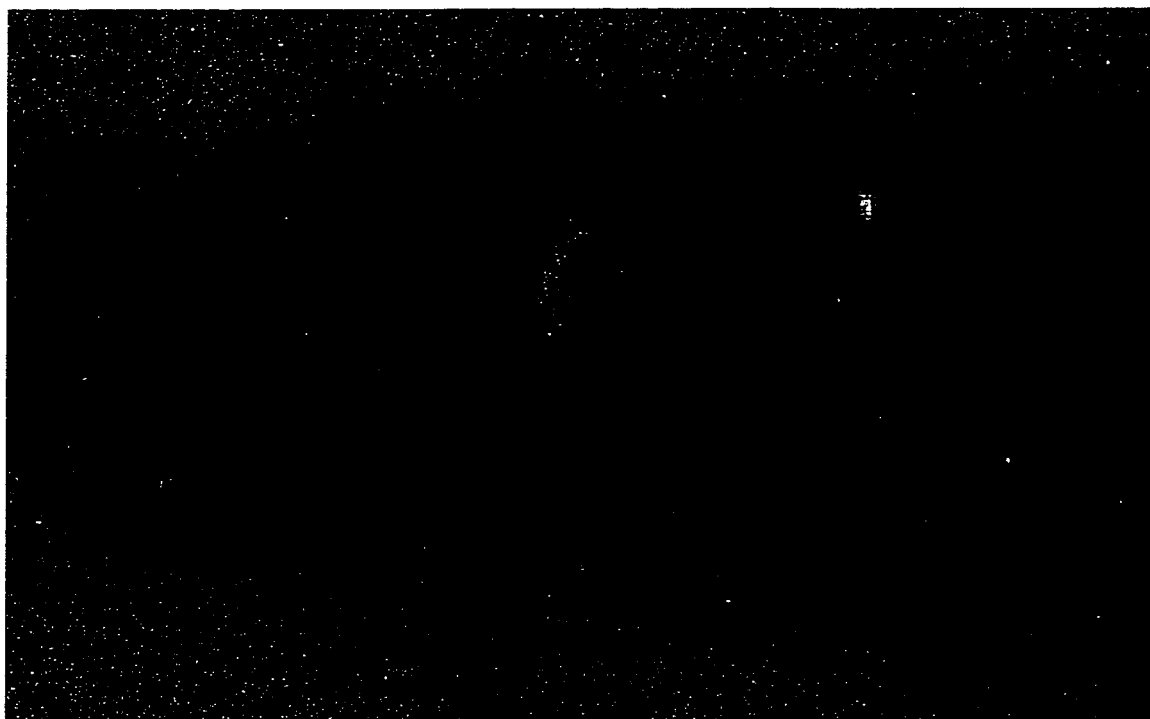


Figure 43. Photograph of a SEM/EDS test specimen treated with 100 mM sodium benzoate before atmospheric exposure.

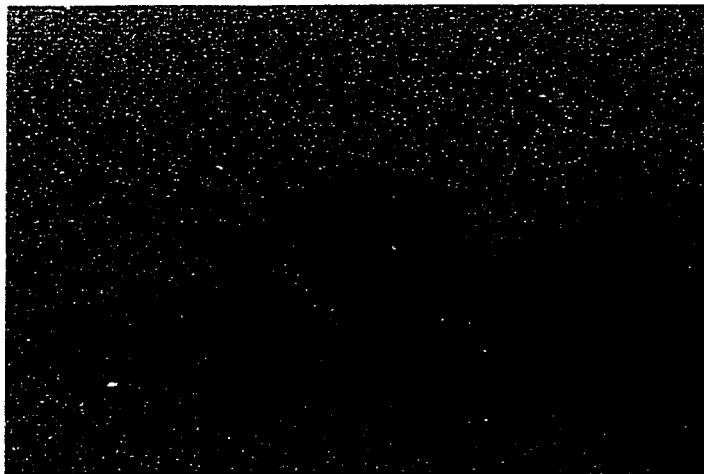


Figure 44. Photograph of a SEM/EDS test specimen exposed to atmosphere for 5 days after treatment with 100 mM sodium benzoate.



Figure 45. Photograph of a SEM/EDS test specimen exposed to atmosphere for 5 days after treatment with 100 mM sodium phosphate.

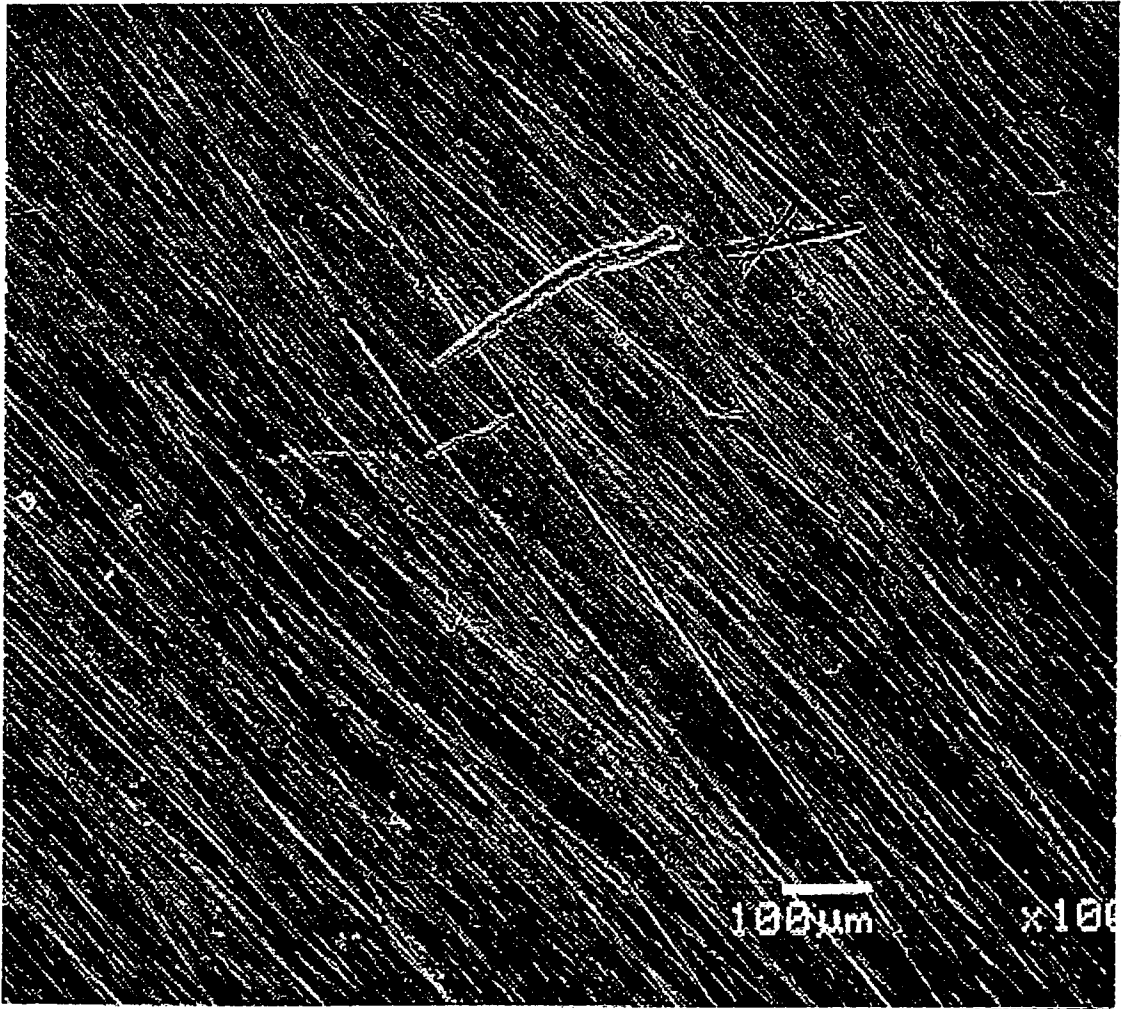


Figure 46. SEM micrograph of an as received steel specimen after polishing (control specimen).

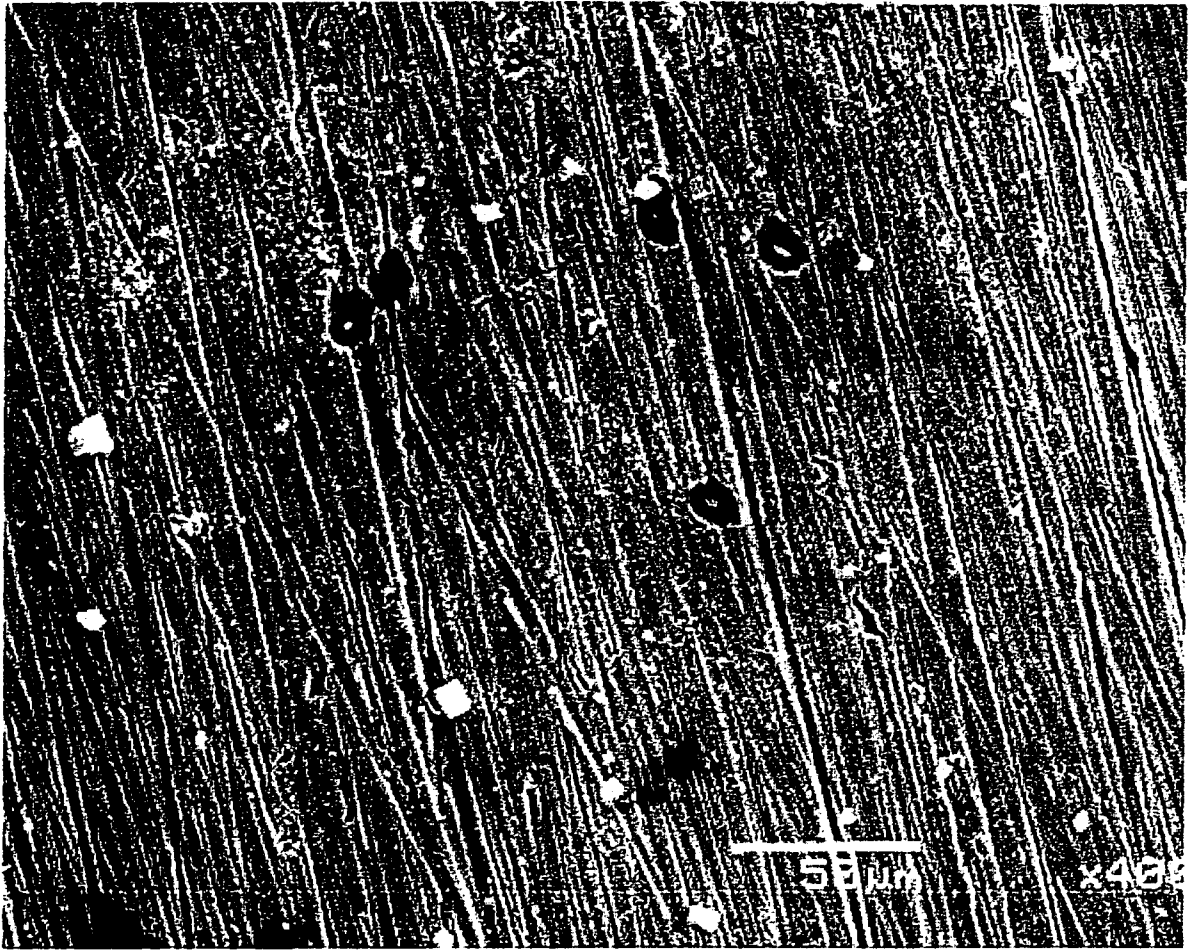


Figure 47. SEM micrograph of an untreated steel specimen after 5 days of atmospheric exposure.

Table 3. EDS analysis of the surface shown in Figure 47 (untreated steel specimen after 5 days of atmospheric exposure). Elemental composition of the control specimen is also included for comparison purposes.

| | C, wt% | O, wt% | Na, wt% | Al, wt% | Si, wt% | Cl, wt% | Mn, wt% | S, wt% | K, wt% | Fe, wt% |
|---|-----------|-----------|------------|------------|------------|------------|------------|-----------|-----------|------------|
| Dark spot near the center | 1.1 | 2.93 | - | 2.69 | 0.23 | 0.12 | 1.76 | 0.43 | - | 90.7 |
| Big white spot at left | 0.61 | 3.41 | - | 4.14 | 2.9 | 0.05 | 0.57 | - | 0.22 | 88.1 |
| Center part away from dark or white spots | 0.94 | 3.21 | - | 2.82 | 0.3 | 0.07 | 0.76 | - | - | 91.9 |
| Control | 0.46 | - | - | 0.26 | 0.14 | 0.14 | 0.2 | 0.01 | - | 98.8 |

Compositions of the three points were not that different from each other. Higher Mn content in the dark spot might indicate that dark spots are steel interior points. Higher Si content in the white spot indicates that it might be sand contamination. Higher oxygen content in all points might be a result of minor corrosion of the specimen during 5 days of atmospheric exposure. Aluminum on the surfaces was probably left during polishing with Alumina solutions.

Figure 48 is an SEM micrograph taken on an unexposed steel specimen treated with 100 mM sodium benzoate (at a part away from the white spot in Figure 43). EDS analysis of the surface is given in Table 4. SEM micrograph and EDS analysis on the white spot of the surface are also presented in Figure 49 and Table 4, respectively.

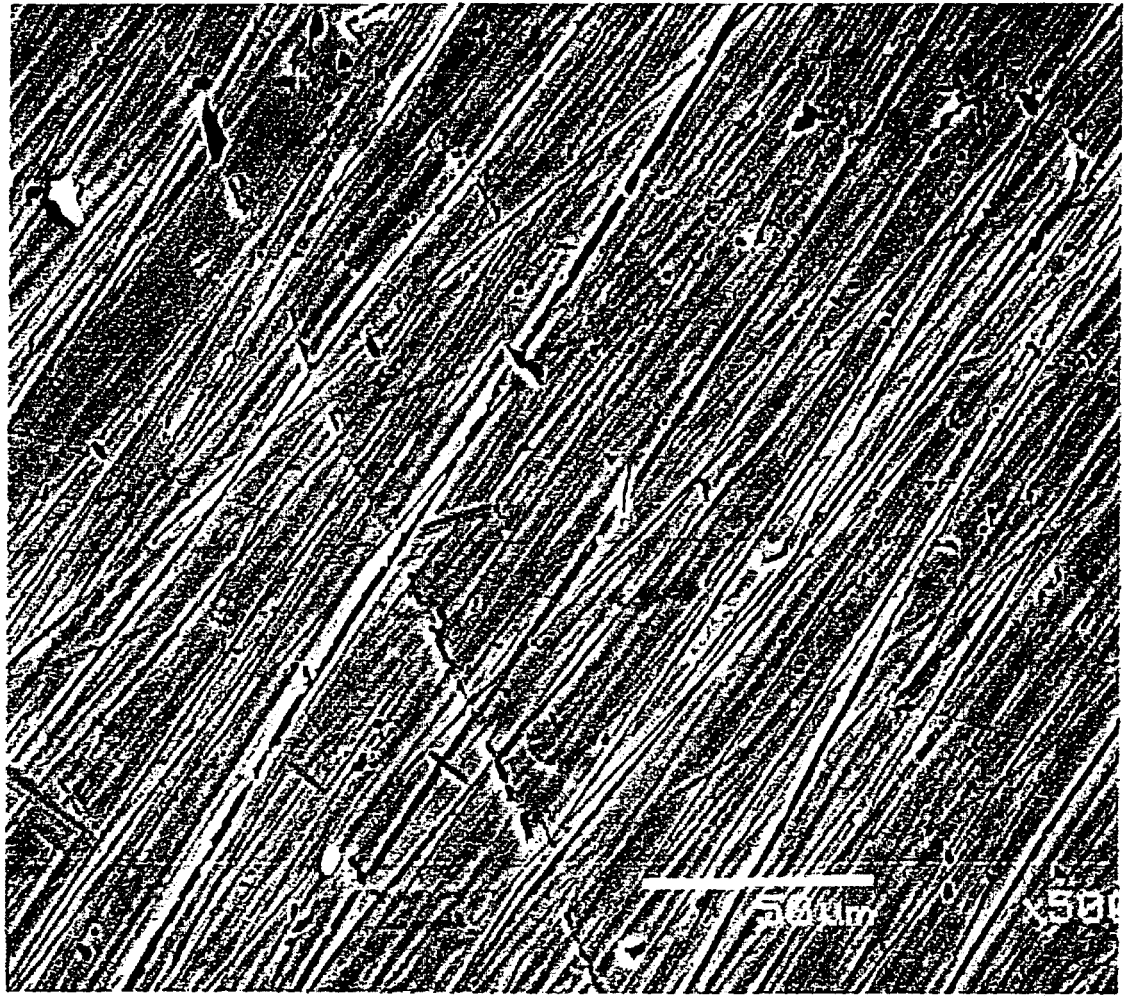


Figure 48. SEM micrograph taken on an unexposed steel specimen treated with 100 mM sodium benzoate (at a part away from the white spot in Figure 43).

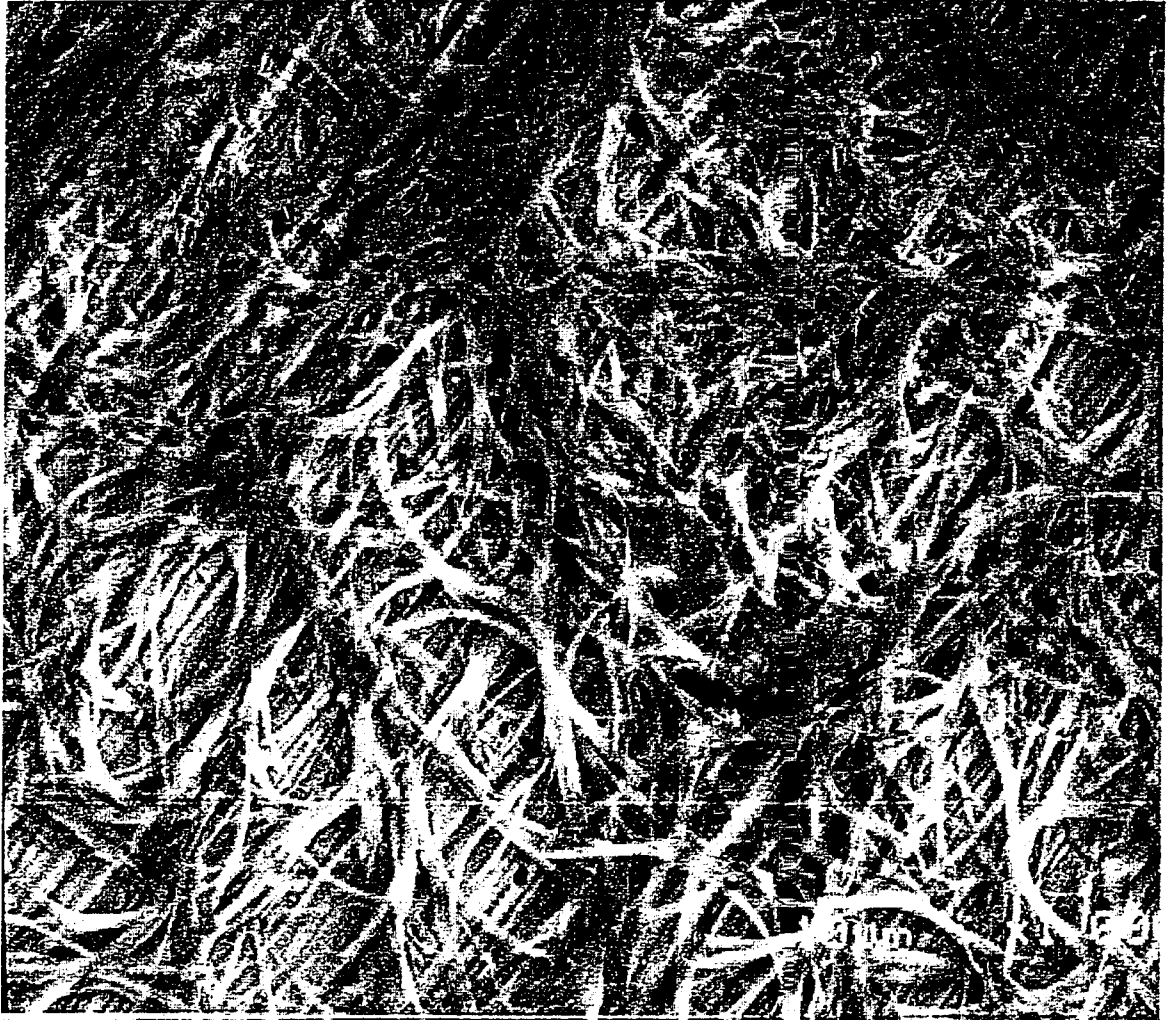


Figure 49. SEM micrograph taken on the white spot of Figure 43.

Table 4. EDS analysis of the surface of an unexposed steel specimen treated with 100 mM sodium benzoate (Figure 43).

| | C, wt% | O, wt% | Na, wt% | Mg, Wt% | Al, wt% | Si, wt% | Cl, wt% | Ca, wt% | Mn, wt% | Fe, wt% |
|---|-----------|-----------|------------|------------|------------|------------|------------|------------|------------|------------|
| Away from the white spot in Figure 43 | 0.7 | - | - | - | 0.41 | 0.24 | 0.17 | 0.1 | 0.68 | 97.7 |
| White spot in Figure 43 | 7.37 | 2.19 | 4.05 | 0.18 | 0.37 | 0.27 | 0.07 | 0.08 | 0.81 | 84.6 |
| Control | 0.46 | - | - | - | 0.26 | 0.14 | 0.14 | - | 0.2 | 98.8 |

Higher Na, O, and C content on the white spot indicates that it is a thicker but loose film of the inhibitor, sodium benzoate, (which comes out easily by washing with water). The elemental composition of the rest of the surface (away from the white spot) was not significantly different than that of the control indicating that the inhibitor film must be very thin which might not contribute much in the EDS analysis.

SEM and EDS analyses were also performed on a sodium benzoate treated specimen after 5 days of atmospheric exposure (a photograph of that specimen was shown in Figure 44). Figure 50 is a micrograph taken at the center part away from the white spots of the surface shown in Figure 44. An SEM micrograph was also taken on one of the white spots (lower one) and shown in Figure 51. EDS analyses of the surfaces are given in Table 5.

Not much corrosion but lots of polishing scratches were observed on the specimen. White loose parts on Figure 50 are contamination, probably sand with higher contents of Ca, Si, and O (Table 5). The rest of the surface in Figure 50 is mostly Fe (the inhibitor film is probably too thin to contribute in the EDS analysis in Table 5). The

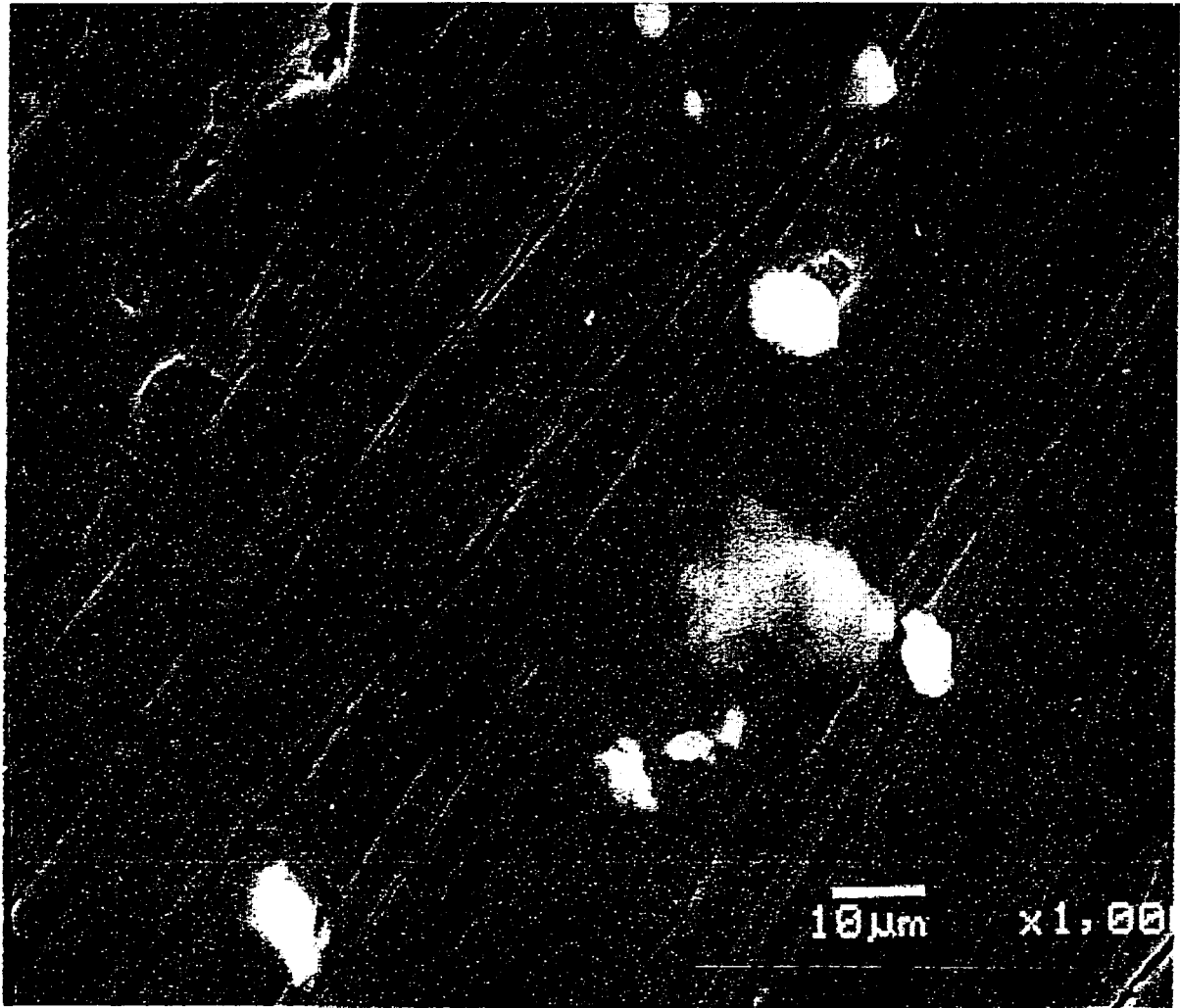


Figure 50. SEM micrograph taken at the center part away from the white spots of the surface shown in Figure 44.

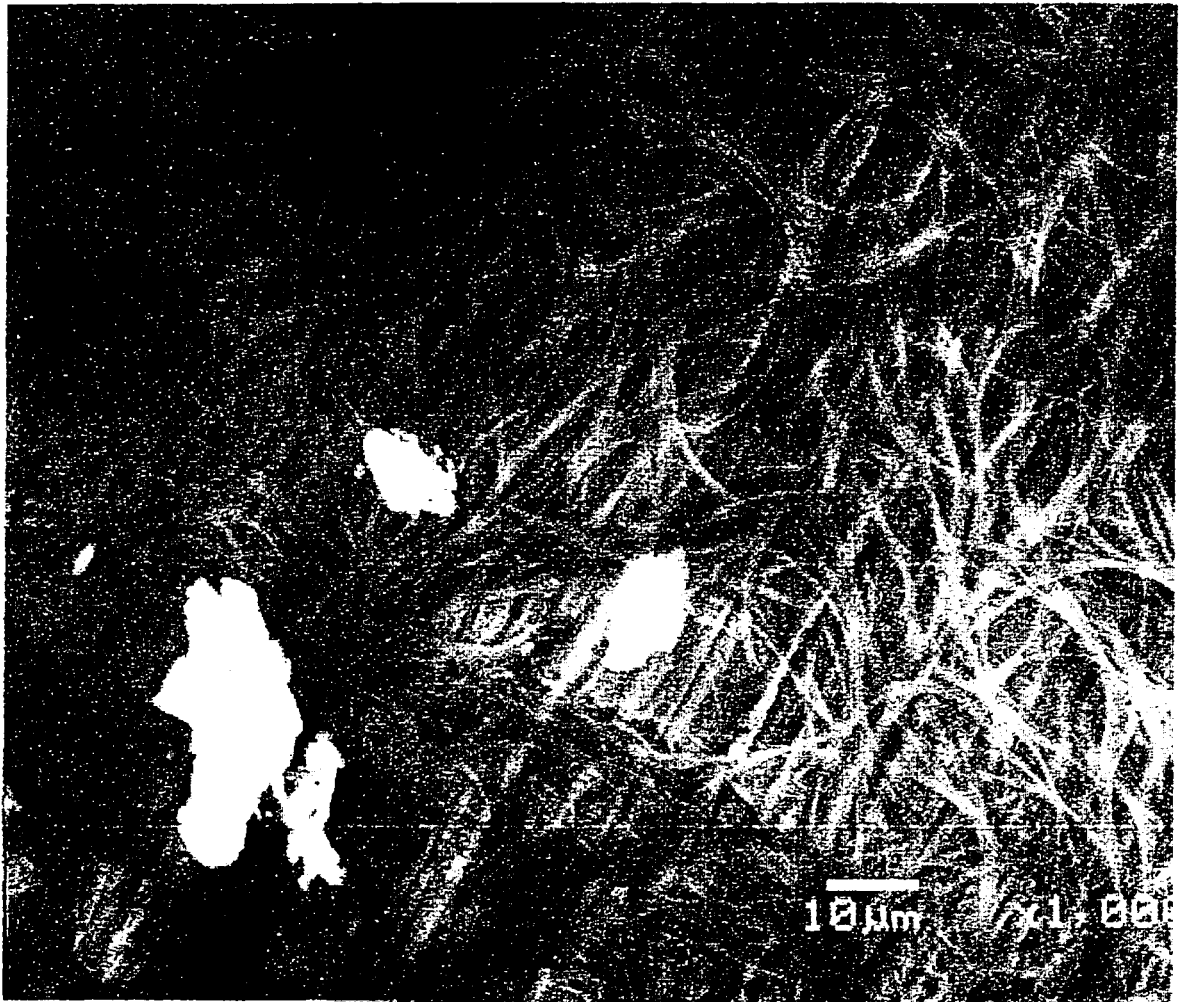


Figure 51. SEM micrograph taken on the lower white spot of the surface shown in Figure 44.

fibrous structure in Figure 51 is a film of the inhibitor sodium benzoate with similar composition to that of the unexposed specimen treated with sodium benzoate (Figure 49 and Table 4). The white loose parts of Figure 51 are probably contamination with higher contents of Si, O, Na and Cl.

Table 5. EDS analysis on a specimen exposed to atmosphere for 5 days after treatment with 100 mM sodium benzoate (a photograph of the specimen and SEM micrographs taken on that specimen are given in Figures 44, 50 and 51).

| | C, wt% | O, wt% | Na, wt% | Mg, wt% | Al, wt% | Si, wt% | Cl, wt% | Ca, wt% | Mn, wt% | Fe, wt% |
|--|-----------|-----------|------------|------------|------------|------------|------------|------------|------------|------------|
| Away from white loose parts in Figure 50 | 0.9 | - | - | - | 0.52 | 0.2 | 0.2 | 0.09 | 0.7 | 97.4 |
| White loose part in Figure 50 | 1.95 | 9.18 | - | 0.16 | 2.31 | 4.34 | 0.29 | 0.78 | 0.69 | 80.3 |
| Away from white loose parts in Figure 51 | 7.62 | 2.83 | 3.32 | 0.07 | 0.82 | 0.18 | 0.16 | - | 0.63 | 84.38 |
| White loose part in Figure 51 | 13.47 | 7.25 | 7.23 | 0.5 | 2.24 | 1.89 | 0.6 | 0.83 | 0.86 | 65.12 |
| Control | 0.46 | - | - | - | 0.26 | 0.14 | 0.14 | - | 0.2 | 98.8 |

Morphological analysis was also done on a specimen exposed to atmosphere for 5 days after treating with sodium phosphate. A photograph of the specimen was shown earlier in Figure 45. A thick inhibitor coating was present on the specimen. No sign of corrosion was noticed. An SEM micrograph taken on that surface is shown in Figure 52 and the EDS analysis of that surface is presented in Table 6. Higher contents of Na, P, and O are indication for the sodium phosphate film on the surface. The loose white spots

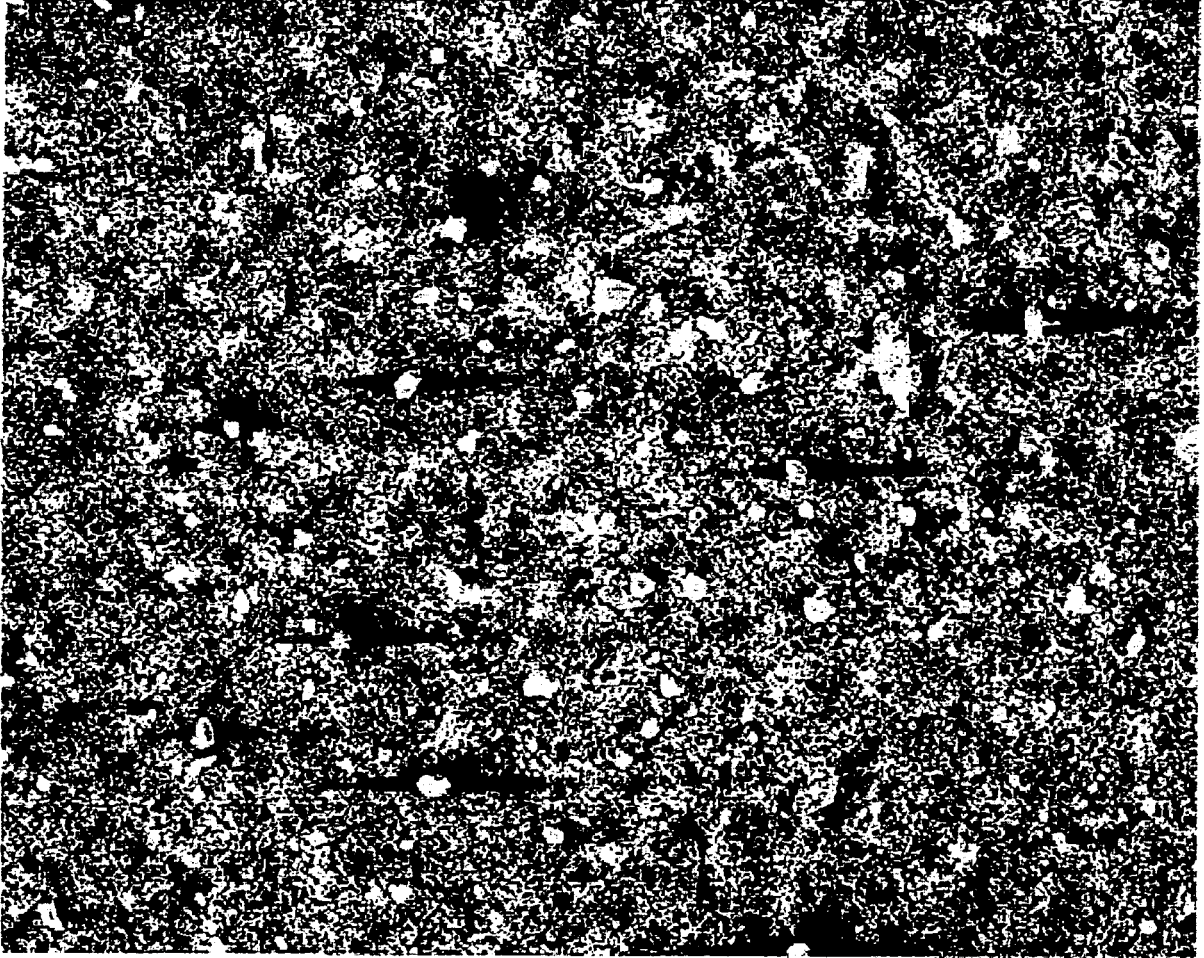


Figure 52. SEM micrograph taken on the surface of a specimen exposed to atmosphere for 5 days after treatment with 100 mM sodium phosphate.

on the surface (see Figure 52) are probably calcium silicate particles with higher Ca and Si content (see Table 6). The dark marks across these particles come from charging.

Table 6. EDS analysis on a specimen exposed to atmosphere for 5 days after treatment with 100 mM sodium phosphate (a photograph of the specimen and SEM micrograph taken on that specimen are given in Figures 45 and 52).

| | C, wt% | O, wt% | Na, wt% | Mg, wt% | Al, wt% | Si, wt% | Cl, wt% | Ca, wt% | P, wt % | S, wt % | K, wt % | Mn, wt% | Fe, wt% |
|-------------------------------|-----------|-----------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| Whole surface of Figure 52 | 1.01 | 34.68 | 4.78 | 0.31 | 0.29 | - | 0.13 | 0.21 | 13.75 | 0.33 | - | - | 44.5 |
| White loose spot in Figure 52 | 1.42 | 53.93 | 1.56 | 0.83 | 1.45 | 4.46 | 0.15 | 20.09 | 4.34 | 0.26 | 0.78 | - | 10.74 |
| Control | 0.46 | - | - | - | 0.26 | 0.14 | 0.14 | - | - | 0.01 | - | 0.2 | 98.8 |

CONCLUSION

Corrosion inhibition of four inhibitors, sodium phosphate, sodium benzoate, sodium nitrate and sodium nitrite, was first tested in a simulated aqueous solution of 2% NaCl and 1% Na₂SO₄ for the purpose of initial screening of inhibitors and inhibitor application conditions. In light of the results obtained, sodium phosphate and sodium benzoate were selected for examination against atmospheric corrosion of steel to be applied at 10 and 100 mM concentrations for 1 day at room temperature.

As expected, the Arabian Gulf Atmosphere was corrosive on the as-received local mild steel. Treatment of steel with either sodium benzoate or sodium phosphate lowered its corrosion rate during initial days of its exposure to atmosphere. Corrosion inhibition performance of sodium phosphate was better than that of sodium benzoate. 100 mM inhibitor concentration functioned better against atmospheric corrosion than 10 mM concentration for the case of sodium benzoate. The difference in their effectiveness was not significant for the case of sodium phosphate.

Atmospheric corrosion inhibition performance of sodium benzoate deteriorated with exposure time for longer exposure durations and the atmospheric corrosion rates of sodium benzoate treated specimens reached that of the unprotected specimens at the end of 90 days of atmospheric exposures.

Atmospheric corrosion rates of sodium phosphate treated specimens, on the other hand, stayed low even after 6 months of exposure.

RECOMMENDATIONS

The following recommendations might be made for future related studies:

- Various inhibitors other than four examined in this study are reported in the literature for protection of metals against atmospheric corrosion. Among them are cyclohexyl amine, dicyclohexylamine nitrite, methylcyclohexylamine, phenylthiourea, sebacic acid and calcium silicate, which were not available in the local market. They should be obtained and their performance in inhibiting atmospheric corrosion of steel should be examined.
- Effects of inhibitor application at higher temperatures should be examined. This is important because it is more practical and economical if the inhibitor application is done in the steel production line during cooling of steel by water spray.

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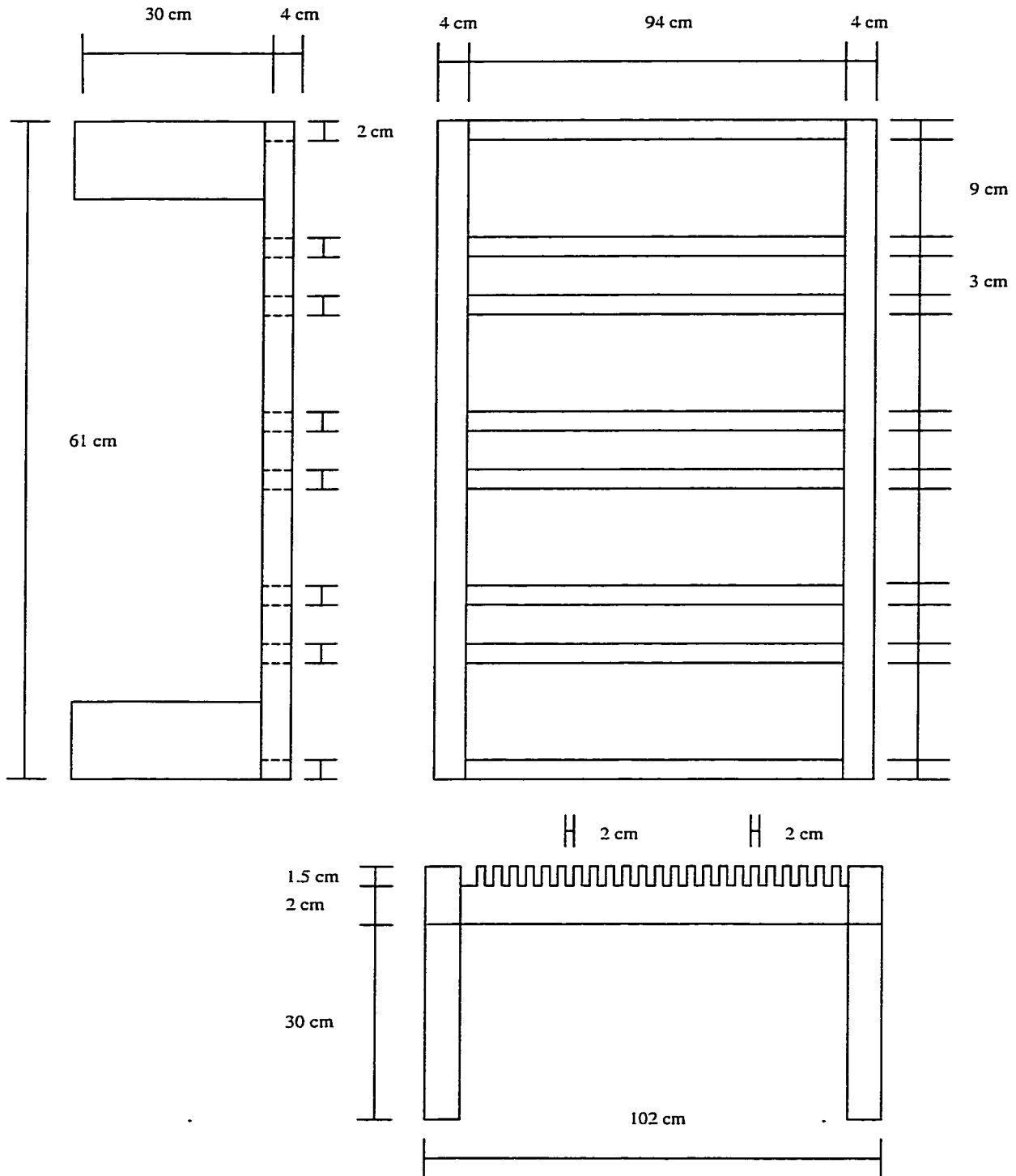
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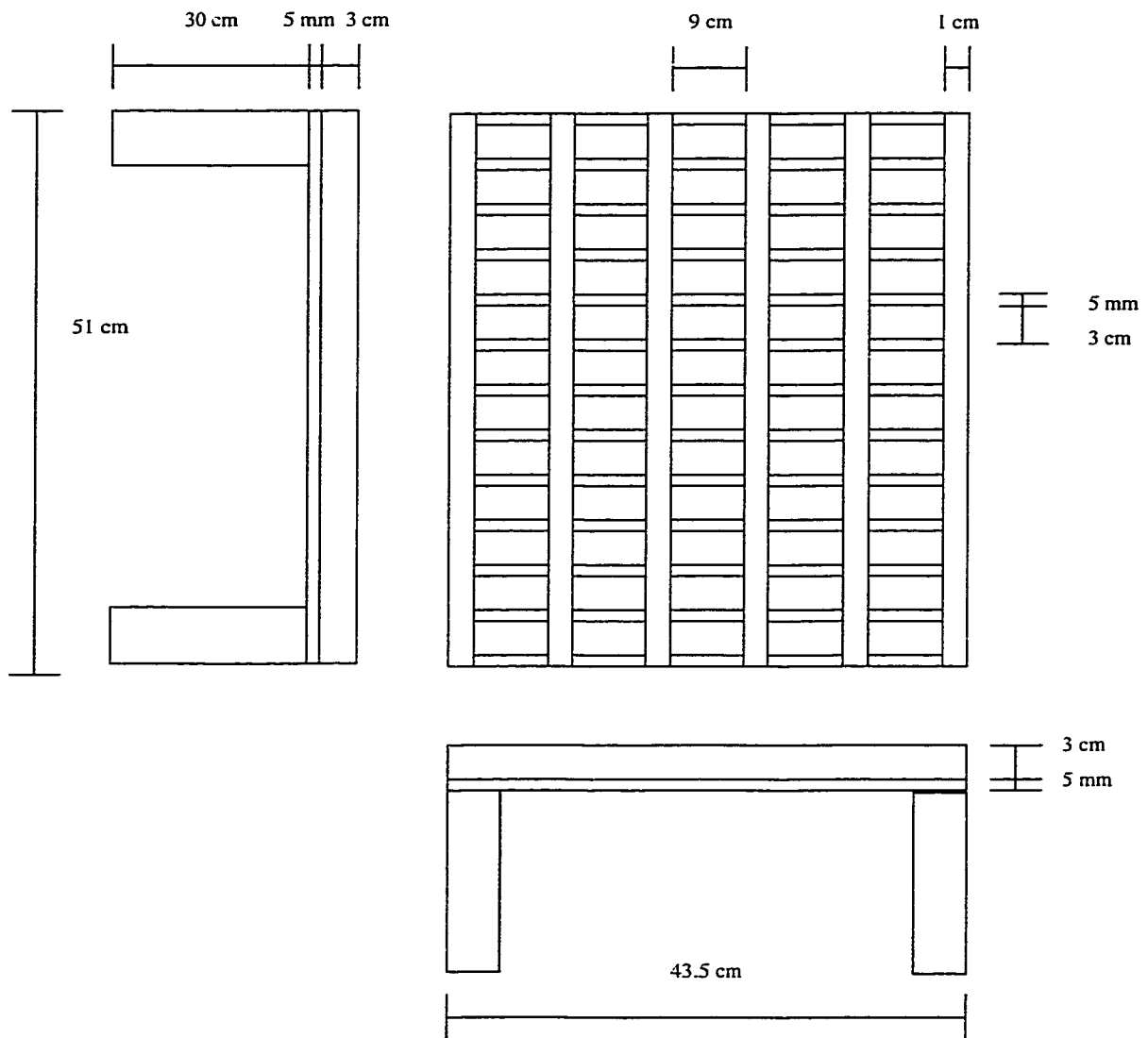
APPENDICES

APPENDIX A

1. SKETCH OF THE RACK DESIGNED TO HOLD 5-INCH SPECIMENS



2. SKETCH OF THE RACK DESIGNED TO HOLD 1-INCH AND DISK SPECIMENS



APPENDIX B

NUMBER OF SPECIMENS FOR EXPOSURE PERIODS

| Exposure Starting Date | Exposure Period | Unprotected Specimens | | | Sodium Phosphate Treated Specimens | | | | | |
|------------------------|-----------------|-----------------------|-----------|---------|------------------------------------|-----------|---------|------------------|-----------|---------|
| | | | | | 10 mM Treatment | | | 100 mM Treatment | | |
| | | W. Sp. | Elec. Sp. | SEM Sp. | W. Sp. | Elec. Sp. | SEM Sp. | W. Sp. | Elec. Sp. | SEM Sp. |
| - | 0 day | | 3 | 1 | | 3 | | | 3 | |
| 23/4/00 | 5 days | 3 | 3 | 1 | 3 | 3 | | 3 | 3 | 1 |
| 23/4/00 | 15 days | 3 | 3 | | 3 | 3 | | 3 | 3 | |
| 24/4/00 | 30 days | 3 | 3 | | 3 | 3 | | 3 | 3 | |
| 22/5/00 | 90 days | 3 | 3 | | 3 | 3 | | 3 | 3 | |
| 24/4/00 | 180 days | 3 | 3 | | 3 | 3 | | 3 | 3 | |

| Exposure Starting Date | Exposure Period | Sodium Benzoate Treated Specimens | | | | | |
|------------------------|-----------------|-----------------------------------|-----------|---------|------------------|-----------|---------|
| | | 10 mM Treatment | | | 100 mM Treatment | | |
| | | W. Sp. | Elec. Sp. | SEM Sp. | W. Sp. | Elec. Sp. | SEM Sp. |
| - | 0 day | | 3 | | | 3 | 1 |
| 23/4/00 | 5 days | 3 | 3 | | 3 | 3 | 1 |
| 23/4/00 | 15 days | 3 | 3 | | 3 | 3 | |
| 24/4/00 | 30 days | 3 | 3 | | 3 | 3 | |
| 22/5/00 | 90 days | 3 | 3 | | 3 | 3 | |
| 24/4/00 | 180 days | 3 | 3 | | 3 | 3 | |

Where W. Sp. Means "specimen for weight loss measurements",
 Elec. Sp. Means "specimen for electrochemical tests",
 SEM Sp. Means "specimen for SEM analysis",

APPENDIX C

WEIGHT LOSS MEASUREMENTS

| Exposure Period | Spec. No. | Rebar Length | Diam. | Initial Weight | Surface Area | Cross-sectional Area | Final Weight | Weight Loss | Corrosion Rate | | Ave. Corrosion Rate |
|---------------------------|-----------|--------------|-------|----------------|-----------------|----------------------|--------------|-------------|----------------|-------|---------------------|
| | | | | | | | | | mm/y | mpy | |
| | | cm | cm | g | cm ² | cm ² | g | mg | | | mm/y |
| 5 Days Untreated | 01 | 12.700 | 1.158 | 107.430 | 46.200 | 2.100 | 107.36 | 60.00 | 0.115 | 4.690 | |
| | 02 | 12.689 | 1.150 | 107.500 | 45.850 | 2.080 | 107.40 | 90.00 | 0.174 | 7.100 | 0.141 |
| | 03 | 12.701 | 1.153 | 107.400 | 46.010 | 2.090 | 107.32 | 70.00 | 0.135 | 5.510 | |
| 5 Days Inhibitor 1 10mM | 111 | 12.730 | 1.173 | 107.240 | 46.910 | 2.160 | 107.20 | 30.00 | 0.057 | 2.330 | |
| | 112 | 12.700 | 1.169 | 107.080 | 46.640 | 2.150 | 107.03 | 40.00 | 0.076 | 3.100 | 0.082 |
| | 113 | 12.723 | 1.171 | 107.460 | 46.810 | 2.150 | 107.39 | 60.00 | 0.114 | 4.650 | |
| 5 Days Inhibitor 1 100mM | 121 | 12.711 | 1.159 | 107.140 | 46.280 | 2.110 | 107.07 | 60.00 | 0.115 | 4.690 | |
| | 122 | 12.710 | 1.165 | 107.040 | 46.520 | 2.130 | 107.00 | 30.00 | 0.057 | 2.330 | 0.070 |
| | 123 | 12.718 | 1.162 | 107.410 | 46.430 | 2.120 | 107.38 | 20.00 | 0.038 | 1.550 | |
| 5 Days Inhibitor 2 10mM | 211 | 12.690 | 1.173 | 107.010 | 46.760 | 2.160 | 106.96 | 40.00 | 0.076 | 3.100 | |
| | 212 | 12.688 | 1.163 | 106.990 | 46.350 | 2.120 | 106.90 | 80.00 | 0.153 | 6.240 | 0.133 |
| | 213 | 12.720 | 1.167 | 107.130 | 46.630 | 2.140 | 107.03 | 90.00 | 0.171 | 6.980 | |
| 5 Days Inhibitor 2 100mM | 221 | 12.688 | 1.157 | 107.600 | 46.120 | 2.100 | 107.51 | 80.00 | 0.154 | 6.290 | |
| | 222 | 12.723 | 1.161 | 107.260 | 46.410 | 2.120 | 107.22 | 30.00 | 0.057 | 2.330 | 0.102 |
| | 223 | 12.708 | 1.160 | 107.110 | 46.310 | 2.120 | 107.05 | 50.00 | 0.096 | 3.920 | |
| 15 Days Untreated | 01 | 12.710 | 1.159 | 107.020 | 46.280 | 2.110 | 106.86 | 150.00 | 0.096 | 3.920 | |
| | 02 | 12.685 | 1.156 | 107.770 | 46.070 | 2.100 | 107.62 | 140.00 | 0.090 | 3.670 | 0.096 |
| | 03 | 12.683 | 1.165 | 106.980 | 46.420 | 2.130 | 106.81 | 160.00 | 0.102 | 4.160 | |
| 15 Days Inhibitor 1 10mM | 111 | 12.683 | 1.153 | 107.350 | 45.940 | 2.090 | 107.28 | 60.00 | 0.039 | 1.590 | |
| | 112 | 12.710 | 1.168 | 107.690 | 46.640 | 2.140 | 107.61 | 70.00 | 0.044 | 1.800 | 0.042 |
| | 113 | 12.720 | 1.173 | 106.940 | 46.880 | 2.160 | 106.86 | 70.00 | 0.044 | 1.800 | |
| 15 Days Inhibitor 1 100mM | 121 | 12.725 | 1.175 | 107.580 | 46.970 | 2.170 | 107.50 | 70.00 | 0.044 | 1.800 | |
| | 122 | 12.720 | 1.170 | 106.910 | 46.750 | 2.150 | 106.84 | 60.00 | 0.038 | 1.550 | 0.036 |
| | 123 | 12.716 | 1.168 | 107.300 | 46.660 | 2.140 | 107.25 | 40.00 | 0.025 | 1.020 | |
| 15 Days Inhibitor 2 10mM | 211 | 12.693 | 1.163 | 107.290 | 46.370 | 2.120 | 107.15 | 130.00 | 0.083 | 3.390 | |
| | 212 | 12.700 | 1.153 | 107.380 | 46.000 | 2.090 | 107.26 | 110.00 | 0.071 | 2.900 | 0.072 |
| | 213 | 12.710 | 1.167 | 106.900 | 46.600 | 2.140 | 106.79 | 100.00 | 0.063 | 2.570 | |
| 15 Days Inhibitor 2 100mM | 221 | 12.685 | 1.155 | 107.240 | 46.030 | 2.100 | 107.12 | 110.00 | 0.071 | 2.900 | |
| | 222 | 12.700 | 1.163 | 106.730 | 46.400 | 2.120 | 106.64 | 80.00 | 0.051 | 2.080 | 0.060 |
| | 223 | 12.679 | 1.159 | 107.500 | 46.170 | 2.110 | 107.40 | 90.00 | 0.058 | 2.370 | |

Where Inhibitor 1 is sodium phosphate and Inhibitor 2 is sodium benzoate.

| Exposure Period | Spec. No. | Rebar Length | Diam. | Initial Weight | Surface Area | Cross-sectional Area | Final Weight | Weight Loss | Corrosion Rate | | Ave. Corrosion Rate |
|----------------------------|-----------|--------------|-------|----------------|-----------------|----------------------|--------------|-------------|----------------|-------|---------------------|
| | | | | | | | | | mm/y | mpy | |
| | | cm | cm | g | cm ² | cm ² | g | mg | | | mm/y |
| 30 Days Untreated | 01 | 12.710 | 1.159 | 107.210 | 46.277 | 2.110 | 106.990 | 210.000 | 0.071 | 2.898 | |
| | 02 | 12.688 | 1.152 | 106.900 | 45.916 | 2.084 | 106.710 | 180.000 | 0.064 | 2.612 | 0.071 |
| | 03 | 12.681 | 1.150 | 107.440 | 45.813 | 2.077 | 107.200 | 230.000 | 0.079 | 3.224 | |
| 30 Days Inhibitor 1 10mM | 111 | 12.730 | 1.173 | 107.360 | 46.910 | 2.161 | 107.290 | 60.000 | 0.019 | 0.776 | |
| | 112 | 12.711 | 1.168 | 107.040 | 46.639 | 2.142 | 106.940 | 90.000 | 0.028 | 1.143 | 0.024 |
| | 113 | 12.720 | 1.173 | 107.370 | 46.877 | 2.161 | 107.280 | 80.000 | 0.025 | 1.020 | |
| 30 Days Inhibitor 1 100mM | 121 | 12.698 | 1.157 | 107.370 | 46.155 | 2.103 | 107.290 | 70.000 | 0.022 | 0.898 | |
| | 122 | 12.832 | 1.153 | 107.320 | 46.484 | 2.090 | 107.210 | 100.000 | 0.032 | 1.306 | 0.026 |
| | 123 | 12.718 | 1.168 | 107.070 | 46.664 | 2.142 | 106.980 | 80.000 | 0.025 | 1.020 | |
| 30 Days Inhibitor 2 10mM | 211 | 12.697 | 1.162 | 107.220 | 46.348 | 2.123 | 106.990 | 220.000 | 0.070 | 2.857 | |
| | 212 | 12.710 | 1.155 | 107.460 | 46.116 | 2.097 | 107.280 | 170.000 | 0.054 | 2.204 | 0.062 |
| | 213 | 12.708 | 1.168 | 107.610 | 46.632 | 2.142 | 107.410 | 190.000 | 0.060 | 2.449 | |
| 30 Days Inhibitor 2 100mM | 221 | 12.683 | 1.157 | 107.11 | 46.103 | 2.103 | 106.97 | 130.000 | 0.042 | 1.714 | |
| | 222 | 12.710 | 1.164 | 107.62 | 46.477 | 2.129 | 107.45 | 160.000 | 0.051 | 2.082 | 0.052 |
| | 223 | 12.673 | 1.158 | 107.4 | 46.103 | 2.103 | 107.19 | 200.000 | 0.064 | 2.612 | |
| 90 Days Untreated | 01 | 12.710 | 1.150 | 107.490 | 45.916 | 2.077 | 100.39 | 710.00 | 0.076 | 3.102 | |
| | 02 | 12.684 | 1.157 | 107.400 | 46.103 | 2.103 | 100 | 740.00 | 0.080 | 3.265 | 0.080 |
| | 03 | 12.701 | 1.153 | 107.220 | 46.006 | 2.090 | 99.52 | 770.00 | 0.083 | 3.388 | |
| 90 Days Inhibitor 1 10mM | 111 | 12.732 | 1.173 | 107.230 | 46.916 | 2.161 | 104.93 | 230.00 | 0.025 | 1.020 | |
| | 112 | 12.712 | 1.155 | 106.970 | 46.129 | 2.097 | 103.97 | 300.00 | 0.032 | 1.306 | 0.030 |
| | 113 | 12.723 | 1.165 | 107.310 | 46.568 | 2.129 | 104.21 | 310.00 | 0.032 | 1.306 | |
| 90 Days Inhibitor 1 100mM | 121 | 12.714 | 1.157 | 107.040 | 46.213 | 2.103 | 104.64 | 240.00 | 0.026 | 1.061 | |
| | 122 | 12.713 | 1.167 | 107.390 | 46.606 | 2.142 | 105.29 | 210.00 | 0.022 | 0.898 | 0.028 |
| | 123 | 12.728 | 1.158 | 106.890 | 46.303 | 2.103 | 103.59 | 330.00 | 0.035 | 1.429 | |
| 90 Days Inhibitor 2 10mM | 211 | 12.690 | 1.173 | 107.120 | 46.761 | 2.161 | 100.22 | 690.00 | 0.072 | 2.939 | |
| | 212 | 12.675 | 1.167 | 107.420 | 46.471 | 2.142 | 99.62 | 780.00 | 0.082 | 3.347 | 0.074 |
| | 213 | 12.725 | 1.166 | 107.330 | 46.613 | 2.135 | 101.03 | 630.00 | 0.066 | 2.694 | |
| 90 Days Inhibitor 2 100mM | 221 | 12.678 | 1.156 | 107.450 | 46.045 | 2.097 | 100.75 | 670.00 | 0.072 | 2.939 | |
| | 222 | 12.723 | 1.161 | 107.180 | 46.406 | 2.116 | 100.68 | 650.00 | 0.069 | 2.816 | 0.069 |
| | 223 | 12.710 | 1.163 | 107.440 | 46.439 | 2.123 | 101.14 | 630.00 | 0.066 | 2.694 | |
| 180 Days Untreated | 01 | 12.710 | 1.170 | 107.530 | 46.716 | 2.148 | 106.250 | 1270.000 | 0.087 | 3.551 | |
| | 02 | 12.690 | 1.157 | 107.480 | 46.129 | 2.103 | 106.030 | 1440.000 | 0.100 | 4.082 | 0.097 |
| | 03 | 12.711 | 1.153 | 107.580 | 46.045 | 2.090 | 106.060 | 1510.000 | 0.105 | 4.286 | |
| 180 Days Inhibitor 1 10mM | 111 | 12.732 | 1.173 | 107.240 | 46.916 | 2.161 | 106.740 | 490.000 | 0.033 | 1.347 | |
| | 112 | 12.700 | 1.165 | 107.020 | 46.484 | 2.129 | 106.600 | 410.000 | 0.028 | 1.143 | 0.032 |
| | 113 | 12.723 | 1.171 | 107.400 | 46.806 | 2.155 | 106.890 | 500.000 | 0.034 | 1.388 | |
| 180 Days Inhibitor 1 100mM | 121 | 12.710 | 1.158 | 107.380 | 46.239 | 2.103 | 106.980 | 390.000 | 0.027 | 1.102 | |
| | 122 | 12.712 | 1.165 | 107.540 | 46.522 | 2.129 | 107.060 | 470.000 | 0.032 | 1.306 | 0.029 |
| | 123 | 12.716 | 1.162 | 106.970 | 46.419 | 2.123 | 106.580 | 380.000 | 0.026 | 1.061 | |
| 180 Days Inhibitor 2 10mM | 211 | 12.680 | 1.172 | 107.510 | 46.684 | 2.155 | 106.200 | 1300.000 | 0.089 | 3.633 | |
| | 212 | 12.740 | 1.163 | 107.390 | 46.548 | 2.123 | 106.050 | 1330.000 | 0.092 | 3.755 | 0.092 |
| | 213 | 12.720 | 1.167 | 107.480 | 46.632 | 2.142 | 106.060 | 1410.000 | 0.097 | 3.959 | |
| 180 Days Inhibitor 2 100mM | 221 | 12.688 | 1.157 | 107.600 | 46.116 | 2.103 | 106.350 | 1240.000 | 0.089 | 3.633 | |
| | 222 | 12.726 | 1.164 | 107.460 | 46.535 | 2.129 | 106.200 | 1250.000 | 0.091 | 3.714 | 0.088 |
| | 223 | 12.718 | 1.150 | 107.230 | 45.948 | 2.077 | 106.020 | 1200.000 | 0.084 | 3.429 | |

Where Inhibitor 1 is sodium phosphate and Inhibitor 2 is sodium benzoate.

APPENDIX D

CALCULATION PROCEDURES OF CORROSION RATE USING ELECTROCHEMICAL TECHNIQUE

1. Calculate polarization resistance (R_p). R_p is the slope of the polarization curve.
2. Calculate corrosion current from this Equation:

$$I_{corr} = \frac{B}{R_p}$$

$$\text{Where; } B = \frac{\beta_a \times \beta_c}{2.3(\beta_a + \beta_c)}$$

3. Calculate corrosion rate from this Equation:

$$\text{Corrosion rate (mm/y)} = \frac{0.0033 \times I_{corr} \times EW}{D}$$

or

$$\text{Corrosion rate (mpy)} = \frac{0.13 \times I_{corr} \times EW}{D}$$

Where; EW = 27.93 (equivalent weight of iron)

$D = 7.87 \text{ g/cm}^3$ (density of steel)

I_{corr} in $\mu\text{A/cm}^2$

(mpy means mils per year and 1 mil = 0.001 in)

APPENDIX E

1. TAFEL RUNS

| Specimen | Inhibitor Concentration | Temp. | Inhibitor Application Duration | β_a | β_c |
|--------------------------|-------------------------|------------|--------------------------------|-----------|-----------|
| Control | - | Room Temp. | - | 0.07261 | 0.2102 |
| Sodium Phosphate Treated | 100 mM | Room Temp. | 24 h | 0.05225 | 0.1587 |
| Sodium Phosphate Treated | 100 mM | 70°C | 5 min | 0.05369 | 0.1353 |
| Sodium Benzoate Treated | 100 mM | Room Temp. | 24 h | 0.06306 | 0.1208 |
| Sodium Benzoate Treated | 100 mM | 70°C | 5 min | 0.06131 | 0.1211 |
| Sodium Nitrate Treated | 100 mM | Room Temp. | 24 h | 0.0671 | 0.1217 |
| Sodium Nitrite Treated | 100 mM | Room Temp. | 24 h | 0.06604 | 0.1224 |

2. ELECTROCHEMICAL MEASUREMENTS-INITIAL SCREENING OF INHIBITORS

The units for all the runs:

R_p : Kohms

I_{corr} : $\mu\text{A}/\text{cm}^2$

Corrosion rate: mm/y or mpy (mils per year)

Control Specimens

| Run # | R_p | I_{corr} | mpy | mm/y |
|-------|--------|------------|-------|-------|
| 1 | 0.1087 | 20.86 | 9.525 | 0.242 |
| 2 | 0.2201 | 10.29 | 4.7 | 0.119 |
| 3 | 0.1365 | 16.6 | 7.582 | 0.193 |

Sodium Phosphate Treated Specimens

| Inhibitor Concentration, Run # | RT, 5 min Treatment | | | | RT, 24 h Treatment | | | |
|--------------------------------|---------------------|------------|------|-------|--------------------|------------|------|-------|
| | R_p | I_{corr} | mpy | mm/y | R_p | I_{corr} | mpy | mm/y |
| 1 mM, 1 | | | | | 0.21 | 7.64 | 3.49 | 0.089 |
| 1 mM, 2 | | | | | 0.16 | 9.36 | 4.27 | 0.108 |
| 10 mM, 1 | 0.18 | 9 | 4.12 | 0.105 | 0.44 | 3.753 | 1.71 | 0.043 |
| 10 mM, 2 | 0.2 | 8 | 3.7 | 0.094 | 0.54 | 3 | 1.38 | 0.035 |
| 100 mM, 1 | | | | | 0.52 | 3.164 | 1.44 | 0.037 |
| 100 mM, 2 | | | | | 0.79 | 2.1 | 0.95 | 0.024 |
| 1000 mM, 2 | | | | | 0.09 | 17.8 | 8.14 | 0.207 |
| 1000 mM, 2 | | | | | 0.09 | 18.4 | 8.4 | 0.213 |

| Inhibitor Concentration, Run # | 70°C, 5 min Treatment | | | | 70°C, 1 h Treatment | | | |
|--------------------------------|-----------------------|------------|------|-------|---------------------|------------|------|-------|
| | R_p | I_{corr} | mpy | mm/y | R_p | I_{corr} | mpy | mm/y |
| 1 mM, 1 | 0.18 | 8.54 | 3.9 | 0.099 | | | | |
| 1 mM, 2 | | | | | | | | |
| 10 mM, 1 | 0.17 | 9.26 | 4.23 | 0.107 | 0.21 | 7.7 | 3.55 | 0.090 |
| 10 mM, 2 | 0.15 | 10.6 | 4.85 | 0.123 | 0.19 | 8.3 | 3.78 | 0.096 |
| 100 mM, 1 | 0.23 | 6.74 | 3.08 | 0.078 | | | | |
| 100 mM, 2 | 0.23 | 6.85 | 3.12 | 0.079 | | | | |
| 1000 mM, 2 | 0.32 | 5.01 | 2.28 | 0.058 | | | | |
| 1000 mM, 2 | 0.19 | 8.33 | 3.8 | 0.097 | | | | |

Sodium Benzoate Treated Specimens

| Inhibitor Concentration, Run # | RT, 5 min. Treatment | | | | RT, 24 h Treatment | | | |
|--------------------------------|----------------------|------------|------|-------|--------------------|------------|------|-------|
| | R_p | I_{corr} | mpy | mm/y | R_p | I_{corr} | mpy | mm/y |
| 1 mM, 1 | | | | | 0.142 | 12.18 | 5.54 | 0.141 |
| 10 mM, 1 | 0.207 | 8.39 | 3.83 | 0.097 | 0.18 | 9.45 | 4.3 | 0.109 |
| 10 mM, 2 | 0.217 | 8.3 | 3.79 | 0.096 | 0.17 | 9.92 | 4.53 | 0.115 |
| 10 mM, 3 | | | | | | | | |
| 100 mM, 1 | | | | | 0.19 | 9.17 | 4.19 | 0.106 |
| 1000 mM, 1 | | | | | 0.17 | 10.16 | 4.64 | 0.118 |
| 1000 mM, 2 | | | | | 0.18 | 9.66 | 4.41 | 0.112 |

| Inhibitor Concentration, Run # | 70°C, 5 min Treatment | | | |
|--------------------------------|-----------------------|------------|------|-------|
| | R_p | I_{corr} | mpy | mm/y |
| 1 mM, 1 | 0.17 | 9.8 | 4.5 | 0.114 |
| 10 mM, 1 | 0.24 | 7.12 | 3.25 | 0.083 |
| 10 mM, 2 | 0.2 | 8.46 | 3.86 | 0.098 |
| 10 mM, 3 | 0.22 | 7.5 | 3.42 | 0.087 |
| 100 mM, 1 | 0.17 | 9.83 | 4.48 | 0.114 |
| 1000 mM, 1 | 0.17 | 9.7 | 4.45 | 0.113 |
| 1000 mM, 2 | | | | |

Sodium Nitrate Treated Specimens

| Inhibitor Concentration, Run # | RT, 5 min. Treatment | | | | RT, 24 h Treatment | | | |
|--------------------------------|----------------------|------------|------|-------|--------------------|------------|------|-------|
| | R_p | I_{corr} | mpy | mm/y | R_p | I_{corr} | mpy | mm/y |
| 1 mM, 1 | 0.16 | 11.36 | 5.18 | 0.132 | | | | |
| 10 mM, 1 | 0.2 | 8.94 | 4.08 | 0.104 | 0.19 | 9.29 | 4.24 | 0.108 |
| 10 mM, 2 | | | | | 0.16 | 10.9 | 4.9 | 0.124 |
| 100 mM, 1 | | | | | 0.15 | 11.43 | 5.21 | 0.132 |
| 1000 mM, 1 | | | | | 0.158 | 11.46 | 5.23 | 0.133 |
| 1000 mM, 2 | | | | | 0.165 | 10.96 | 5 | 0.127 |

| Inhibitor Concentration, Run # | 70°C, 5 min Treatment | | | |
|--------------------------------|-----------------------|------------|------|-------|
| | R_p | I_{corr} | mpy | mm/y |
| 1 mM, 1 | | | | |
| 10 mM, 1 | 0.18 | 9.75 | 4.45 | 0.113 |
| 10 mM, 2 | 0.2 | 8.9 | 4.06 | 0.103 |
| 100 mM, 1 | 0.17 | 10.65 | 4.86 | 0.123 |
| 1000 mM, 1 | | | | |
| 1000 mM, 2 | | | | |

Sodium Nitrite Treated Specimens

| Inhibitor Concentration, Run # | RT, 5 min. Treatment | | | | RT, 24 h Treatment | | | |
|-----------------------------------|-------------------------|------------|------|-------|-----------------------|------------|-------|-------|
| | R_p | I_{corr} | mpy | mm/y | R_p | I_{corr} | mpy | mm/y |
| 1 mM, 1 | | | | | 0.15 | 11.38 | 5.19 | 0.132 |
| 10 mM, 1 | 0.19 | 9.33 | 4.26 | 0.108 | 0.12 | 14.19 | 6.47 | 0.164 |
| 10 mM, 2 | 0.14 | 12.5 | 5.7 | 0.145 | | | | |
| 10 mM, 3 | 0.21 | 9.23 | 4.21 | 0.107 | | | | |
| 100 mM, 1 | | | | | 0.19 | 9.135 | 4.17 | 0.106 |
| 100 mM, 2 | | | | | 0.19 | 9.237 | 4.218 | 0.107 |
| 100 mM, 3 | | | | | 0.19 | 9.382 | 4.28 | 0.109 |
| 1000 mM, 1 | | | | | 0.2 | 8.9 | 4.06 | 0.103 |
| 1000 mM, 2 | | | | | 0.18 | 9.736 | 4.44 | 0.113 |

3. ELECTROCHEMICAL TESTS ON EXPOSED SPECIMENS

Exposure Duration: 0 Day

| Run # | Unprotected Specimens | | | | | | | |
|-------|------------------------------------|------------|-------|-------|--------|------------|-------|-------|
| | R_p | I_{corr} | mpy | | mm/y | | | |
| 1 | 0.2305 | 10.62 | 4.849 | | 0.123 | | | |
| 2 | 0.231 | 10.6 | 4.84 | | 0.123 | | | |
| 3 | 0.1832 | 13.36 | 6.102 | | 0.155 | | | |
| | Sodium Phosphate Treated Specimens | | | | | | | |
| | 10 mM | | | | 100 mM | | | |
| | R_p | I_{corr} | mpy | mm/y | R_p | I_{corr} | mpy | mm/y |
| 1 | 0.311 | 5.733 | 2.618 | 0.066 | 0.619 | 2.879 | 1.315 | 0.033 |
| 3 | 0.3112 | 5.729 | 2.616 | 0.066 | 0.6717 | 2.655 | 1.212 | 0.031 |
| 3 | 0.3403 | 5.239 | 2.393 | 0.061 | 0.46 | 3.876 | 1.77 | 0.045 |
| | Sodium Benzoate Treated Specimens | | | | | | | |
| | 10 mM | | | | 100 mM | | | |
| | R_p | I_{corr} | mpy | mm/y | R_p | I_{corr} | mpy | mm/y |
| 1 | 0.2385 | 7.878 | 3.598 | 0.091 | 0.2155 | 8.718 | 3.981 | 0.101 |
| 2 | 0.1876 | 10.02 | 4.574 | 0.116 | 0.26 | 7.22 | 3.3 | 0.084 |
| 3 | | | | 0.000 | 0.2466 | 7.62 | 3.48 | 0.088 |

Exposure Duration: 5 Days

| Run # | Unprotected Specimens | | | | | | | |
|-------|------------------------------------|------------|------------|-------|--------|------------|-------|-------|
| | R_p | | I_{corr} | | mpy | | mm/y | |
| 1 | 0.1633 | | 13.76 | | 6.282 | | 0.160 | |
| 2 | 0.21 | | 11.58 | | 5.189 | | 0.132 | |
| 3 | | | | | | | | |
| | Sodium Phosphate Treated Specimens | | | | | | | |
| | 10 mM | | | | 100 mM | | | |
| | R_p | I_{corr} | mpy | mm/y | R_p | I_{corr} | mpy | mm/y |
| 1 | 0.268 | 6.654 | 3.039 | 0.077 | 0.274 | 6.27 | 2.867 | 0.073 |
| 3 | 0.2393 | 7.188 | 3.283 | 0.083 | 0.304 | 5.86 | 2.676 | 0.068 |
| 3 | 0.3388 | 5.262 | 2.403 | 0.061 | 0.584 | 3.053 | 1.394 | 0.035 |
| | Sodium Benzoate Treated Specimens | | | | | | | |
| | 10 mM | | | | 100 mM | | | |
| | R_p | I_{corr} | mpy | mm/y | R_p | I_{corr} | mpy | mm/y |
| 1 | 0.189 | 9.943 | 4.541 | 0.115 | 0.292 | 6.433 | 2.938 | 0.075 |
| 2 | 0.2329 | 8.068 | 3.684 | 0.094 | 0.215 | 8.735 | 3.98 | 0.101 |
| 3 | 0.2495 | 7.532 | 3.44 | 0.087 | 0.247 | 7.59 | 3.467 | 0.088 |

Exposure Duration: 15 Days

| Run # | Unprotected Specimens | | | | | | | |
|-------|------------------------------------|------------|------------|-------|--------|------------|-------|-------|
| | R_p | | I_{corr} | | mpy | | mm/y | |
| 1 | 0.1911 | | 12.81 | | 5.848 | | 0.149 | |
| 2 | 0.1614 | | 15.16 | | 6.925 | | 0.176 | |
| 3 | 0.1862 | | 13.15 | | 6.004 | | 0.153 | |
| | Sodium Phosphate Treated Specimens | | | | | | | |
| | 10 mM | | | | 100 mM | | | |
| | R_p | I_{corr} | mpy | mm/y | R_p | I_{corr} | mpy | mm/y |
| 1 | 0.294 | 5.611 | 2.56 | 0.065 | 0.3344 | 5.332 | 2.435 | 0.062 |
| 3 | 0.504 | 3.535 | 1.615 | 0.041 | 0.4733 | 3.767 | 1.72 | 0.044 |
| 3 | 0.335 | 5.317 | 2.428 | 0.062 | 0.323 | 5.52 | 2.521 | 0.064 |
| | Sodium Benzoate Treated Specimens | | | | | | | |
| | 10 mM | | | | 100 mM | | | |
| | R_p | I_{corr} | mpy | mm/y | R_p | I_{corr} | mpy | mm/y |
| 1 | 0.1772 | 10.61 | 4.844 | 0.123 | 0.224 | 8.389 | 3.831 | 0.097 |
| 2 | 0.2168 | 8.666 | 3.958 | 0.101 | 0.251 | 7.486 | 3.419 | 0.087 |
| 3 | 0.1875 | 10.02 | 4.578 | 0.116 | 0.19 | 9.892 | 4.517 | 0.115 |

Exposure Duration: 30 Days

| Run # | Unprotected Specimens | | | | | | | |
|-------|------------------------------------|------------|------------|-------|--------|------------|-------|-------|
| | R_p | | I_{corr} | | mpy | | mm/y | |
| 1 | 0.169 | | 14.48 | | 6.613 | | 0.168 | |
| 2 | 0.1460 | | 16.77 | | 7.659 | | 0.195 | |
| 3 | 0.154 | | 15.9 | | 7.259 | | 0.184 | |
| | Sodium Phosphate Treated Specimens | | | | | | | |
| | 10 mM | | | | 100 mM | | | |
| | R_p | I_{corr} | mpy | mm/y | R_p | I_{corr} | mpy | mm/y |
| 1 | 0.3388 | 5.262 | 2.403 | 0.061 | 0.3318 | 5.374 | 2.454 | 0.062 |
| 3 | 0.3834 | 4.647 | 2.122 | 0.054 | 0.4 | 4.457 | 2.036 | 0.052 |
| 3 | 0.2514 | 7.091 | 3.238 | 0.082 | 0.2346 | 7.598 | 3.47 | 0.088 |
| | Sodium Benzoate Treated Specimens | | | | | | | |
| | 10 mM | | | | 100 mM | | | |
| | R_p | I_{corr} | mpy | mm/y | R_p | I_{corr} | mpy | mm/y |
| 1 | 0.157 | 11.97 | 5.465 | 0.139 | 0.164 | 11.46 | 5.232 | 0.133 |
| 2 | 0.1146 | 16.4 | 7.491 | 0.190 | 0.17 | 11.06 | 5.049 | 0.128 |
| 3 | 0.165 | 11.37 | 5.193 | 0.132 | 0.15 | 12.53 | 5.723 | 0.145 |

Exposure Duration: 90 Days

| Run # | Unprotected Specimens | | | | | | | |
|-------|------------------------------------|------------|------------|-------|--------|------------|--------|-------|
| | R_p | | I_{corr} | | mpy | | mm/y | |
| 1 | 0.015 | | 91.4 | | 41.255 | | 1.048 | |
| 2 | 0.018 | | 90.7 | | 41.246 | | 1.048 | |
| 3 | 0.011 | | 91.8 | | 42.508 | | 1.080 | |
| | Sodium Phosphate Treated Specimens | | | | | | | |
| | 10 mM | | | | 100 mM | | | |
| | R_p | I_{corr} | mpy | mm/y | R_p | I_{corr} | mpy | mm/y |
| 1 | 0.049 | 34.46 | 15.726 | 0.399 | 0.0543 | 30.13 | 13.345 | 0.339 |
| 3 | 0.043 | 35.83 | 16.772 | 0.426 | 0.052 | 30.88 | 14.59 | 0.371 |
| 3 | 0.045 | 35.66 | 16.372 | 0.416 | 0.055 | 29.9 | 13.246 | 0.336 |
| | Sodium Benzoate Treated Specimens | | | | | | | |
| | 10 mM | | | | 100 mM | | | |
| | R_p | I_{corr} | mpy | mm/y | R_p | I_{corr} | mpy | mm/y |
| 1 | 0.019 | 90.35 | 40.37 | 1.025 | 0.024 | 86.09 | 38.797 | 0.985 |
| 2 | 0.011 | 91.7 | 42.40 | 1.077 | 0.022 | 87.84 | 39.843 | 1.012 |
| 3 | | | | | | | | |

Exposure Duration: 180 Days

| Run # | Unprotected Specimens | | | | | | | |
|-------|------------------------------------|------------|------------|-------|---------|------------|-------|-------|
| | R_p | | I_{corr} | | mpy | | mm/y | |
| 1 | 0.00016 | | 148.84 | | 68.67 | | 1.744 | |
| 2 | 0.00017 | | 139.82 | | 64.5 | | 1.638 | |
| 3 | | | | | | | | |
| | Sodium Phosphate Treated Specimens | | | | | | | |
| | 10 mM | | | | 100 mM | | | |
| | R_p | I_{corr} | mpy | mm/y | R_p | I_{corr} | mpy | mm/y |
| 1 | 0.0003 | 57.3 | 26.44 | 0.672 | 0.0004 | 44.3 | 20.36 | 0.517 |
| 2 | 0.00012 | 73 | 33.68 | 0.855 | 0.0003 | 54.7 | 25.28 | 0.642 |
| 3 | | | | | | | | |
| | Sodium Benzoate Treated Specimens | | | | | | | |
| | 10 mM | | | | 100 mM | | | |
| | R_p | I_{corr} | mpy | mm/y | R_p | I_{corr} | mpy | mm/y |
| 1 | 0.00012 | 152 | 70.13 | 1.781 | 0.00015 | 122.9 | 56.7 | 1.440 |
| 2 | 0.00013 | 139.43 | 64.33 | 1.634 | 0.00012 | 153.54 | 70.84 | 1.799 |
| 3 | | | | | | | | |