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A STUDY OF THE EFFECT OF SOME INHIBITORS ON THE CORROSION RATES OF AUSTENITIC STAINLESS STEELS IN SULFURIC ACID

BY SHANG-YINN CHIOU

Thesis Submitted to the Faculty of the Graduate School of the New Jersey Institute of Technology in Partial Fullfillment of the Requirements for the Degree of Master of Science in Chemical Engineering 1989

APPROVAL OF THESIS

Title of Thesis: A Study Of The Effect Of Some Inhibitors On The Corrosion Rates Of Austenitic Stainless Steels In Sulfuric Acid

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ABSTRACT

Title of Thesis: A Study of The Effect of Some Inhibitors on The Corrosion Rates of Austenitic Stainless Steels in Sulfuric Acid.

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Four sulfur-containing and three nitrogen-containing organic compounds have been tested as inhibitors for four different austenitic stainless steels—SS304, SS316, SS317L, and SS410—in 10-50 weight% sulfuric acid solutions respectively. Results confirmed that the sulfur-containing compounds were more effective than the nitrogen-containing compounds. The effect of sodium iodide additions on the behaviours of two of the nitrogen-containing compounds was also studied The synergistic effect caused by the I⁻ ion was essential for nitrogen-containing compounds as inhibitors in sulfuric acid solution.

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ACKNOWLEDGEMENT

I wish to thank all of the people who have helped and inspired me, in various ways, in the progress of this study. I am much indebted to each of my committee members, Dr. L. Suchow and Dr. J. M. Grow, for their valuable reviews and suggestions. A special appreciation goes to my thesis advisor, Dr. R. P. T. Tomkins, for his meritorious guidance, thoughtful comments, and endless encouragement throughout the course of this study.

Finally, to my family goes my eternal gratitude for their love, support, and dedication.

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Chapter 1 Introduction And Theory

Definition of Corrosion

When a metal is subject to corrosion, its properties are changed due to the unintentional but destructive reaction with the exposed environment. The corrosion process is continuous and irreversible. Usually it consists of a set of electrochemical redox reactions (1). Thus the metal is oxidized to a corrosion product at anodic sites (e.g., $M \rightarrow M^{2+} + 2e^-$) and some species are reduced at cathodic sites (e.g., $2H^+ + 2e^- \rightarrow H_2$). Because of the electrochemical nature of most corrosion processes, electrochemical methods are useful tools for studying corrosion. More specifically, electrochemical techniques can be used to measure the kinetics of electrochemical processes(e.g., corrosion rates) in specific environments and also measure or control the oxidizing power (i.e., potential) of the environment (2).

Importance of Corrosion

Metals and alloys are used widely in industry. The development of many new technologies employs the use of some uncommon and expensive metals. Furthermore, the increasing pollution of the environment produces a more corrosive medium. Therefore there is a much greater need for corrosion protection techniques.

Corrosion results in a tremendous financial loss both directly and indirectly. For example, there is added cost in using protection methods, replacing of corroded equipment, using other more expensive resistant metals, as well as production and efficiency loss and industrial accidents due to corrosion. Research is needed in order to better understand the detailed mechanisms of corrosion and as a result find more efficient methods of corrosion control.

Environment

Our environment is becoming increasingly more corrosive to all materials including every kind of metal and alloy. Polluted air and water and many industrial by-products such as chlorine, ammonia, sulfur dioxide, and fuel gases are contributing factors. Inorganic acids such as hydrochloric, sulfuric, and nitric, are particularly corrosive. Other harmful materials include steam, solvents, alkalies and organic acids.

Sulfuric acid (H_2SO_4) is the most widely used inorganic acid. Consequently, sulfuric acid corrosion is the most frequently encountered in chemical processing. The behavior of stainless steels in sulfuric acid, the subject of this investigation, poses some highly complex problems. Essentially, the acid is neither highly oxidizing nor highly reducing. The stainless steels may be either passivated or activated depending on the oxidizing or reducing agents present in the solution (3). Also some impurities could affect the corrosion behavior in some systems. These impurities come from the materials treated with the acid as well as being present in the manufactured acid.

Some of these impurities accelerate the attack, while others may slow it down slightly. On the other hand some impurities may have no effect on the corrosion behavior of materials while others may make the acid much less corrosive. Table 1 lists some of the common impurities present in sulfuric acid and includes comments on their corrosion effects. In addition to the effects of impurities, concentration, velocity, temperature and degree of aeration also affect corrosion rates.

Table 1 Influence of impurities on the corrosion behavior of sulfuric acid (3)

Harmful	Neutral	Beneficial
Sulfurous ions	Ferrous ions	Ferric ions
Hyposulfurous ions	Lead ions	Copper ions
Gelatine	Chlorides	Arsenic ions
Nitrogenous Compounds	Ammonium salts	Nitric ions
Sulfurous Compounds		Nitrous ions
Vegetable matter		

Prevention of Corrosion

There are many methods that can be applied to control and minimize the corrosion of a material in a specific environment. First, the selection of the appropriate metal or alloy for a particular corrosive system is the most common method. Judicious use of the proper materials of construction and good design practices can maintain corrosion rates within tolerable limits. Second, alteration of environmental conditions can produce marked changes in corrosion properties. Typical changes in the medium that are often used are (1) lowering temperature, (2) decreasing velocity, (3) removing oxygen or oxidizers, and (4) changing concentration. Another method is the addition of substances called inhibitors to an environment. Further, application of a protective coating to the material surface, and cathodic and anodic protection are also used to combat corrosion (1).

Theory

Corrosion attack is basically a chemical reaction accompanied by the passage of an electric current. For this to occur a potential difference must exist in the system. The primary reaction in the region at the lower potential, the anode, is the dissolution of metal in the form of ions. The electrons liberated migrate through the metal to the solution at the higher potential, the cathode, where they are utilized in the reduction of either ions or oxygen. The overall effect is the passage of a current through the circuit formed by metal and solution(4-7).

Some examples of electrochemical corrosion reactions follow. The anodic reaction is the oxidation of a metal to its ion. Typically, the general form is (1):

 $\mathbf{M} \to \mathbf{M}^{+n} + \, \mathrm{ne}$

Some examples are:

$$Ag \rightarrow Ag^{+} + e$$

$$Zn \rightarrow Zn^{2+} + 2e$$

$$Al \rightarrow Al^{3+} + 3e$$

$$Fe \rightarrow Fe^{2+} + 2e$$

The metal is oxidized to a higher valency state. The valence of the metallic ion is equal to the number of electrons produced.

On the other hand, the cathodic reaction is the reduction of some species. The most frequently encountered examples are:

$$2H^+ + 2e \rightarrow H_2$$

$$O_2$$
+ 4H⁺+ 4e \rightarrow 2H₂O
M³⁺+ e \rightarrow M²⁺
M⁺+ e \rightarrow M

Obviously, the cathodic reactions use up electron(s) produced at the anode.

Therefore, corrosion reactions include at least one oxidation and one reduction reaction. Electrons generated at the metal are totally consumed by some species in solution. Electrochemical equilibrium is established between the metal and the solution. When corrosion occurs, the rate of oxidation of the metal is equal to the rate of reduction of some species. The net measurable current is zero. However, a potential is generated due to the reactions. This potential is a function of the characteristics of the metal and the nature of the solution. It is referred to as the corrosion potential, E_{CORR} (8).

In any corroding system, at least two co-existing electrochemical reactions are present.

$$M^+ + e^- \rightleftharpoons M$$
$$Z^+ + e^- \rightleftharpoons Z$$

where M is the corroding metal and Z is usually a species in solution. The current-potential relationship of such a mixed-couple system is shown in Figure 1 (8). The equilibrium potentials of the couples in the above equations are labeled $E_{EQ,M}$ and $E_{EQ,Z}$, respectively. When the corrosion potential is removed far from $E_{EQ,M}$ and $E_{EQ,Z}$, the rate of reduction of M⁺ becomes insignificiant compared to the rate of oxidation of M, and the rate of oxidation of Z becomes insignificant with respect to the rate of reduction of Z⁺. The corrosion potential, E_{CORR} , is the potential at which the rate of oxidation of M (defined by current $i_{O,M}$) is equal to the rate of reduction of Z⁺ (defined by current $i_{R,Z}$). Since the net current is the difference between the oxidation and reduction currents, the current measured with an external device will be zero.

$$i_{MEAS} = i_{O,M} - i_{R,Z} = 0$$
 at E_{CORR}

and

To calculate the corrosion rate, i_{CORR} must be determined.



Figure 1: Potential-Current Relationship for a Mixed-Electrode System

When an electrochemical method is used to measure the corrosion, the fundamental concept is based on the determination of the oxidation current at the corrosion potential. The Tafel technique is commonly used to determine the corrosion rate of a material. By this method, a controlled-potential scan is typically applied to a metal sample. The range of this potential starts from E_{CORR} , and extends into either the anodic or the cathodic direction for a few hundred millivolts.

When the resultant potential-current relationship is plotted on semi-log paper, it characteristically exhibits a linear region. This is true for both anodic and cathodic plots. The plot itself is known as a Tafel Plot and the slope of the linear region in V/decade of current is known as the Tafel Constant (Figure 2) (8). A projection of the linear region defines I_{CORR} at the intersection with E_{CORR} , and thus the corrosion rate.



Figure 2: Tafel Plot

According to Faraday's Law (8):

$$Q = \frac{nFW}{M}$$

where

Q=Coulombs

n=number of electrons involved in the electrochemical reaction

F=the Faraday, 96487 coulombs

W=weight of electroactive species

M=molecular weight of electroactive species

By rearrangement and since equivalent weight=M/n and Q=it, therefore

$$W/t = \frac{i(E.W.)}{F}$$

W/t is the corrosion rate (C.R.) in grams per second. It is convenient and customary to express corrosion rate as milli-inches per year (mpy). This unit gives an indication of penetration.

Dividing the above equation by the electrode area and the density gives

$$C.R.(cm/sec) = \frac{i(E.W.)}{dFA}$$

After converting seconds to years, centimeters to milli-inches, and the Faraday (amp-sec/eq) to microamps, this becomes

$$C.R.(mpy) = \frac{i(E.W.) \times 31.6 \times 10^{6} \times 10^{3}}{dFA \times 2.5 \times 10^{6}}$$

Expressing the term i/A as current density and combining all the constants gives:

Corrosion
$$Rate(mpy) = \frac{0.13I_{CORR}(E.W.)}{d}$$

where

 I_{CORR} = Corrosion current density, $\mu A/cm^2$

E.W. = Equivalent weight of the corroding species

d = Density of the corroding species, g/cm^3

This equation is used to calculate the corrosion rate directly from I_{CORR} .

The potential is an indication of the "willingness" of a species to gain or lose electrons, i.e., reduce or oxidize. The current is a measure of electron flow when a reduction or oxidation reaction occurs. The corrosion potential or open-circuit potential is the potential a metal will assume when placed in contact with a conductive medium. It is due to a chemical equilibrium established at the metal-solution interface.

The Tafel Plot technique provides an extremely rapid means of determining the corrosion rate when compared with weight-loss measurements. The technique can be very advantageous for such studies as inhibitor evaluations, oxidizer effects, and alloy comparisons.

Experimentally, it can happen that the extrapolations of the anodic and cathodic linear Tafel regions do not intersect at E_{CORR} . The true value of the

corrosion current will then be subject to interpretation. If this occurs, the inference must be drawn that there is an error in the measurement, since the rate of oxidation must equal the rate of reduction at E_{CORR} . In most cases, the error is probably in the anodic measurement. Since the metal specimen is corroding, the surface is changing and the mechanism of corrosion may be extremely complex. As a result, the measured Tafel Plot could then reflect the combination of several different Tafel slopes. If this behavior is observed, it is probably safest to measure I_{CORR} at the point where the cathodic Tafel extrapolation intersects E_{CORR} .

The electrochemical technique of Polarization Resistance (Linear polarization) is another method of measuring corrosion rates (8). This method involves the application of a controlled-potential scan over a small range, typically ± 25 mV with respect to E_{CORR} . The resulting current is plotted versus potential, as shown in Figure 3. The slope of this potential-current function at E_{CORR} is the Polarization Resistance. It is used together with the Tafel Constants to determine I_{CORR} .



Figure 3: Polarization Resistance Plot

When a potential is imposed on the metal specimen from an external voltage source, such as a potentiostat, a current will pass according to the following equation.

$$i_{MEAS} = i_{O,M} - i_{R,Z}$$

The anodic and cathodic currents obey the Tafel equations.

$$\eta = \beta_A \log \frac{i_{O,M}}{i_{CORR}}$$

and

$$\eta = -\beta_C \log \frac{i_{R,Z}}{i_{CORR}}$$

where

 η =overvoltage, the difference between the potential imposed on the specimen and the corrosion potential, η =E_{APP}-E_{CORR}.

By rearrangement

$$10^{\eta/\beta_A} = \frac{i_{O,M}}{i_{CORR}}$$
$$10^{-\eta/\beta_C} = \frac{i_{R,Z}}{i_{CORR}}$$

Substitution of these equations into $i_{MEAS} = i_{O,M} - i_{R,Z}$ gives

$$i_{MEAS} = i_{CORR} (10^{\eta/\beta_A} - 10^{-\eta/\beta_C})$$

 10^{x} can be approximately by the following power series

$$10^{x} = 1 + 2.3 + \frac{(2.3x)^{2}}{2!} + \dots + \frac{(2.3x)^{n}}{n!}$$

If x in this series is small, the third and later terms of the series can be truncated without significant error. Replacing η/β_A and $-\eta/\beta_C$ for x gives

$$10^{\eta/\beta_A} = 1 + 2.3^{\eta/\beta_A}$$

$$10^{-\eta/\beta_c} = 1 - 2.3^{\eta/\beta_c}$$

Substituting these equations into the ones defining i_{MEAS} and simplifying produces

$$i_{MEAS} = 2.3 \ i_{CORR} \ \eta \frac{\beta_A + \beta_C}{\beta_A \beta_C}$$

Rearrangement to solve for polarization resistance gives

$$\eta/i_{MEAS} = \frac{\beta_A \beta_C}{2.3 \ (i_{CORR})(\beta_A + \beta_C)}$$

or

$$\Delta E / \Delta I = \frac{\beta_A \beta_C}{2.3(i_{CORR})(\beta_A + \beta_C)}$$

It is important to realize that this equation is valid only if η/β is small. This means that η must be small compared to β . A typical value of β is 100 mV/decade. The overvoltage in this case should be less than 10 mV. Experimentally, linear polarization data can exhibit significant curvature within 10-20 mV of the corrosion potential. This deviation from linearity is theoretically recognized (8).

Passivity

Passivity involves a strongly reduced corrosion tendency of metals due to a protecting layer of corrosion products or some other protective film, which reduces their chemical reactivity (1,4–7). In other words, certain metals and alloys under specified conditions are basically inactive and act as if they were noble metals. Formation of a surface film or a stable protective barrier is essential and accounts for this unusual characteristic. However, the passive state in which the corrosion rate is very low is relatively unstable and subject to damage due to the environmental changes, thereby causing a great increase in corrosion rate.

Three behaviors can be observed for a metal or alloy if it possesses passivity: active, passive, and transpassive. In the active region the behavior of the material is identical to that of a normal metal. The increase in corrosion rate is proportional to the amount of oxidizing power in the system. However, an abrupt decrease in corrosion rate is seen after a critical amount of the oxidizing agent is added and passivity sets in. This critical point varies in different systems, depending on the nature of the solution, the metal and the film formed on the metal surface. Further increases in oxidizing agents yield little, if any, change in the corrosion rate of the material. Finally, at very high concentrations of oxidizers or in the presence of very powerful oxidizers, a breakdown of the protective film occurs, resulting in a great increase in corrosion rate. The system is activated again and passes into the transpassive region.

If a plot of electrode potential vs. current density is constructed, a typ-

ical S-shaped dissolution curve will be shown for a passive metal or alloy, as in Figure 4(1). There is a decrease in dissolution rate accompanying the active-to-passive transition. This decrease in dissolution rate is the result of film formation on the surface of metal or alloy. Figure 4 demonstrates three general possible cases which may occur when an active-passive metal is placed in a corrosive environment such as an acid solution. In case 1, there is only one stable intersection point, point A, which is in the active region, and a high corrosion rate is observed. Case 2 is particularly interesting since there are three possible intersection points, B, C, and D. At each point, although the total rate of oxidation and total rate of reduction are equal, point C is electrically unstable and, as a result, the system cannot exist at this point. The other two points B and D are stable. B is in the active region corresponding to a high corrosion rate, while D is in the passive region with a low corrosion rate. This system may exist in either the active or passive state. That is, both active and passive states are stable under identical environmental conditions. In case 3, there is only one stable point, in the passive region at point E. For such a system, the metal or alloy will spontaneously passivate and remain passive. The system cannot be made active and always shows a very low corrosion rate. From an engineering viewpoint, the passive state is the most desirable, since the metal will remain almost inert and corrode very slowly.



Figure 4: Behavior of an Active-Passive Metal under Corrosive Conditions

Environmental effects (1)

Effect of Oxygen and Oxidizers

The effect of oxidizers on corrosion rate is dependent on both the medium and the metals involved. Oxidizers may increase or decrease the corrosion rate, or have no effect on it.

Some examples of corrosion behavior in systems which contain oxidizers are in Table 2.

Table 2

Corrosion behavior	Examples
(1) Always active	Monel in HCl + O_2 Cu in H ₂ SO ₄ + O_2 Fe in H ₂ O + O_2
(2) Initially active, then passive	$\begin{array}{r} 18 \text{Cr-8Ni in } \text{H}_2 \text{SO}_4 \ + \ \text{Fe}^{3+} \\ \text{Ti in } \text{HCl} \ + \ \text{Cu}^{2+} \end{array}$
(3) Always passive	18Cr-8Ni in HNO ₃ Hastelloy C in FeCl ₃
(4) Initially passive, then active	18Cr-8Ni in $HNO_3 + Cr_2O_3$
(5) Initially active, passive follows, then active again	18Cr-8Ni in concentrated H ₂ SO ₄ + HNO ₃ mixtures at elevated temperature

Corrosion behaviors of some metals (1)

In general, when an oxidizing agent is added to a corroding system containing a nonpassivating metal, the corrosion rate is increased and the corrosion However, if we increase the amount of potential shifts in the noble direction. oxidizers in a passive corroding system, the corrosion behavior corresponding to case 5 in Table 2 can be observed. In other words, a passive state where the corrosion rate is low is reached when the concentration of the oxidizer in the system is increased to a certain amount and is maintained until on further increase in concentration, corrosion proceeds again (transpassive state). Before and after the passive condition, the corrosion rate of the metal is directly proportional to the concentration of oxidizer. In principle, the amount of oxidizer necessary to cause passivation is greater than that required to maintain passivity. On the other hand, although lower concentrations of oxidizers can maintain the passive state, surface damage may produce a transition from the passive to active state. Therefore, to safely guarantee passivity, oxidizer concentration should be equal to or greater than the minimum necessary to produce spontaneous passivation.

Effects of Velocity

The effects of velocity on corrosion rate are, like the effect of oxidizer additions, complicated and related to the characteristics of the metal and the exposed environment(1). When corrosion occurs, the rate of electrochemical reaction is limited by many physical and chemical factors. There are two types of polarization: activation polarization and concentration polarization (diffusion control). If the reaction sequence at the metal-electrolyte interface dominates the electrochemical process, it refers to activation polarization. It is caused by a certain slow step in the electrode process requiring an activation energy to overcome the reaction barrier. Activation polarization often happens in media containing a high concentration of active species. On the other hand, if the diffusion of species in the electrolyte controls the electrochemical reactions, it is called concentration polarization. It is caused by a difference of the concentration on the electrode surface film from that of the bulk solution. Concentration polarization generally predominates when the concentration of the reducible species is small.

Agitation and velocity will have no effect on the corrosion rate if activation polarization dominates the corrosion process. Examples are Fe in dilute HCl and 18Cr-8Ni in H₂SO₄. If the corrosion process is under cathodic diffusion control, then agitation increases the corrosion rate. This effect is generally seen when small quantities of oxidizer are added to the system. If the process is under diffusion control and the metal is easily passivated, the metal will follow an active-to-passive transition when velocity or agitation is increased. Examples are 18Cr-8Ni in H₂SO₄ + Fe³⁺ and Ti in HCl + Cu⁺².

Effects of Corrosive Concentration

Many systems such as Ni in NaOH, 18Cr-8Ni in HNO₃, Hastelloy B in HCl, and Ta in HCl that exhibit passivity effects are only negligibly affected by wide changes in corrosive concentration (1). Other systems such as Monel in HCl and Pb in H_2SO_4 show similar behavior except at very high corrosive concentrations, where the corrosion rate increases rapidly. A third possibility also exists: initially, as the concentration of corrosive is increased, the corrosion rate is likewise increased. This is primarily due to the fact that the amount of hydrogen ions, which are the active species, are increased as acid concentration is increased. However, as acid concentration is increased further, corrosion rate reaches a maximum and then decreases. This is due to the fact that at very high concentrations of acids, ionization is reduced. Because of this, many of the common acids—such as sulfuric, acetic, hydrofluoric, and others—are virtually inert when in the pure state and at moderate temperatures.

Effect of Temperature

Increasing temperature increases (except in some cases) the rate of corrosion reactions in a manner similar to that of other chemical reactions (5). In addition, the increase in both the diffusion of oxygen and the conductivity of the solution will result in more rapid corrosion. When the temperature approaches the boiling point of water, the rapid decrease in oxygen solubility will be a mitigating factor (6). Two typical behaviors can be seen with increasing temperature: a very rapid or exponential rise in corrosion rate and an almost negilgible temperature effect followed by a very rapid rise in corrosion rate at higher temperatures (Figure 5). 18Cr-8Ni in H_2SO_4 , Ni in HCl, and Fe in HF are examples of the former. On the other hand, 18Cr-8Ni in HNO₃, monel in HF, and Ni in NaOH are examples of the latter.



Figure 5: Effect of Temperature on Corrosion

Corrosion Resistance of Stainless steel (3)

The corrosion resistance of stainless steels depends not only on the exposed environment but also on the elements that constitute the steel. Following are some generalizations about the corrosion resistance of stainless steels, which relate to their major constituents:

1. Chromium content: Chromium is the most important alloying element in steel. It promotes the attainment of passivity and thus increases the corrosion resistance of the steel. A minimum chromium content of approximately 12% is required to effect passivity. With chromium content above 12%, further improvement in corrosion resistance is effected. However, steels containing chromium are liable to attack by chlorine. The negative chloride ion in aqueous solutions causes the localized corrosion known as pitting.

2. Nickel content: Nickel stands next to chromium in importance as an alloying element in stainless steel. It not only confers valuable mechanical properties but also considerably extends the resistance to corrosion by neutral chloride solutions and by acids of low oxidizing capacity. A minimum amount of 6 or 7% is required to achieve this superiority. For engineering properties and corrosion resistance, the chromium-nickel steels provide the finest of all stainless alloys. Furthermore, nickel broadens the range of passivity established by the chromium.

3. Carbon content: Carbon is always present in stainless steel as well as other commercial steels. It slightly decreases corrosion resistance when dissolved, but decreases it considerably when present as free carbide.

4. Molybdenum content: Molybdenum, with certain exceptions, expands the passivity range, counteracts the tendency to pit, and improves corrosion resistance of the steels. It is particularly useful in sulfuric and sulfurous acids at high temperatures and pressures and in neutral chloride solutions, specifically in sea water.

5. Copper content: Copper additions to stainless steel are restricted but particularly useful in increasing resistance to sulfuric acid.

6. Silicon: Silicon primarily enhances oxidation and carburization resistance at high temperatures. In strong sulfuric acid solution, 1.0% or more is sometimes added to improve corrosion resistance. However, it offers little improvement against dilute sulfuric acid and is unfavorable in nitric acid.

Chapter 2

Corrosion Inhibitors

Classification

Corrosion of an exposed metal can be reduced by addition of small amounts of chemicals to a corrodent. This is a preventive process known as inhibition and the chemicals used to reduce the corrosion process are called Inhibitors. Inhibitors can be classified as (5,9-11):

- (1) Anodic inhibitors (reduce the rate of anodic oxidation).
- (2) Cathodic inhibitors (reduce the rate of cathodic reduction).
- (3) Mixed inhibitors (reduce the rate of both).

They can also be classified according to:

- (1) Chemical nature (organic and inorganic substances).
- (2) Inhibitor characteristics (oxidizing or nonoxidizing compounds).
- (3) Field of applications (pickling, descaling, acid cleaning, cooling water system etc.).
- (4) Mechanisms of operations (barrier layer formers, neutralizers, scavengers, and miscellaneous types).

Anodic inhibitors are chemicals that stifle the reaction at the anode. Generally, they react with the initially formed corrosion product and form an extremely insoluble and thick film which adheres tightly to the metal surface, preventing the corrosive solution from entering into contact with the metal surface. Thus corrosion is disminished or avoided. For example, nitrite seems to act by oxidizing the corrosion products to compounds which have lower solubility and therefore form protective films more easily (6).
$$NO_2^- + 8H^+ + 6e = NH_4^+ + 2H_2O$$

Some chromates such as Na_2CrO_4 or K_2CrO_4 also act as anodic inhibitors. Their action partly consists of an oxidation of corrosion products to less soluble forms (6).

 $CrO_4^{2-} + 8H^+ + 3e = Cr^{3+} + 4H_2O$

Cathodic inhibitors, on the other hand, reduce corrosion indirectly by stifling the cathodic reactions. Divalent cations react with the hydroxyl anions and form precipitates over the cathodic areas, avoiding the cathodic reaction. As an example, the anodic reaction is (10):

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$

And the cathodic reaction is:

$$2H^+ + 2e^- \rightarrow 2H^\circ$$

and

$$H^{\circ} + H^{\circ} \rightarrow H_2$$

Hydrogen ions from solution are converted into hydrogen atoms by utilization of the electrons left by the anodic reaction. The hydrogen atoms then combine into a hydrogen molecule at the metal surface. These cathodic reactions are based on the reduction of hydrogen ions and will occur in acidic solutions. As the solution becomes neutral, the concentration of hydrogen ions decreases greatly and the main cathodic reaction then becomes one of the conversion of oxygen to hydroxyl ions:

$$O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

The ferrous ions that were dissolved at the anode then will react with the

hydroxyl ions to precipitate ferrous hydroxide either at the surface or near it in solution:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

In most cases there is sufficient oxygen in the solution to oxidize the ferrous hydroxide to ferric hydroxide:

$$4 \text{Fe}(\text{OH})_2 + \text{O}_2 + 2 \text{H}_2 \text{O} \rightarrow 4 \text{Fe}(\text{OH})_3$$

The interesting phenomenon of all these reactions is the formation of a protective layer of hydrogen atoms over the cathode, preventing hydrogen ions from reaching the electrons that are at the metal surface. The cathodic reaction is stifled and consequently the anodic reaction is forced to slow down and stop.

The cathodic inhibitors are less effective than anodic inhibitors due to the fact that the precipitates do not tightly bond to the metal surface. Good examples of cathodic inhibitors are salts of zinc and calcium.

There is no universal inhibitor. Each inhibitor is specific for a particular corrosion problem. However it is possible to use the same inhibitor at different pH values for different corrosion problems.

Corrosion Mechanisms in Acid Solutions

Aqueous acid solutions cause severe corrosion with metals and alloys. Organic compounds such as triple-bonded hydrocarbons, acetylenic alcohols, sulfoxides, sulfides, mercaptans, and aliphatic, aromatic, or heterocyclic compounds containing nitrogen, and sulfur as well as many other families of simple organic compounds can be added to the metal-electrolyte as inhibitors to reduce corrosive effects. Table 3 shows some organic inhibitors. Efficient inorganic compounds include metal salts and oxidizing agents such as $SnSO_4$, CuSO₄, FeSO₄, K₂Cr₂O₇, KIO₄, KIO₃, K₄Fe(CN)₆, Na₂SO₄, NiSO₄, MnSO₄, (NH₄)₂SO₄, HNO₃, H₂O₂, etc.

Table 3

Classification	Compounds
N-containing compounds	2-aminobicyclohexyl, aniline, benzylallylamine, unsaturated ethoxylated amines, hexamethylene tetramine (urotropine), toluidines, acetoxime, 4-methoxybenzonitrile, cinnamonitrile, 1-hexyne-3-ol, pyridinium, nitrobenzene, etc.
S-containing compounds	alkylmercaptanes, benzylmercaptanes, mercaptobenzthiazol, thiocresoles, etc.
Acetylenic alcohols	propargylalcohol, 1,4-butyne-diol, 1-phenoxy-2-butyne-4-ol, etc.
Sulfides	dibenzylsulfide, dipropargylsulfide, diethylsulfide
Sulfoxides	dibenzylsulfoxide, ditholylsulfoxide
Others	thioaldehydes, thioureas, thionamides, thiocyanates, thiazoles, sulfonamides, etc.

Examples of Organic Inhibitors (39)

The first step in the mechanism of the inhibitor in an aggressive acid media is the adsorption of the inhibitor by the metal surface. This process depends on several factors (12):

- (1) The nature and surface charge of the metal.
- (2) The chemical structure of the organic inhibitor.
- (3) The type of aggressive electrolyte.

The basic types of interaction between an organic inhibitor and a metal surface are physical (or electrostatic) adsorption and chemisorption. Physical adsorption is caused by electrostatic attractive forces between the inhibitor ions and the metal surface which is electrically charged. An electric field is produced at the metal surface, which is responsible for the surface charge. The electric field exists at the outer Helmholtz plane of the electrical double layer that is present at the metal/solution interface. This surface charge can be defined by the potential of the metal (E_{CORR}) vs. its zero-charge potential $(E_{g=0})$ (13). Helmholtz suggested a model in which the charges at the interface were regarded as the two plates constituting a parallel plate capacitor, e.g. a plate of metal with excess electrons (the inner Helmholtz plate I.H.P.) and a plate of excess positively charged ions (the outer Helmholtz plate O.H.P.) in the solution adjacent to the metal. The charges balance one another so that the electrical double layer is neutral as a whole (Figure 6) (5).



Figure 6: Helmholtz Double Layer

When the difference $E_{CORR}-E_{q=0}=\phi$ is negative, cation adsorption is favored, while a positive difference favors the adsorption of anions. This pattern is seen in compounds with positive or negative charges and in dipoles whose orientation is determined by the value of the ϕ potential.

Adsorbable anions such as halide ions which may be present in the solution are adsorbed on the metal surface by creating oriented dipoles (5, 14). In aqueous solution the potential difference is large due to adsorption of water molecules, although adsorption of other molecules in solution can also have an effect. Although the water molecule is electrically neutral as a whole, the fact that the two binding electrons are closer to the oxygen atom than to the hydrogen atoms, resulting in an electric dipole with a positively charged (hydrogen) end and a negatively charged (oxygen) end, and consequently a potential difference exists across the molecule (Figure 7-a).



Figure 7: Adsorption of Water Dipoles

If the metal has a large negative excess charge, the adsorbed water molecules will be oriented with their positive ends towards the metal and their negative ends towards the solution. This layer of oriented dipoles will contribute an additional potential difference to the layer (Figure 7-b). The converse situation will arise when the metal has a large positive charge, and again the dipoles will contribute to the potential difference (Figure 7-c). In the case of a metal with only a small excess charge, dipoles of both orientations will adsorb, and the potential difference will be proportional to the excess number of one or the other (Figure 7-d)(5).

The above behavior increases the adsorption of the organic cations on the dipole and creates a positive synergistic effect (When two or more inhibiting compounds are added to a corrosive system, the inhibiting effect is sometimes greater than that which would be obtained by either of the two or more substances alone.), so that the degree of inhibition when adsorbable anions and inhibitor cations are present, is higher than the sum of the individual effects.

In some chemicals, electrostatic adsorption is responsible for their inhibiting properties. The inhibitor interacts rapidly but weakly with the electrode surface, and thus, it can be easily removed. This adsorption process is characterized by having a low activation energy and being relatively independent of temperature. However, it depends on other factors such as (15):

- (1) The electrical characteristics of the organic inhibitors.
- (2) The position of the corrosion potential with respect to the zero-charge potential.
- (3) The type of adsorbable anions present in the aggressive solution.

Chemisorption is the other main type of metal/inhibitor interaction. In chemisorption, charges are shared or transported from the inhibitor to the metal surface, creating a coordinate type of bond. An example of chemisorption is the adsorption of hydrogen gas onto the surface of tungsten (5). The hydrogen molecules contact with the surface, dissociate and form a chemical bond. Each atom of hydrogen combines with an atom of tungsten to form a monolayer so that the layer is chemically bonded by covalent (or ionic) forces to the metal. This process has a higher activation energy than physical adsorption but is slower. Unlike physical adsorption, chemisorption depends on the temperature. At higher temperatures, the inhibition effect increases. Also, it is specific for certain metals, creating strong bonds with the metal surface. The nature of the metal and the nature of the organic inhibitor will determine the bonding when electrons are transferred. The transfer occurs when metals have vacant and low energy electron orbitals, as in the transition metals. In inhibitors by contrast, electron transfer occurs in molecules having relatively loosely bonded electrons. This situation may arise because the adsorbed inhibitor contains multiple bonds or aromatic rings, whose electrons have a π character. Besides, electron transfer is favored when the adsorbed molecule presents heteroatoms with one-pair electrons. Usually, molecules of organic inhibitors have at least one functional group which behaves as a reaction center for the chemisorption process. The electron density and polarization of the heteroatom will determine the strength of the adsorption bond.

Inhibitor efficiency may increase, when there are lateral interactions between inhibitor molecules, which is produced when the coverage at the metal surface by the inhibitor increases. These lateral interactions produce a strong adsorption and thus, a high inhibitor efficiency. An example of this effect is seen in molecules with long hydrocarbon chains, whose lateral interaction is enhanced by van der Waals forces (16,17). However inhibition efficiency can be diminished when a repulsive interaction occurs due to the presence of ions or molecules containing dipoles which will cause a weak adsorption.

The purpose of using inhibitors is to avoid or disminish the acid corrosion of metals. This can be accomplished by retarding either the acidic dissolution of metals, the cathodic hydrogen evolution reaction or both. This process consists of different mechanisms involving the following (12):

Changes in the Electrical Double Layer

One of the inhibitor effects is produced by changing the structure of the electrical double layer at the metal/solution interface. This effect is produced by electrostatic adsorption of ionized inhibiting species. Adsorption of organic cations or anions results in a positive or negative adsorption potential jump. Adsorption of cations (i.e., quaternary ammonium ions or pyridinium ions) (18) to the iron surface in acid solution causes a positive shift in the potential known as **positive adsorption potential jump**. In this case the hydrogen evolution reaction is reduced in deaerated acid solutions. In aerated solutions, the hydrogen evolution is inhibited in the presence of organic cations, and the oxygen reduction reaction may become important. Selective inhibitors can retard the hydrogen evolution better than the oxygen reduction reaction. By contrast, the adsorption of anions stimulates the hydrogen evolution reaction. Thus, a **negative adsorption potential jump** is produced.

Formation of a Physical Barrier

A different type of inhibitor effect is the formation of a multimolecular layer on the metal surface which interferes with the diffusion of ions to or from the metal surface. The hindering of mass transfer causes inhibition of the corrosion reaction. Inhibitors such as sulfoxides, acetylene derivatives, or substances with a high number of carbon atoms in the hydrocarbon chain possess this property. The physical barrier formed is independent of the nature of the adsorption force between the molecules of the inhibitor and the metal surface. Attractive lateral interactions, chemisorption bonds, electron interactions and hydrogen bonds can also be involved in this process.

Reduction of Metal Reactivity

A third type of inhibition mechanism is a reduction of metal reactivity. This mechanism does not necessarily involve total or partial coverage of the metal surface by the inhibitor. Interacting forces, such as chemisorption, are very important in this process and the stronger the bond, the higher is the efficiency obtained. In this process the inhibitor adsorbs on sites active with respect to the partial electrochemical reactions. When this occurs, active sites are blocked and the reduction of either the anodic or cathodic reaction is increased. Consequently, the reaction rate decreases proportionally to the blockage of the active sites by the inhibitor.

Participation of the Inhibitor in Partial Electrochemical Reactions

Anodic and cathodic reactions include steps involving adsorbed intermediates on the metal surface. The adsorbed inhibitor can affect the intermediate formation by increasing or decreasing the rate of electrode reaction. This effect depends on the stability of the adsorbed surface intermediate. When an organic molecule produces a decrease in corrosion rate, the formation of a stable surface complex with the inhibitor can be considered. As an example, we may consider the anodic process of iron dissolution. The formation of intermediates such as adsorbed (FeOH) is generally assumed. In the presence of organic inhibitors (Inh), the formation of a stable chelate [(FeOH) Inh_n] adsorbed to the iron surface is considered. The presence of this surface complex reduces the rate of anodic dissolution of iron. As a result, a variation in the anodic Tafel slope is observed (12).

Selection of the wrong inhibitor in acid solutions may cause corrosion stimulation instead of inhibition and/or hydrogen penetration into the metal.

Acid corrosion of iron, for example, is accelerated when low concentra-

tions of inhibitor are used (19). Some examples of inhibitors that enhance the corrosion of iron are mercaptans, sulfoxides, nitriles, and quinoline. This effect depends on the type of acid. Steel corrosion can be inhibited by using bis(4-dimethylaminophenyl) antipyrilcarbinol and its derivatives in 10^{-4} M hydrochloric acid solutions. By contrast, these same inhibitors in sulfuric acid solution have the opposite effect, by stimulating corrosion.

The causes of adverse stimulating effects of organic inhibitors may be classified as follows (20):

- Stimulation caused by inhibitor decomposition products. This process seems to be basically related to the use of critical concentrations of organic inhibitors containing sulfur-thiourea and its derivatives, thiocyanates, etc. For example, thiourea shows a maximum in the concentration-efficiency curves. Beyond this maximum, thiourea progressively loses its efficiency and eventually becomes a corrosion promoter (42).
- 2. Stimulation through preferential paths of partial electrochemical reactions in corrosion processes. When an additive is present in an aggressive environment it can provide a catalytic path of lowered activation energy for an electrochemical reaction, and therefore enhance the process. Examples of inhibitors which have this characteristic are amines.
- 3. Stimulation caused by inhibitor participation in the metal dissolution process. According to this mechanism, the acceleration of corrosion in the presence of organic compounds is related to the oxidative tendency of the surface chelates. Inhibition persists until the chelate is adsorbed. If charge transfer comes about with desorption of the complex ions, the additive will undoubtedly act as a stimulator. For example, Bockris (21) has suggested the following mechanism for iron dissolution:

Fe + OH⁻ = (FeOH)_{ads} + e⁻
(FeOH)_{ads}
$$\rightarrow$$
 (FeOH)⁺ + e⁻

$$(\text{FeOH})^+ \rightarrow \text{Fe}^{2+} + \text{OH}^-$$

If the effect of the inhibitor (I) is on the adsorbed intermediate:

$$(\text{FeOH})_{ads} + nI \rightleftharpoons [\text{(FeOH) } I_n]_{ads}$$

$$[\text{(FeOH) I}_n]_{ads} \rightarrow [\text{(FeOH) I}_n]^+ + e^-$$

The adsorbed intermediate interacts with n molecules of inhibitor I to form a complex which is adsorbed on the surface. This complex can undergo charge transfer and desorb as a complex ion. A postulated inhibitor may in fact be an accelerator.

The application of organic inhibitors for pickling and acid cleaning treatments presents the problem of hydrogen penetration into the metal (12). Any additive covering the metal surface usually decreases the amount of hydrogen produced and also decreases the molcular hydrogen further, so that hydrogen penetration into the metal can be increased.

Although some chemicals are very effective corrosion inhibitors for ferrous metals, they can provoke hydrogen penetration. Examples are organic compounds such as thiourea and its derivatives and mercaptans that contain =C=S or $\equiv C-SH$ bonds (22). Apparently, these chemicals are reduced in the cathodic area, forming hydrogen sulfide which is the promoter of hydrogen penetration that creates the embrittlement of the metal.

Certain chemicals have the property of inhibiting corrosion by interfering with the cathodic and/or anodic reaction occuring at the site where the inhibitor adsorbs onto the metal surface (11). The corrosion reaction can be significantly reduced when the metal coverage is total due to a complete adsorption process. An example of this effect is seen with acetylenic alcohols on steel in hydrochloric acid (23). The same effect can be found in organic nitrogen compounds such as quinoline, aromatic amines and some quaternary salts in strong acid solutions (24). Other effective inhibitors are organic compounds containing 5A or 6A periodic chart elements. Inorganic compounds such as sulfides, arsenic, antimony, and halides also act as adsorbed layer inhibitors in strongly acid solutions.

Strong acid inhibition is usually used in oil-well acidizing, metal pickling and acid cleaning. The most effective inhibitors act by interfering in one or more steps of the dissolution process. Usually they interfere with both anodic and cathodic reactions so that there is no measurbable shift in corrosion potential.

Corrosion Mechanisms in Neutral Solution

Efficient inhibitors in acid solutions have little or no effect in near-neutral solutions. This is due to differences in the mechanism of the corrosion processes. In acid solutions the inhibitor action is caused by adsorption on oxidefree metal surfaces. In these media the main cathodic process is hydrogen evolution. On the other hand, in neutral aqueous solutions the corrosion processes result in the formation of insoluble surface products such as oxides, hydroxides, or salts. The cathodic reaction is oxygen reduction. The inhibitors influence the oxide-covered surface by increasing or maintaining the protective characteristics of the oxide or of the surface compounds in the aggressive solutions. If the concentration of inhibitors, the pH value of the inhibitive anion (favored in alkaline solution), the dissolved oxygen concentration and supply in the solution, aggressive anion concentration, the nature of the metal surface, and temperature of the solution are well known and controlled (5), this effect can be accomplished. The basic step of inhibition is the replacement of preadsorbed water molecules by adsorbing inhibitor molecules. Chemical or electrochemical reactions of the inhibitor at the surface may also participate

in order to explain the inhibitor efficiency and these reactions may consume more inhibitor (25-27).

In many cases inorganic compounds are used as inhibitors in near-neutral solutions:

- Ca²⁺ and Mg²⁺ ions are usually present in industrial waters. They produce local alkalinity in the system and react with anions to form carbonate precipitates on the metal surface. Corrosion attack is thus prevented.
- 2. Ni²⁺, Co²⁺, Zn²⁺, Fe²⁺ are intentionally added to water to modify surface film protective properties. They also tend to form insoluble hydroxyles, especially at cathodic areas, and are more alkaline due to the hydroxyl ions produced by reduction of oxygen. In the case of corrosion inhibition of zinc in 3% NaCl solution by the action of diluted cobalt chloride, Leidheiser and Suzuki (28) attributed the inhibiting efficiency to the introduction of Co atoms into the zinc surface oxide, which led to inhibition of cathodic oxygen reduction. On the other hand, the inhibiting efficiency of Fe²⁺ against corrosion of Cu-Ni alloys in water is attributed to the formation of a γ -FeOOH protective layer.
- 3. Inorganic anions such as polyphosphates, phosphates, silicates, and borates all contribute to the formation and maintenance of protective films according to various mechanisms (29). Their action limits diffusion of dissolved oxygen to the metal surface and therefore affects the cathodic reaction and in some cases even the anodic reaction. For example, polyphosphates in the presence of zinc or calcium can produce a thin amorphous salt film. This salt film restricts diffusion of dissolved oxygen to the metal surface. The film is a poor electronic conductor so that oxygen reduction does not occur on the film surface (5).
- 4. Oxidizing inhibitors such as chromates and nitrites are commonly used to reduce the corrosion rate of metals and alloys with active-passive anodic

behavior. They function by causing self-passivation of the metallic material due to the fact that the oxide films on metals offer high resistance to the diffusion of metal ions and the anodic reaction of metal dissolution is inhibited (5, 30).

Sodium salts of organic acids such as benzoate, salicylate, cinnamate, tartrate, and azelate are alternatives to the inorganic compounds mentioned above, particularly with ferrous metals. The action of these substances is assumed to involve the adsorption of the anion on the oxide surface (26). Other inhibitor formulations for ferrous metals include organic phosphoruscontaining compounds, often in conjunction with zinc ions. Compounds such as salts of aminomethylenephosphonic acid, hydroxyethylidenediphosphonic acid, and phosphinocarboxylic acid have also been suggested (31,32).

Corrosion Mechanisms in Alkaline Solutions

A third group of inhibitors are used in alkaline solutions. If the metal hydroxides are amphoteric or the protective oxides are easily destroyed in the presence of alkalies, the metals are liable to caustic attack. Useful inhibitors consist of organic substances such as tannins, gelatine, saponin, thiourea, substituted phenols and naphthols, beta-diketones, and quinalizarine (33). They act by expanding the pH stability range of amphoteric oxide and hydroxide layers, protecting pores in oxide and hydroxide films, decreasing the diffusion rate of reactant to the surface, and removing corrosion products from the surface (9).

Other Inhibitors (11)

Passivators—oxidizing inhibitors—are another important class of barrier– layer former. They are useful in neutral aqueous solutions. These inhibitors shift the electrochemical potential of the corroding metal into a region where a stable, water-repellent oxide or hydroxide is produced which protects the metal surface. This type of inhibitor is especially effective on steels, although it is also effective on copper base alloys and certain other alloy systems. Chromates and nitriles are very effective for inhibiting steel in neutral environments. The main benefits of this type of inhibitor are that they are relatively inexpensive, are efficient at low concentrations, and greatly reduce the corrosion rate of steel. However, chromates and nitrosamine formation can pollute the environment. Molybdates and tungstates are alternatives to overcome this problem.

In many systems, although corrosive agents are present in small quantities or concentrations, they can induce severe damage to the metals or alloys. Scavengers are designed to remove such small amounts of detrimental species. One of the most widely used scavenger systems is employed in boilers to remove oxygen from the feedwater. Typical techniques such as stream stripping can remove the bulk of dissolved oxygen from water. However, the lower the concentration of oxygen present in the feedwater, the more difficult and expensive it is to remove. In this case, chemical techniques for oxygen removal become much more attractive. The two most widely used scavengers in boiler systems are hydrazine and sodium sulfite.

In chemical processing, many organic compounds are used for cleaning and finishing. However some of these organic compounds can break down into acidic products which are corrosive to metals. For example, chlorinated hydrocarbons in the presence of water can decompose into hydrochloric acid especially at higher temperatures. The hydrochloric acid is of course detrimental to steel, aluminum and other structural materials. This problem can be overcome by adding small quantities of inhibitors, such as volatile amines or dioxane, which either react with the hydrochloric acid or impede the decomposition process (11). Chemical bond formation can also play a role in inhibition. The functional polar group of the organic inhibitor bonds to the metal surface to form a protective film.

Some inhibitors are not only corrosion inhibitors but also beneficial compounds in certain systems (34). Examples are biocides such as quaternary ammonium compounds which are used in cooling water applications. They can interfere with the corrosion process and preclude the harmful bacteria from fouling the equipment.

Scale deposits, such as precipitates of calcium carbonate on heat transfer surfaces are another type of corrosion (34). This localized darnage can result in pitting and perforation. It causes leakage of solution and partial area overheating which is a safety hazard. Scale inhibitors react to interfere with the normal crystal growth and form soft nonadherent precipitates in solution rather than on the metal surface. Typical inhibitors for this purpose are phosphonates, gluconates, and polyacrylic acids. In addition, chelating agents such as ethylene diamine tetraacetic acid (EDTA) can be used as descaling agents. Nevertheless, the protective corrosion products can sometimes be dissolved if chelating agents are used. The amount of chelating agents in solution needs to be carefully controlled in order to maintain the corrosion rate below an acceptable value.

Finally and surprisingly, water is a effective inhibitor in some systems. It is added to liquid ammonia to enhance the formation of a protective corrosion product on carbon steels and thereby reduce stress corrosion cracking (35). Similarly, it is also applied ($\sim 1\%$) to anhydrous ethylene glycol to protect aluminum from corrosion.

Corrosion Inhibitors in Sulfuric Acid Media

The corrosion prevention of stainless steels in sulfuric acid can be achieved by adding some inorganic sulfates or oxidizing agents to the electrolyte. Additives like SnSO₄, NiSO₄, MnSO₄, HNO₃, Na₂Cr₂O₇, CrO₃, K₂Cr₂O₇, KIO₄, $KMnO_4$, H_2O_2 , $HgCl_2$, KIO_3 , and $K_4Fe(CN)_6$ can inhibit attack in sulfuric acid (36–37). Small additions of the sulfates of copper, cerium, silver, or mercury can effectively passivate stainless steels in sulfuric acid. The sulfates of ammonium, sodium, iron (ferrous), manganese and nickel lower the corrosion rate in dilute acids, but their more or less inhibiting action does not amount to passivation. Kiefer and Renshaw (36) showed that the presence of any of the sulfates (ammonium, sodium, ferrous, copper, or stannous sulfate) greatly lowers the corrosion rate of both Types 304 and 316 in 5 percent sulfuric acid. However, as the temperature increases to 55C, the effect becomes less pronounced, particularly with Type 304, except when copper or stannous sulfate is present. In 30 percent sulfuric acid, the influence of sulfates on the corrosion rate is not so strong as in 5 percent acid, except for copper or stannous sulfate. Copper and stannous sulfates are quite powerful passivating agents, especially with respect to 18/8/Mo steels. In 30% acid, additions of ferrous or nickelous sulfate have the opposite effect of increasing the corrosion rate, whereas stannous sulfate maintains its passivating action at this concentration.

The passivating film formed by using oxidizing agents resists breakdown for a long time after the transfer of the passivated metal to the electrolyte (H_2SO_4) containing no oxidizing agents (37). This reveals that stainless steel equipment may be passivated periodically by the use of oxidizing agents incorporated in the electrolytes. During the intervals between two passivation treatments, the equipment should be able to handle normal electrolytes.

Arsenic is a common impurity in industrial sulfuric acid and its effect on the corrosion of iron and mild steel are well known (3). For stainless steels, arsenic in sulfuric acid media exerts a great protective action, acting as an anodic inhibitor which reacts with the corrosion product to form an insoluble film on the metal surface, especially in the presence of molybdenum because it expands the range of passivity.

Nitric acid has a very powerful passivating effect on stainless steels, but their behavior is essentially a function of their surface finish and the acid concentration (3). After mechanical polishing, an austenitic 18/8 steel requires between 2 and 7% nitric acid to passivate it in hot sulfuric acid solutions of strength 5 to 60%, whereas when the surface has been pickled a smaller proportion will suffice. As the sulfuric acid concentration is increased, the amount of nitric acid required to passivate the stainless steels decreases. This is due to the fact that at high concentrations of sulfuric acid, ionization is reduced, and the corrosion strength of the concentrated acid is not so strong as in dilute acid.

Passivation by nitric acid is greatly facilitated when the steel contains molybdenum because it extends the passivity range and improves corrosion resistance of the steel. (3). At 100-110 C, for example, the 18/8 grade with 2.5% molybdeum is passivated by as little as 2% nitric acid at all sulfuric acid concentrations up to about 70%; this passivity is obtained regardless of whether the surfaces have been pickled or polished.

It was also found that a 0.5 to 1% concentration of nitric acid in stagnant 65% sulfuric acid significantly reduces the corrosion rate (38). The action of nitric acid is unusual. Initially, corrosion is very significant, then it drops to less than 5 mpy. This is due to the replacement of the normal ferrous sulfate film by a more protective ferric sulfate surface film. Conditions leading to this kind of inhibition of carbon steel at 70 to 100 F are (1) quiescent conditions, so that the HNO₃ reaction may proceed via buildup of NO⁺ at the corroding surface, and (2) a relatively narrow range of nitric acid concentration.

Bonhoeffer (39) showed that HNO_2 is involved in the passivation of iron in concentrated HNO_3 . The nitrous acid acts as a cathodic depolarizer. Although it lowers the redox potential of the nitric acid slightly, it increases the anodic current density to the level required for passivation.

McKinnell, Lockwood, Speiser, and Fontana found that nitric oxide causes passivation of abraded Type 302 stainless steel surfaces in 10 percent H_2SO_4 solution (40). This passivation apparently is due to the presence of HNO_2 in the acid. The specimens were passivated by bubbling nitric oxide through the solution. Bubbling oxygen through the solution did not passivate these abraded specimens. And removal of HNO_2 from the solutions by the addition of urea destroys the passivating effect of nitric oxide-treated H_2SO_4 solutions.

S-containing inhibitors are useful in sulfuric acid (41). Sulfoxides, sulfides, and thioureas are mostly used in commercial inhibitor formulations, with dibenzyl sulfoxide, dibenzyl sulfide, thiourea and di-o-tolythiourea being the most prominent representatives of these groups of compounds. Physical adsorption is responsible for the corrosion mechanism. The inhibitor covers some portion of the metal surface, causing a hindrance for the corrosive, so that the metal is protected. These inhibitors also exhibit good efficiencies at higher temperatures.

Thiourea has long been known as an inhibitor for the acid corrosion of iron (42-48). It has been characterized as either an anodic, cathodic or mixed inhibitor due to the controversy of its mechanism of inhibition. Unlike many other inhibitors, thiourea shows a maximum in the concentration-efficiency curves. Beyond this maximum, thiourea progressively loses its efficiency and eventually becomes a corrosion promoter. At all temperatures, the efficiency increases with concentration up to a critical concentration, above which it drops. The extent of this drop depends upon concentration, temperature, and pH. At concentrations less than critical point, the protection efficiency increases with temperature.

As an inhibitor, thiourea can undergo specific adsorption, i.e. it adsorbs in the inner part of the Helmholtz double layer. Thiourea and its protonated species (see below) can replace some of the H⁺ ions from the outer Helmholtz plane. This limits the accessibility of the reacting ion H⁺ to the metal surface, i.e. the additive blocks part of the surface and hence decreases the reaction rate (42).

Thiourea could undergo protonation resulting in loss of efficiency at higher concentrations:



The protonated species catalyzes the hydrogen evolution reaction and hence increases the corrosion reaction. Thiourea could also gradually yield corrosion promoting species, e.g., HS⁻ ion, during the corrosion-inhibition process and its efficiency is reduced when the ion concentration is high in the corroding system.

Some imidazole derivatives, especially 2-mercaptobenzimidazol, proved to be valuable inhibitors for steel in low concentrations of sulfuric acid at temperatures up to 70 C (41). Imidazole has strong intermolecular hydrogen bonding in the solid state and in the acid solution the binding of the cations, H^+ , was found to have a significant effect on the hydrogen bonding (49). Thus, as an inhibitor, imidazole is chemically adsorbed on the surface of metal to form a polymeric film which is a insoluble corrosion-inhibiting layer (50). Improved results were obtained using 2-mercapto-benzimidazole in combination with alkynols, especially propargyl alcohol or 1-hexyl-3-ol, since the alcohol was used as a medium for the reaction. As these mixed inhibitors are also effective against sulfuric acid attack on copper, brass, and aluminum, they seem useful for the inhibition of cleaning acids.

Highly efficient inhibitors based on N-containing organic compounds include, e.g., alkylamines, benzylquinolinium, alkylbenzylquinolinium halides, n-alkyltrimethylammonium, n-alkylpyridinium, n-alkyl-benzylpyridinium, nalkylquinolinium, n-alkylisoquinolinium halides, and p-alkylbenzylquinolinium halides (the alkyl part generally being a C_8-C_{12} straight chain), preferably in combination with potassium iodide (41). The substances, applied in concentrations of $10^{-2}-10^{-3}$ mol/l, provide efficient corrosion inhibition for steel at 20-60 C in sulphuric acid of 5-30 mass%. It was suggested that the inhibition adsorption is assisted by interaction between the π -electrons of the heterocyclic ring system and the metal surface, as in the chemisorption mechanism.

Long-chain n-alkylisoquinolinium compounds are very good inhibitors of the corrosion of steel by sulfuric, hydrochloric and hydrobromic acids, giving up to 99% protection in the best cases (51). Again, the π -electrons of the heterocyclic ring system play an important role in the inhibition mechanism. Also, the inhibition increases with increasing alkyl chain length except at the highest levels. The effect of the alkyl chain length on corrosion inhibition by n- alkylisoquinolinium compounds is more clearly seen at higher temperature due to better solubility of the alkyl chain. Above about 93% inhibition there is no longer a direct relationship between alkyl chain length and corrosion inhibition and the highest maximum values are again obtained with the C_s, C₁₀ and C₁₂ compounds. This is probably related to the perfection of packing of the ions in the adsorbed layer. At the maximum inhibition the adsorbed ions are probably almost close- packed. The corrosion protection persists for a long time after transfer of the steel from the inhibited to the uninhibited acid solution. Another advantage of these compounds is that they give significiant corrosion inhibition in neutral aqueous media. In this case, the anodic reaction:

$$Fe_{metal} + x H_2O \rightarrow Fe x H_2O^{2+} + 2e$$

is the same in acid solution, but the hydrogen ion discharge reaction is replaced by a cathodic reaction involving the reduction of oxygen:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-$$

The corrosion rate is relatively low, since it is limited by the rate which oxygen can diffuse from the atmosphere to the metal surface. The inhibition is predominantly anodic and the steel surfaces in the inhibitor solutions become water repellent, indicating that the adsorbed films are very stable as in acid solutions.

N-containing inhibitors such as amines or quaternary ammonium salts are relatively ineffective in preventing corrosion of iron in sulfuric acid unless certain anions, especially halide (except fluoride) and pseudo-halide ions, are present. The oriented dipoles created due to interaction between the anions and the metal account for this corrosion mechanism, as in physical adsorption (pages 24 & 25). This long known synergistic effect, which increases in the order Cl⁻ <Br⁻ <I⁻, is widely used in inhibitor formulation.

The effect of inorganic halides on certain inhibitors used for low-carbon steel in sulfuric acid has been reported (52). The degree of inhibition was found to be greatly dependent upon the concentration of the halide. The authors attributed the observed inhibitor characteristics of halides to the formation of a monomolecular film of the iron halide. Halides functioned as inhibitors by increasing the polarization of the local anodes on the steel. This meant that the apparent single potential of steel moved in a cathodic (noble) direction if a halide was added to the sulfuric acid where the steel was immersed. The iodide has a relative superiority over the other halides. The ability of the halides to limit hydrogen absorption was not outstanding. Halide addition significantly improved the inhibitor performance of many organic compounds.

Acetylenic alcohols also exert inhibitive activity in sulfuric acid, but generally higher concentrations $(5.10^{-2}-10^{-2} \text{ mol/l})$ are needed than those used in hydrochloric acid $(10^{-2}-10^{-3} \text{ mol/l})$ (41). However, an enormous synergistic effect is observed in the presence of halide ions (except fluoride). Thus the corrosion rate of steel in boiling 15% H₂SO₄ was found to be 1751 g/m²h and 1355 g/m²h in the presence of 0.4% propargyl alcohol or 0.4% 1-hexyn-3ol, respectively, whereas the introduction of KCl decreased the rate of metal dissolution to 5 and 1.5 g/m²h, respectively. This example again emphasises the high value of acetylenic alcohols, especially of 1-hexyn-3-ol as inhibitor compounds for service at high temperatures.

Mild steel in contact with an aqueous solution of sulfurous acid can be protected from corrosion by the use of inhibitors consisting of ammonium oxalate and hexamine (53). It was found that hexamine gives good temporary protection and that ammonium oxalate gives good protection of a more permanent nature. However, a combination of the two materials is much surperior to either one alone. The dark solid film produced by the combination is harder and much more adherent to the steel and has less free and active poles than that produced by ammonium oxalate alone. Also, large amounts of sulfuric acid can be present in the sulfurous acid without materially changing the protective value obtained with ammonium oxalate alone. The presence of a combination of hexamine and ammonium oxalate in sulfuric acid will considerably reduce the corrosion rate of low carbow steel in that acid.

Limitations in Use of Inhibitors

Although inhibitors can be used to great advantage to suppress the corrosion of metals in many environment, there are certain limitations of this type of corrosion prevention which should be recognized. First, it may not be possible to add inhibitors to all corrosive systems because they may contaminate the environment. Further, many inhibitors are toxic, and their application is limited to those media that will not be used directly or indirectly in the preparation of food or other products that will come in contact with humans. Arsenic salts, which exert a powerful inhibitors are primarily used in closed systems where the corrosive environment is either contained for long periods or recirculated. Inhibitors are usually not practical in "once-through" systems. Finally, inhibitors generally rapidly lose their effectiveness as the concentration and temperature of the environment change.

Chapter 3

Experimental

Four types of stainless steels, Type 304, 316, 317L, and 410, were tested in the present investigation. The samples of the four standard stainless steels were obtained from regular mill production and represent material commercially available. No chemical analysis was made of the material. Table 4 shows the average composition of the tested materials.

Table 4 Compositions of the tested materials in wt $\%$		
Elements: C-0.060; Mn-1.34; P-0.029; S-0.011; Si-0.61;		
	Cr-18.08; Ni-8.33; Cu-0.32; Mo-0.28; N-0.08	
Alloy: 316		
Elements:	C-0.040; Si-0.52; Mn-1.59; P-0.035; S-0.003;	
	Cr-17.7; Ni-10.8; Mo-2.08; N-0.054.	
Alloy: 317	L	
Elements:	C-0.022; Si-0.50; S-0.006; P-0.026; Mn-1.66;	
	Cr-18.32; Ni-12.96; Mo-3.01; N-0.038.	
Alloy: 410		
Elements: C-0.128; Mn-0.64; P-0.015; S-0.004; Si-0.54;		
	Cu-0.07; Ni-0.16; Cr-11.74; Mo-0.11; N-0.046.	

Reagent-grade sulfuric acid (specific gravity, 1.84) and distilled water were used to make all test solutions. Table 5 shows the impurities present in sulfuric acid. As in Table 1, some of these impurities can increase or decrease the corrosion strength of the acid. However, because they are present in very small amounts in reagent-grade sulfuric acid, their effects can be neglected. Seven reagent-grade organic compounds. i.e., p-toluidine, ammonium oxalate, hexamethylenetetramine, p-toluene sulfonic acid, p-toluenesulfonylhydrazine, thiourea, and 1,3-diethyl-2-thiourea, were used as corrosion inhibitors. After the test solution was prepared, it was transferred to the test cell (Figure 8) and heated to the desired temperature in a constant-temperature bath. The bath is equipped with a heater, model PORTA TEMP, made by Precision Scientific Group, GCA Corporation, and a cooler, model Cryocool, made by Neslab Instruments, INC. The heating and cooling capacity were well adjusted so that the temperature of the water bath could be controlled at the desired setting. A thermometer was used to indicate the temperature of the bath.

Table 5

Impurities present in reagent-grade sulfur	ic acid
--------------------------------------------	---------

Impurities	Concentration in ppm
Ammonium (NH ₄) Chloride (Cl) Nitrate (NO ₃) Phosphate (PO ₄) Arsenic (As) Barium (Ba) Cadmium (Cd) Copper (Cu) Iron (Fe) Lead (Pb) Lithium (Li) Manganese (Mn) Potassium (K) Silver (Ag) Sodium (Na) Zinc (Zn)	$<1 \\< 0.1 \\< 0.2 \\< 0.5 \\< 0.004 \\< 0.02 \\< 0.002 \\0.0004 \\0.01 \\0.0004 \\< 0.02 \\< 0.0001 \\< 0.1 \\0.0001 \\0.02 \\< 0.002 \\< 0.002 \\< 0.002 $

Corrosion measurements were undertaken under stagnant conditions at a temperature of 30 C. Although it is recognized that velocity of the solution can have pronounced effects on corrosion rates, stagnant conditions were preferred in this study as the main objective was to examine the effects of The corrosion rates for uninhibited and inhibited sodifferent inhibitors. lutions in four concentrations of H_2SO_4 were measured and compared. Flat metal specimens obtained from Metal Samples Company, INC. Alabama, were prepared by polishing and wet grinding until any scratches and burrs were removed before being subjected to tests. The dry sample was polished using No. 600 grit emery paper. Each side of the sample was polished until the surface was clean. The clean specimen should be free of surface oxides or organic contamination and have a smooth test surface. This procedure was followed by degreasing in 1,1,1-trichloroethane solution for 2 minutes and then rinsing in distilled water. Surface preparation was critical as surface roughness has a marked effect on the initial potential of specimens (35).



Figure 8: Model K47 Corrosion Cell System Components

In carrying out the testing program, every precaution was taken to provide uniform conditions. One of the most important factors, particularly where sulfuric acid is concerned, is the chemical condition of the surface. For stainless steel, unless the samples are activated immediately prior to immersing in the testing medium, irregularities in results will be obtained (36). Even duplicate samples of the same steel, when not previously activated, frequently require widely different periods of time to become active in the testing environment and unless the tests involve relatively long periods of time, the calculated corrosion rates appear erratic. Therefore, in order to avoid such a source of error, all specimens were activated immediately before testing. The method used to activate the samples in this work involved the use of hydrochloric acid as an activating medium (36). The samples were immersed in a 15 percent by volume hydrochloric acid solution for several seconds until hydrogen bubbles appeared on the surface. In the meantime, graphite counter electrodes and reference electrode (a saturated calomel electrode) were placed in the test cell. After the sample was activated, it was rinsed again with distilled water and then was mounted in the electrode holder and transferred to the test cell. The test then commenced immediately.

The calibration experiment used a cylindrical sample of a standard ferritic Type 430 stainless steel in 1.0 N H_2SO_4 solution. The cleaning and activation procedures were the same as those described above. The corrosion rate obtained was compared to the literature value.

The Tafel method was used to determine the corrosion current density, from which the rate of the corrosion reaction was calculated. The corrosion potentials of the stainless steel specimens were measured against a saturated calomel electrode immersed in the test solution. Data were recorded as potential vs. current or log current.

The method of linear polarization is another method for determining the

corrosion rate of a construction material. As in Figure 3 of Chapter 1, it is observed that the applied current density is a linear function of the electrode potential within 10 mV more noble or more active than the corrosion potential. The slope of this linear-polarization curve is related to the Tafel Constants. β_a and β_c , as follows:

$$slope = R_p = \frac{\Delta E}{\Delta I} = \frac{\beta_a \beta_c}{2.3(i_{CORR})(\beta_a + \beta_c)}$$

The beta values for the reactions were determined by the Tafel method. Thus, corrosion rates may be calculated.



Figure 9: Model 273 Experimental Connections

The electrochemical instrumentation used to measure and record the corrosion process was a Model 273 potentiostat (EG&G Princeton Applied Research Co.) (8) in combination with a computer (a PC processor), model 3100, made by Philips Corporation, using corrosion software provided by the A schematic of the experimental set up is shown in Figure 9. company. The corrosion software provides a step-by-step procedure to guide the user in setting up each parameter, to run the experiment, to record the potential and current produced by the corrosion reactions, and to calculate the results (see Appendix). To set up the parameters, the exposed area, the equivalent weight and the density of the sample were needed for calculating the corrosion rate. The exposed area of the sample was provided by the supplier. Α equation was used to calculate the total surface area of the specimen (ASTM, G31).

$$A = \frac{\pi}{2(D^2 - d^2)} + t\pi D + t\pi d$$

where

A = total surface area

t = thickness of the sample

D = diameter of the specimen

d = diameter of the mounting hole

In this work, the exposed area was 1 cm^2 . The weights of the specimens were obtained with an analytical balance. The densities of the specimens were obtained by reference to the ASTM, G1. It lists the densities of many alloys. The densities of the samples, stainless steels Types 304, 316, 317L, and 410, used in this study were 7.94, 7.98, 7.98, and 7.7 g/cm³ respectively. Also, in the experiment, the initial applied potential was -250 mV vs. the corrosion potential and the final applied potential was 250 mV vs. the corrosion potential. The measurement of E_{CORR} was made by means of a high-impedence voltmeter connected to the metal and to a convenient reference electrode dipping into the electrolyte. In this work, the saturated calomel electrode (SCE) was used. The scan rate was chosen as 0.25 mV per second so that the running time of the experiment was about 45 minutes which is typical for using the Tafel technique to predict the corrosion rate of the metal. In addition, an initial delay was required to stablize the potential. It specifies an open-cell interval before the application of the initial potential. The initial delay is the duration that the specimen remains unpolarized at the start of the scan so that it can reach E_{CORR} , the equilibrium potential.

Electrochemical measurements of corrosion phenomena require a cell system that is versatile, convenient to use, and that can provide reproducible conditions from one experiment to another so that a rational comparison between specimens and/or environments can be drawn. The K47 Corrosion Cell System (Figure 8) (8) fulfills these requirements by incorporating the necessary cell, glassware, and hardware for performing rapid, accurate, and reproducible corrosion measurements.

Figure 8 shows the Cell System disassembled. The corrosion flask, which has a capacity of one liter, is fitted with five openings to hold the other components. The specimen holder is mounted in the large center hole, and the reference electrode bridge tube is placed in the angled opening forming a ball joint which is secured with the spring loaded clamp provided. The purge and vent tube is situated directly opposite the reference electrode bridge tube, and the counter- electrode holders are placed in the remaining two holes. The reference electrode plugs into the reference electrode bridge tube. The various components mentioned above are briefly considered below.

(1) COUNTER ELECTRODE

Two high density graphite rods are used as counter electrodes. Each rod mounts in a glass counter-electrode holder and is secured by a nut that compresses an O-ring against the rod. The rods are simply inserted into the adapters and secured with the compression nuts. The adapters containing the rods are then inserted into the 24/40 joints on either side of the flask, and the penetration depth adjusted to where the rods just clear the bottom of the flask, after which the compression nuts should be tightened to secure the rods.

(2) SPECIMEN HOLDER

Two different models are available. One is designed to hold a cylindrical specimen, the other a flat specimen. Both are illustrated in Figure 10. In this work, the flat specimen holder was used in the inhibitor tests and the cylindrical specimen was used in the calibration experiment. The flat specimen holder is designed to accept specimens $15.88\pm.25$ mm in diameter and up to 3.18 mm thick. The sealing washer is made of Kalrez, a new fluorocarbon elastomer with a chemical resistance approaching that of Teflon. The Kalrez washer exposes 1 cm² of the specimen to the test solution.

Cylindrical specimens should be 12.7 mm long, 9.53 mm in diameter, and should be drilled to a depth of 6.35 mm and tapped to accept a 3-48 thread. (Other specimen geometries can be accommodated, as long as the specimen can clear the 45 mm diameter opening provided for the electrode holder.) A Teflon compression gasket between the specimen and the glass electrode holder ensures a leakproof assembly. The specimen should be threaded on the assembly to finger tightness only. Too much pressure will break the holder; too little will cause leakage. The Teflon compression gasket will freeze flow under continuous stress and should be replaced when leakage is detected or distortion of the gasket becomes excessive.



Figure 10: Specimen Holders

Electrical contact between the console and the specimen is made via one of the leads emerging from the rectangular electrometer box (Figure 11). The correct lead is easily identified in that it is the only one terminated in a green alligator clip, green being the color used to denote the working electrode connection.

(3) REFERENCE ELECTRODE BRIDGE TUBE

The reference electrode bridge tube is special in that its operational life can be divided into two periods, before wetting, and after wetting: When dry, this frit has an almost indefinite life. Once wetted, however, it will be severely stressed if it is allowed to dry out again. What this means practically is that the frit will have a longer life if care is taken to keep it wet once it has been wetted for the first time. The bridge tube should be in solution all the time. An individual frit might undergo drying many times without cracking, but its life will certainly be shortened. Electrical contact between the reference electrode and the electrolyte in the flask is via the porous Vycor frit at the end of the reference electrode bridge tube.



Figure 11: Electrometer

Before mounting the bridge tube in the flask's ball and socket joint, the bridge tube should be rinsed with distilled or deionized water. The bridge tube should then be filled with the electrolyte to be used in the flask, or with any other suitable electrolyte. Next the reference electrode should be inserted into the bridge tube, making sure that the bottom of the electrode contacts the solution in the bridge tube. Be sure the reference electrode is filled (saturated potassium chloride solution), and that the filling hole is left exposed. Then insert the entire assembly into the ball and socket joint and clamp loosely. Adjust the bridge tube so that the Vycor tip is positioned about 1 mm from the surface of the specimen. Then tighten the clamp to secure it in that position.

Electrical contact between the reference electrode and the console is made by way of the reference electrode output lead which simply plugs into the corresponding pin jack on the electrometer box (Figure 11).

(4) REFERENCE ELECTRODE

The reference electrode bridge tube accepts the Saturated Calomel Reference Electrode (SCE). Before this electrode can be used, it must be filled with saturated KCl solution, which is injected through the filling hole in the side of the electrode. A rubber band around the electrode is used to cover the filling hole when the electrode is not in use, thereby preventing accidental spillage of the electrode solution. When the electrode is in use, the filling holes should be exposed. These electrodes are highly reliable. About the only problems likely to occur are bubbles on the wire or at the frit, or damage to the frit(unglazed Vycor). Bubbles can be avoided by shaking and tapping the electrode while it is being filled.

(5) PURGE/VENT TUBE

This tube allows purge gas to be admitted to the flask. It also acts as a vent for the flask. The gas is connected to the upper tube, from where it is routed down into the electrolyte. By maintaining a stream of nitrogen bubbling through the solution, the oxygen reduction reaction interference will be prevented. If some other gas is being vented as well, particularly hydrogen or some other flammable gas, take care to safely vent it as it exits from the lower tube. Hydrogen gas was used in this work.

There are two additional minor points worth noting. First, be sure the electrolyte is deep enough to completely cover the specimen. Second, do not be concerned with the "unused' lead that emerges from the electrometer housing. This black lead is a ground. Except for Galvanic Corrosion studies, it is generally not used, and the user's only precaution is to see that it doesn't short against one of the other leads. If there is a piece of nearby apparatus, such as an electrostatic shield that should be grounded, this lead can be used for that purpose, if desired.
Chapter 4 Results

The results of this study are given in Tables 6 to 22. The corrosion rates were calculated from the current densities obtained from each Tafel Plot and Polarization Resistance Plot respectively. The reported corrosion rates in Tables 6-22 are the average values of the results of the Tafel Plot analysis and the Polarization Resistance Plot analysis. The percent inhibition (P) is defined as:

$$P = (1 - \frac{corrosion \ rate \ in \ inhibited \ solution}{corrosion \ rate \ in \ uninhibited \ solution}) \times 100\%$$

To calculate the corrosion rate from the Tafel Plot, the following procedure was used:

- 1. A typical Tafel Plot is shown in Figure 2. The intersection of the cathodic and anodic curves in the plot is the equilibrium point of the corrosion reaction. The corresponding potential is the corrosion potential E_{CORR} , and the corresponding current is the current density, I_{CORR} , of the reaction. Two straight lines are drawn based on these experimental cathodic and anodic curves. The ordinate of the point of intersection is E_{CORR} and the abscissa of the point of intersection is I_{CORR} (Figure 12).
- 2. The value of I_{CORR} is then inserted into the equation:

Corrosion Rate
$$(mpy) = \frac{0.13I_{CORR}(E.W.)}{d}$$

so that one can directly obtain the corrosion rate. The E.W. (equivalent weight) and d (density) are the entered parameters during the experimental setup. The units for I_{CORR} , E.W., and d are $\mu A/cm^2$, gram, and g/cm^3 , respectively.



Figure 12: Indication of E_{CORR} and I_{CORR} from a Tafel Plot

To calculate the corrosion rate from the Polarization Resistance Plot, the following procedure was used:

1. Calculate the slopes of the cathodic and anodic curves in the Tafel Plot. These are the beta values of the reaction, β_C and β_A . In doing this, take two values of potentials, P_1 and P_2 , and two values of currents, I_1 and I_2 , on the cathodic curve of the experimental Tafel Plot (Figure 13). The slope of the cathodic curve was obtained from:

$$slope = rac{(P_2 - P_1)}{(I_2 - I_1)} = eta_C$$



Figure 13: Calculation of the Beta Values from a Tafel Plot

For the value of β_A , the same method is used except that the values of potentials and currents on the anodic curve of the Tafel Plot are used. The appropriate equation is:

$$slope = \frac{(P'_2 - P'_1)}{(I'_2 - I'_1)} = \beta_A$$

- 2. Calculate the slope of the experimental Polarization Resistance Plot, which is the polarization resistance of the reaction, R_p or $\Delta E/\Delta I$.
- 3. Substitute values of the various quantities above into the equation to obtain the current density, i_{CORR}:

$$\Delta E / \Delta I = \frac{\beta_A \beta_C}{2.3(i_{CORR})(\beta_A + \beta_C)}$$

4. Again, use the Tafel equation to calculate the corrosion rate.

For calculations of the corrosion rates, the uncertainty of the intersection point of the cathodic and anodic curves is a factor. Different straight lines may be drawn from the cathodic and anodic portion of the Tafel Plot, as in Figure 14, thus, different points of intersection may be generated, resulting in different values of corrosion currents and therefore variation in the corrosion rates. For example, in Figure 14, different values of corrosion currents are produced because of three pairs of the cathodic and anodic curves:(a) 1050, (b) 950, and (c)880 $\mu A/cm^2$. If the E.W. and the density of the test material is 27.6 g and 7.98 g/cm³, the corrosion rates are:

(a) Corrosion Rate
$$(mpy) = \frac{0.13 \times 1050 \times 27.6}{7.98} = 472.1$$

(b) Corrosion Rate
$$(mpy) = \frac{0.13 \times 950 \times 27.6}{7.98} = 427.14$$

(c) Corrosion Rate
$$(mpy) = \frac{0.13 \times 880 \times 27.6}{7.98} = 395.67$$



Figure 14: Variation of Corrosion Currents

And the average corrosion rate is:

$$\frac{472.1 + 427.14 + 395.67}{3} = 431.64 \quad (mpy)$$

Therefore, the average deviations in the values of corrosion rates are:

(a)
$$\frac{472.1 - 431.64}{431.64} \times 100\% = +9.37\%$$

(b)
$$\frac{427.14 - 431.64}{431.64} \times 100\% = -0.9\%$$

(c)
$$\frac{395.67 - 431.64}{431.64} \times 100\% = -8.33\%$$

The mean (\overline{I}) of the corrosion currents in this example is:

$$\bar{I} = \frac{1050 + 950 + 880}{3} = 960$$

The sum of squares of deviations from mean is (54):

$$\sum_{i=1}^{N} (I_i - \bar{I})^2 = (1050 - 960)^2 + (950 - 960)^2 + (880 - 960)^2$$
$$= 14600$$

The standard deviation (s) is (54):

$$s = \sqrt{\frac{\sum_{i=1}^{N} (I_i - \bar{I})^2}{N - 1}} = \sqrt{\frac{14600}{3 - 1}} = 85.44$$

The reported value for the corrosion currents in this example should be $960.00(\pm 85.44)$. The corrosion rate based on this value is:

$$\frac{0.13 \times 960(\pm 85.44) \times 27.6}{7.98} = 431.64$$

The variance is (54):

$$\left(\frac{\pm 85.44}{960}\right)^2 = 7.92 \times 10^{-3}$$

The coefficient of variation is (54):

$$\sqrt{7.92 \times 10^{-3}} = 0.089 = 8.9\%$$

Therefore, the reported value for the corrosion rate should be:

Corrosion Rate
$$(mpy) = 431.64(\pm 431.64 \times 0.089)$$

= 431.64(±38.42)

Therefore the uncertainty in the values of corrosion rates is ± 38.42 . This is a statistical error analysis. On the other hand, the experimental uncertainty is based upon an estimate of uncertainties in corrosion currents, equivalent weights, densities, etc. To obtain this, a limit of error is defined as $\pm \lambda$ in the result of the final corrosion rates. The expression for λ can be deduced (55):

$$\lambda(C.R.) = \left| \frac{\partial(C.R.)}{\partial i_{CORR}} \right| \lambda(i_{CORR}) + \left| \frac{\partial(C.R.)}{\partial(E.W.)} \right| \lambda(E.W.) + \left| \frac{\partial(C.R.)}{\partial d} \right| \lambda(d)$$
$$= \frac{0.13(E.W.)}{d} \lambda(i_{CORR}) + \frac{0.13i_{CORR}}{d} \lambda(E.W.) + \frac{0.13i_{CORR}(E.W.)}{d^2} \lambda(d)$$

From Figure 14, the value of $\lambda(i_{CORR})$ is estimated as 90, and the values of $\lambda(E. W.)$ and $\lambda(d)$ are assigned as 0.1 and 0.01 respectively. Therefore:

$$\lambda(C.R.) = \frac{0.13 \times 27.6}{7.98} (90) + \frac{0.13 \times 960}{7.98} (0.1) + \frac{0.13 \times 960 \times 27.6}{(7.98)^2} (0.01)$$
$$= 40.47 + 1.56 + 0.54$$
$$= 42.57$$

Therefore the experimental uncertainty is ± 42.57 in this example which is within 10 percent of the calculated corrosion rate (431.64 mpy).

Table 6: Results of Calibration ExperimentCorrosion rate of stainless steel Type 430in 1.0 N sulfuric acid solution at 30 C

Run	Corrosion Rate (mpy)
1	1085.63
2	1083.26
3	743.89
4	979.19
5	837.97
6	1789.45
7	959.73
8	1115.40

Table 7: Corrosion rates in mpy and percent inhibition of stainless steel 304 in 1 weight% sulfuric acid solutions containing organic compounds at 30 C. The corrosion rate of this steel in 1 weight% sulfuric acid solution is 87.23 mpy.

Inhibitor	Concentration (wt%)	Corrosion Rate (mpy)	Percent Inhibition
p-toluidine	0.01	66.95	23.25%
Hexamethyl- enetetramine	0.01	55.69	36.16%
Ammonium Oxalate	0.01	58.66	32.75%
Ammonium Oxalate + Sodium Iodide	0.01 + 0.005	36.83	57.78%
p-toluene sulfonic acid	0.01	42.92	50.80%
p-toluenesulf- onylhydrazine	0.01	29.06	66.69%
Thiourea	0.01	21.75	75.07%
1,3-diethyl- 2-thiourea	0.01	13.55	84.47%

Table 8: Corrosion rates in mpy and percent inhibition of stainless steel 316 in 1 weight% sulfuric acid solutions containing organic compounds at 30 C. The corrosion rate of this steel in 1 weight% sulfuric acid solution is 73.19 mpy.

Inhibitor	Concentration (wt%)	Corrosion Rate (mpy)	Percent Inhibition
p-toluidine	0.01	63.07	13.83%
Hexamethyl- enetetramine	0.01	51.07	30.22%
Ammonium Oxalate	0.01	31.9	56.43%
Ammonium Oxalate + Sodium Iodide	0.01 + 0.005	26.79	63.40%
p-toluene sulfonic acid	0.01	34.32	53.11%
p-toluenesulf- onylhydrazine	0.01	32.42	55.70%
Thiourea	0.01	17.08	76.66%
1,3-diethyl- 2-thiourea	0.01	11.13	84.80%

Table 9: Corrosion rates in mpy and percent inhibition of stainless steel 317L in 1 weight% sulfuric acid solutions containing organic compounds at 30 C. The corrosion rate of this steel in 1 weight% sulfuric acid solution is 41.77 mpy.

Inhibitor	Concentration (wt%)	Corrosion Rate (mpy)	Percent Inhibition
p-toluidine	0.01	27.69	33.71%
Hexamethyl- enetetramine	0.01	23.68	43.31%
Ammonium Oxalate	0.01	26.99	35.38%
Ammonium Oxalate + Sodium Iodide	0.01 + 0.005	12.74	69.50%
p-toluene sulfonic acid	0.01	25.53	38.71%
p-toluenesulf- onylhydrazine	0.01	25.12	39.86%
Thiourea	0.01	23.37	44.05%
1,3-diethyl- 2-thiourea	0.01	6.87	83.55%

Table 10: Corrosion rates in mpy and percent inhibition of stainless steel 410 in 1 weight% sulfuric acid solutions containing organic compounds at 30 C. The corrosion rate of this steel in 1 weight% sulfuric acid solution is 609.13 mpy.

Inhibitor	Concentration (wt%)	Corrosion Rate (mpy)	Percent Inhibition
p-toluidine	0.01	558.80	8.26%
Hexamethyl- enetetramine	0.01	531.66	12.72%
Ammonium Oxalate	0.01	525.86	13.67%
Ammonium Oxalate + Sodium Iodide	0.01 + 0.005	119.35	80.40%
p-toluene sulfonic acid	0.01	495.04	18.73%
p-toluenesulf- onylhydrazine	0.01	418.23	31.33%
Thiourea	0.01	55.84	90.83%
1,3-diethyl- 2-thiourea	0.01	39.05	93.59%

Table 11: Corrosion rates in mpy and percent inhibition of stainless steel 304 in 10 weight% sulfuric acid solutions containing organic compounds at 30 C. The corrosion rate of this steel in 10 weight% sulfuric acid solution is 211.52 mpy.

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Inhibitor	Concentration (wt%)	Corrosion Rate (mpy)	Percent Inhibition
p-toluidine	0.1	144.14	31.86%
Hexamethyl- enetetramine	0.2	136.14	35.64%
Ammonium Oxalate	0.4	103.01	51.30%
p-toluidine + Sodium Iodide	0.1 + 0.1	111.47	47.30%
p-toluene sulfonic acid	0.2	137.70	34.90%
p-toluenesulf- onylhydrazine	0.2	132.66	37.28%
Thiourea	0.1	68.67	67.53%
1,3-diethyl- 2-thiourea	0.2	58.45	72.37%

Table 12: Corrosion rates in mpy and percent inhibition of stainless steel 316 in 10 weight% sulfuric acid solutions containing organic compounds at 30 C. The corrosion rate of this steel in 10 weight% sulfuric acid solution is 203.83 mpy.

Inhibitor	Concentration (wt%)	Corrosion Rate (mpy)	Percent Inhibition
p-toluidine	0.1	195.88	3.90%
Hexamethyl- enetetramine	0.2	159.23	21.88%
Ammonium Oxalate	0.4	102.31	49.81%
p-toluidine + Sodium Iodide	0.1 + 0.1	80.68	60.42%
p-toluene sulfonic acid	0.2	159.04	21.97%
p-toluenesulf- onylhydrazine	0.2	133.69	34.41%
Thiourea	0.1	83.37	59.10%
1,3-diethyl- 2-thiourea	0.2	48.09	76.41%

Table 13: Corrosion rates in mpy and percent inhibition of stainless steel 317L in 10 weight% sulfuric acid solutions containing organic compounds at 30 C. The corrosion rate of this steel in 10 weight% sulfuric acid solution is 192.45 mpy.

Inhibitor	Concentration (wt%)	Corrosion Rate (mpy)	Percent Inhibition
p-toluidine	0.1	164.13	14.72%
Hexamethyl- enetetramine	0.2	137.90	28.35%
Ammonium Oxalate	0.4	125.30	34.89%
p-toluidine + Sodium Iodide	0.1 + 0.1	97.65	49.26%
p-toluene sulfonic acid	0.2	155.98	18.95%
p-toluenesulf- onylhydrazine	0.2	118.74	38.30%
Thiourea	0.1	54.14	71.87%
1,3-diethyl- 2-thiourea	0.2	44.57	76.84%

Table 14: Corrosion rates in mpy and percent inhibition of stainless steel 410 in 10 weight% sulfuric acid solutions containing organic compounds at 30 C. The corrosion rate of this steel in 10 weight% sulfuric acid solution is 3753.82 mpy.

Inhibitor	Concentration (wt%)	Corrosion Rate	Percent Inhibition
p-toluidine	0.1	1037.91	72.35%
Hexamethyl- enetetramine	0.2	986.34	73.72%
Ammonium Oxalate	0.4	728.24	80.60%
p-toluidine + Sodium Iodide	0.1 + 0.1	415.91	88.92%
p-toluene sulfonic acid	0.2	1062.11	71.71%
p-toluenesulf- onylhydrazine	0.2	584.87	84.42%
Thiourea	0.1	405.63	89.20%
1,3-diethyl- 2-thiourea	0.2	201.15	94.64%

Table 15: Corrosion rates in mpy and percent inhibition of stainless steel 304 in 30 weight% sulfuric acid solutions containing organic compounds at 30 C. The corrosion rate of this steel in 30 weight% sulfuric acid solution is 1732.44 mpy.

Inhibitor	Concentration (wt%)	Corrosion Rate (mpy)	Percent Inhibition
p-toluidine	0.3	1027.26	40.70%
Hexamethyl- enetetramine	0.4	335.33	80.64%
Ammonium Oxalate	0.4	497.70	71.27%
Ammonium Oxalate + Sodium Iodide	0.4 + 0.2	179.26	89.65%
p-toluene sulfonic acid	0.4	399.09	76.97%
p-toluenesulf- onylhydrazine	0.4	345.79	80.04%
Thiourea	0.3	153.38	91.15%
1,3-diethyl- 2-thiourea	0.4	47.87	97.24%

Table 16: Corrosion rates in mpy and percent inhibition of stainless steel 316 in 30 weight% sulfuric acid solutions containing organic compounds at 30 C. The corrosion rate of this steel in 30 weight% sulfuric acid solution is 887.45 mpy.

Inhibitor	Concentration (wt%)	Corrosion Rate (mpy)	Percent Inhibition
p-toluidine	0.3	553.68	37.61%
Hexamethyl- enetetramine	0.4	272.45	69.30%
Ammonium Oxalate	0.4	478.41	46.09%
Ammonium Oxalate + Sodium Iodide	0.4 + 0.2	99.05	88.84%
p-toluene sulfonic acid	0.4	365.19	58.85%
p-toluenesulf- onylhydrazine	0.4	148.24	83.30%
Thiourea	0.3	89.74	89.89%
1,3-diethyl- 2-thiourea	0.4	34.32	96.13%

Table 17: Corrosion rates in mpy and percent inhibition of stainless steel 317L in 30 weight% sulfuric acid solutions containing organic compounds at 30 C. The corrosion rate of this steel in 30 weight% sulfuric acid solution is 752.83 mpy.

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Inhibitor	Concentration (wt%)	Corrosion Rate (mpy)	Percent Inhibition
p-toluidine	0.3	378.63	49.71%
Hexamethyl- enetetramine	0.4	213.18	71.68%
Ammonium Oxalate	0.4	242.67	67.77%
Ammonium Oxalate + Sodium Iodide	0.4 + 0.2	51.38	93.18%
p-toluene sulfonic acid	0.4	268.50	64.33%
p-toluenesulf- onylhydrazine	0.4	87.48	88.38%
Thiourea	0.3	59.45	91.87%
1,3-diethyl- 2-thiourea	0.4	39.21	94.79%
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Table 18: Corrosion rates in mpy and percent inhibition of stainless steel 410 in 30 weight% sulfuric acid solutions containing organic compounds at 30 C. The corrosion rate of this steel in 30 weight% sulfuric acid solution is 5838.72 mpy.

Inhibitor	Concentration (wt%)	Corrosion Rate (mpy)	Percent Inhibition
p-toluidine	0.3	3387.63	41.98%
Hexamethyl- enetetramine	0.4	2047.14	64.94%
Ammonium Oxalate	0.4	2176.53	62.72%
Ammonium Oxalate + Sodium Iodide	0.4 + 0.2	757.00	87.03%
p-toluene sulfonic acid	0.4	2298.64	60.63%
p-toluenesulf- onylhydrazine	0.4	731.74	87.47%
Thiourea	0.3	321.95	94.49%
1,3-diethyl- 2-thiourea	0.4	193.38	96.69%

Table 19: Corrosion rates in mpy and percent inhibition of stainless steel 304 in 50 weight% sulfuric acid solutions containing organic compounds at 30 C. The corrosion rate of this steel in 50 weight% sulfuric acid solution is 2426.81 mpy.

Inhibitor	Concentration (wt%)	Corrosion Rate (mpy)	Percent Inhibition
p-toluidine	0.5	1562.56	35.61%
Hexamethyl- enetetramine	0.5	1275.1	47.46%
Ammonium Oxalate	0.5	679.47	72.00%
Ammonium Oxalate + Sodium Iodide	0.5 + 0.2	206.35	91.50%
p-toluene sulfonic acid	0.5	894.09	63.16%
p-toluenesulf- onylhydrazine	0.5	164.83	93.21%
Thiourea	0.5	97.91	95.96%
1,3-diethyl- 2-thiourea	0.5	58.18	97.60%

Table 20: Corrosion rates in mpy and percent inhibition of stainless steel 316 in 50 weight% sulfuric acid solutions containing organic compounds at 30 C. The corrosion rate of this steel in 50 weight% sulfuric acid solution is 1524.51 mpy.

Inhibitor	Concentration (wt%)	Corrosion Rate (mpy)	Percent Inhibition
p-toluidine	0.5	786.82	48.39%
Hexamethyl- enetetramine	0.5	416.59	72.67%
Ammonium Oxalate	0.5	497.17	67.39%
Ammonium Oxalate + Sodium Iodide	0.5 + 0.2	171.27	88.77%
p-toluene sulfonic acid	0.5	361.18	76.31%
p-toluenesulf- onylhydrazine	0.5	138.75	90.89%
Thiourea	0.5	102.22	93.30%
1,3-diethyl- 2-thiourea	0.5	35.07	97.7%
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Table 21: Corrosion rates in mpy and percent inhibition of stainless steel 317L in 50 weight% sulfuric acid solutions containing organic compounds at 30 C. The corrosion rate of this steel in 50 weight% sulfuric acid solution is 1270.68 mpy.

Inhibitor	Concentration (wt%)	Corrosion Rate (mpy)	Percent Inhibition
p-toluidine	0.5	367.23	71.10%
Hexamethyl- enetetramine	0.5	216.14	82.99%
Ammonium Oxalate	0.5	260.34	79.51%
Ammonium Oxalate + Sodium Iodide	0.5 + 0.2	51.35	95.96%
p-toluene sulfonic acid	0.5	267.51	78.95%
p-toluenesulf- onylhydrazine	0.5	136.60	89.25%
Thiourea	0.5	71.50	94.37%
1,3-diethyl- 2-thiourea	0.5	32.01	97.48%

Table 22: Corrosion rates in mpy and percent inhibition of stainless steel 410 in 50 weight% sulfuric acid solutions containing organic compounds at 30 C. The corrosion rate of this steel in 50 weight% sulfuric acid solution is 6613.26 mpy.

Inhibitor	Concentration (wt%)	Corrosion Rate (mpy)	Percent Inhibition
p-toluidine	0.5	4127.54	37.59%
Hexamethyl- enetetramine	0.5	3133.25	52.62%
Ammonium Oxalate	0.5	3731.17	43.58%
Ammonium Oxalate + Sodium Iodide	0.5 + 0.2	1864.08	71.81%
p-toluene sulfonic acid	0.5	2624.73	60.31%
p-toluenesulf- onylhydrazine	0.5	783.29	88.16%
Thiourea	0.5	196.93	97.02%
1,3-diethyl- 2-thiourea	0.5	165.93	97.50%
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Chapter 5 Discussion

This study involved the behavior of S-containing and N-containing corrosion inhibitors in sulfuric acid using various stainless steels. It was found that the corrosion prevention efficiency of S-containing compounds varies con-P-toluene sulfonic acid was the least efficient while 1,3-diethyl-2siderably. thiourea was the most efficient at all test concentrations as shown in Tables 7-22. P-toluenesulfonylhydrazine is more effective than p-toluene sulfonic acid, but less than thiourea or 1,3-diethyl-2-thiourea. Thiourea behaved somewhat unusual in that the higher the acid concentration, the higher was the efficiency of the inhibitor. Thiourea has been claimed to be either an effective inhibitor or a corrosion promoter in some studies (42-48), but behaved as an efficient inhibitor in this work. The inhibitor, 1,3-diethyl-2-thiourea gave the best performance in protecting the metals. Thiourea and 1,3-diethyl-2thiourea could be specifically adsorbed by the electrically charged metal. The sulfur molecule of these two inhibitors is expected to be directed toward the metal, causing an increased double bond character of the carbon to nitrogen bond.

The adsorption process limits the access ability of the aggressive H^+ ion to the surface of the metal, hence decreasing the reaction rate and therefore aiding inhibition. It is therefore suggested that these two inhibitors inhibit the hydrogen evolution reaction via adsorption. Particularly, 1,3-diethyl-2-thiourea has more double bonds generated in the adsorption process, and the force of adsorption is so strong that it requires more energy to break. Although it was believed that these two inhibitors could undergo protonation and produce HS⁻ which promote the hydrogen evolution reaction (Chapter 2), the extent of protonation and HS⁻ production was assumed to be small. For these four S-containing compounds, the effectiveness of the inhibitors in the higher concentrations of sulfuric acid was greater than that in the lower concentrations of sulfuric acid as seen in Table 7-22.

The effect of N-containing compounds (p-toluidine and hexamethylenetetramine) was also studied. Both compounds did not show any significant inhibition effects in sulfuric acid solutions, suggesting that the organic cations were minutely adsorbed. The mechanism of hexamine decomposition in the presence of acid seems to involve a protonation step with the formation of the hexamine-sulfuric acid complex:

$$[(CH_2)_6N_4H]^{+2} - ^2SO_4$$

However, this only gives temporary protection. The effectiveness of ptoluidine is increased by incorporating sodium iodide at 10 weight% sulfuric acid solution. The halide ion of sodium iodide facilitates the adsorption of the inhibitors onto the metal surface by producing an oriented dipole (explained in Chapter 2). The water molecules in the aqueous solution direct their positively charged ends towards the metal and their negatively charged ends towards the solution, resulting in an increase in the adsorption of the inhibitor cations onto the metal surface. i.e., the I⁻ ions may be chemisorbed so that they become integrated with the metal surface, causing a net negative charge and thus favoring the adsorption of organic cations of the inhibitors. Also, the presence of the halide ions produced a competitive adsorption with the aggressive ions in the sulfuric acid solution.

Ammonium Oxalate was also tested as an inhibitor for austenitic stainless steels in sulfuric acid solution. Results indicated that it did not reduce the corrosion rate greatly. However, once again, a synergistic effect was produced in combination with sodium iodide: the effect of inhibition produced when ammonium oxalate and sodium iodide were present in the corrosive was greater than that produced by ammonium oxalate alone, as shown in Table 7–22. The inhibition effect gained by using ammonium oxalate and sodium iodide is even better than that by using S-containing compounds such as p-toluene sulfonic acid or p-toluenesulfonylhydrazine.

It is seen in Figure 15, that the inhibitors used in this study decreased the cathodic and anodic currents of the corrosion reactions with respect to the uninhibited case. It was suggested that this happened at the sites in which the inhibitors adsorbed onto the metal surface. The inhibitors with higher effectiveness exhibited complete adsorption processes, resulting in total coverage on the metal surface. In addition, the corrosion potentials of the reactions did not change significantly when the inhibitors participated in the reactions.

In summary, the inhibitors used in this work decrease the metal dissolution rate and their adsorptions onto the metal surface cause a blocking effect of the surface and decrease the effective area of the attack. The adsorption of the inhibitors changes the structure of the corrosion compound on the metal surface and decreases the available area for the hydrogen discharge or the number of active centers on the metal surface. The inhibitors are selective in the sense that they retard much more effectively the H_2 evolution than the O_2 reduction in sulfuric acid solution.



Figure 15: Effect of inhibitors

Typical Tafel Plots of stainless steels, Types 304, 316, 317L, and 410 in sulfuric acid solution at 30 C in the presence of N-containing and S-containing compounds. ••••• without inhibitor ---- with N-containing compounds with S-containing compounds

Chapter 6 Conclusions

(1) It can be seen that the stainless steels containing molybdenum, Types 316 and 317L, show the best resistance to sulfuric acid. Type 304 exhibits better resistance than Type 410 but not quite as good as the molybdenum Types 316 and 317L. The fact that the elements of one material play an important role in the resistance of this material to the medium is shown in this study. In addition to molybdenum, chromium and nickel contents are also crucial to the corrosion resistance of the steels. For Type 410, which contains the least content of these two elements (Cr and Ni), and the lack of molybdenum, the corrosion resistance is the weakest of these four materials.

(2) The results show that the sulfur and nitrogen containing organic inhibitors can be used to improve the corrosion resistance of stainless steels in sulfuric acid as they cause reduction of the corrosion rates, with the extent of reduction ranging significantly. 1,3-diethyl-2-thiourea is the most efficient inhibitor, whereas p-toluidine is the least efficient. At the concentration of 50 weight% of sulfuric acid, in which the corrosion rates are believed to be very high, the use of 1,3-diethyl-2-thiourea could produce a percent inhibition up to 97%. In this work, the concentration of inhibitors used was 0.01 of the concentration of sulfuric acid, which proved reasonable and sufficient.

Generally speaking, for steels in sulfuric acid solution, the inhibition effec-

tiveness of sulfur-containing compounds is much greater than that of nitrogencontaining compounds. Thiourea and 1,3-diethyl-2-thiourea again emphasize this superiority in the present work.

(3) The inhibition produced by nitrogen-containing compounds could be significantly enhanced by the addition of the iodide ion. The ion is known to facilitate the adsorption of organic cations, thus producing an inhibition synergism. Results show that the iodide ion plays an essential part in the inhibition.

Appendix

Model 342 Corrosion Measurement Software

Overview

The Model 342 Softcorr Corrosion Measurement Software performs corrosion measurement experiments quickly, easily, and reliably. The Model 342 software and a computer communicate with a potentiostat to control experiments.

The software runs on hardware connected by a National Institutes PC-2A GPIB card. The host computer (an IBM-compatible personal computer with 320 Kbytes of memory) provides memory, data processing, input-output, and interface capabilities between the operator and system.

The model 342 software is contained on 5-1/4-inch 360K byte floppy disks. When the working disk is booted, the hardware automatically loads the software and the video monitor displays the Main Menu. From there, the menudriven software lets you branch to sub-menus that allow you to perform the system functions.

The Model 342 software is versatile. From the system menus, you can select any one of nine experiments listed below.

1. Potentiodynamic Polarization

2. Tafel Plots

- 3. Polarization Resistance
- 4. Cyclic Polarization(Pitting Scans)
- 5. Potentiokinetic Reactivation
- 6. Potentiostatic
- 7. Galvanostatic
- 8. Galvanic Corrosion
- 9. Ecorr(Open Circuit Potential) vs. Time

Parameter entry is easy. You can use the displayed default parameters and begin the experiment as soon as the parameter entry menu appears or you can select one or more of the parameters and enter a new value by responding to the prompts. When you are satisfied with the parameter values, the experiment will run automatically as soon as you select RUN EXPERIMENT.

The Model 342 software can perform three types of calculation –PARCalc Tafel Analysis, Polarization Resistance Analysis, and Potentiokinetic Reactivation Analysis. The PARCalc Tafel Analysis routine statistically fits the experimental data to the corrosion theory. The routine automatically selects the data that lie within the Tafel region ($\pm 200 \text{ mV}$ with respect to the corrosion potential). It then calculates the corrosion current and the corrosion rate (in milli-inches per year) and displays the results. The Polarization Resistance routine uses a linear regression analysis to calculate the polarization resistance, and then uses this value to determine the corrosion current and corrosion rate. The routine automatically selects data within $\pm 10 \text{ mV}$ with respect to the corrosion potential. It then performs the calculation.

System Hardware

An IBM-compatible personal computer with at least 320K bytes of memory and a PARC potentiostat/galvanostat are the core of the system. An output printer and other components, including the K47 corrosion Cell Kit, support the computer and the potentiostat.

System Software

The following resources make up the full Model 342 software package: an operating system, a non-bootable distribution disk containing the Model 342 programs, a bootable set of working disks (A and B) containing the Model 342 programs and other necessary software, a source disk containing the ASCII-formatted source code, a data disk containing some sample data, and an effective menu format. The Model 342 software is supplied on 5 1/4-inch IBM-formatted floppy diskettes.

System Disks

The two working disks containing the Model 342 software are labeled A and B. Before booting the system, each must be inserted into its corresponding disk drive. After the system is booted, the Model 342 software uses Drive B for data storage. The operator must replace Working Disk B with a data disk to run experiments.

Booting The Model 342 Software

Before applying power to the system, the operator should carefully review the hardware installations. When satisfied that all connections are correct, use the following procedures to boot the Model 342 software.

- 1. Apply power to all peripheral equipment except the potentiostat-that is, turn the power switches on the video monitor and printer to ON.
- 2. Apply power to the Model 273 by holding the LOCAL key in and turning the power switch on.
- 3. Insert Working Disk A into drive A.
- 4. Insert Working Disk B into drive B.
- 5. Apply power to the computer by turning the power switch at the rear of the computer to ON.
- 6. The system will begin reading the disks (the red indicators will light to indicate the disk being read) and after several moments, will display the Main Menu on the video monitor.
- 7. When the Main Menu appears, remove Working Disk B from Drive B and replace it with a data disk. Operator must have a data disk in Drive B to operate the system.

Initial Checkout

The purpose of the initial checkout is to make sure that the entire system, including the potentiostat, is communicating correctly. The following procedure serves as a good initial checkout.

- 1. Make sure that the system connections are completed and the system is properly booted.
- 2. From the Main menu, select SETUP AND RUN MENU.
- 3. From the Setup and Run menu, select the ECORR VS. TIME technique.

- 4. Select 0 on this menu, type in "TEST" for the experiment name and press the RETURN key.
- 5. Select 1 and enter a "1" for number of seconds per point.
- 6. Select 2 and enter a "5" for run time in seconds.
- 7. Turn the EXT/DUMMY switch on the electrometer to DUMMY
- 8. Select RUN EXPERIMENT. The following sequence will occur:
 - (a) The message "CHECKING SYSTEM" will appear on the screen.
 - (b) The REMOTE indicator on the potentiostat 273 will light.

The message "SETTING UP PSTAT" will appear on the screen.

The system will collect 5 data points in 5 seconds, the experiment will end, and the Main menu will appear on the screen, indicating that the experiment ran successfully and the computer is communicating properly with the potentiostat.

When you have successfully booted the model 342 working disk, the Main Menu will appear on the screen. From the main Menu, you can make one of the selections and begin operations.

Running Experiments

The following step-by-step procedures tell the operator to perform the Tafel Plot and Polarization Resistance experiments which were the methods used in this work.

- 1. From the MAIN MENU (Figure A-1), select (S) SETUP/RUN MENU.
- 2. The SETUP and RUN MENU will appear on the screen (Figure A-2).
Select (5) TAFEL PLOT METHOD.

- The PARAMETERS SCREEN PAGE 1 (RUN PARAMETERS) will be displayed (Figure A-3). Enter a valid file name and press the RETURN key. File names can contain up to 7 alphanumeric characters and must begin with a letter.
- 4. After you enter the file name, the software will direct you to choose one of the other options. Select the first parameter you wish to change and enter the desired value from the keyboard. Simply skip over the default values that you do not want to change. The default values are reasonable for many experiments. PASS is used to denote a parameter that is not included in the default routine for the experiment, but which can be included if desired. CONDITION E, CONDITION T, and INIT DELAY are Tafel Plot PASS parameters. If values are specified for these parameters, they will be included in the experiment's run routine.
- Repeat step 4 for each parameter you wish to enter from Page 1 of the RUN PARAMETERS screen. For the Tafel Plot experiment, the following RUN PARAMETERS are needed to be considered.

INITIAL E (MV): the initial potential is the potential at which scan begins. Since Tafel Plot scans typically extend 250 mV on both sides of E_{CORR} , a reasonable value for the initial potential would be -250 mV~ E_{CORR} . The allowable range is ±10 V~ E_{CORR} for this parameter.

FINAL E (MV): the final potential is the potential at which the scan ends. Since Tafel Plot scans typically extend 250 mV on both sides of E_{CORR} , a reasonable value for the final potential would be 250 mV~ E_{CORR} . The allowable range for this parameter is ±10 V~ E_{CORR} .

SCAN RATE (MV/S): The scan rate is the rate at which the applied potential changes during the scan. The range of values that the Model 342 software accepts is from 0 to 20 mV/SEC.

CONDITION E (MV): The conditioning potential is the potential at which the specimen is polarized for a specified duration before the scan begins. Normally, the specimen is not conditioned, so the default value for this parameter is PASS. For the present work, although the specimens were polarized by a 15 percent by volume hydrochloric acid solution, the weight loss resulting from the activation procedure was very small and could be ignored (36). A PASS value was given for this parameter.

CONDITION T (S): The conditioning time is the duration for which the specimen is polarized at a specified potential before the scan begins. Normally, the specimen is not conditioned, so the default value for this parameter is PASS. As same reason indicated above for the CONDITION E parameter, a entered PASS value was satisfactory for this parameter in this work.

INITIAL DELAY (MV/S OR S): The initial delay is the duration that the specimen remains unpolarized at the start of the scan so that it can reach E_{CORR} (the equilibrium potential). An initial delay is usually required for a Tafel Plot. The default value of PASS is acceptable when there is no need for the specimen to equilibrate. You can enter a value in seconds or millivolts per second by selecting the desired units on the screen. For the "seconds" parameter to be valid, the specimen must not be immersed until just before the start of the run. If you choose millivolts per second, the delay will continue until the rate of change of the specimen potential becomes less than the entered value. PLOT MAX I RANGE: The maximum current range is the current interval at which the scan stops if the specified value is exceed. The default value of 100 μ A is satisfactory for many measurements.

6. Each technique has three parameter entry pages. Page 2, titled "SAM-PLE PARAMETERS", lets you enter values for sample characteristics, Tafel constants, and potentiostat options (Figure A-4). Page 3, titled "LEGEND", lets you record remarks, such as the date, operator name, solution composition, specimen conditioning, or any other useful remark (Figure A-5). To enter sample parameters, select NEXT PAGE at the bottom of the RUN PARAMETERS screen. This will bring you to the SAMPLE PARAMETERS screen, where you can enter parameter values as you did on Page 1. For the Tafel plot experiment, the following sample parameters are required:

AREA (CM²): the specimen area is required for i_{CORR} and corrosion rate calculations. Since these are the sought-after results of a Tafel Plot, you should enter the specimen area. If you do not enter during this step, you can do so before calculations. The default value for the AREA parameter is 1 cm^2 , the area for the standard flat specimen used with the Flat Specimen Holder. After a new value is entered, the last entered value will be displayed on the data entry screen.

EQUIVALENT WEIGHT (G): The equivalent weight is required only if the area has been entered and you intend to calculate the corrosion rate (MPY) after running the experiment. In this work, this parameter is required. Originally, the default value is PASS, thus a new value for the Tafel Plot experiment should be entered. It can also be entered after running the experiment and before calculations.

DENSITY (G/CM³): the density is required only if the area has been entered and you intend to calculate the corrosion rate (MPY) after running the experiment. The default value is PASS, but a new value was needed for this work. It can also be entered after running the experiment and before calculations.

CATHODIC TAFEL (MV) OR ANODIC TAFEL (MV): The cathodic and anodic Tafel Constant values (in millivolts per decade) must be entered if you intend to calculate i_{CORR} and the corrosion rate from a Polarization Resistance Plot. The Tafel Constants can also be entered after the experiment and before calculations. Generally, one will not know in advance the Tafel Constant values for the specimen being investigated. However, the PARCalc routine will determine the Tafel Constants if the data is good enough. The found values can then be entered into the Sample Parameters screen and used by the software to calculate the Polarization Resistance. LINE SYNC (Y/N): This function lets you determine whether or not data acquisition will be synchronized with the power line frequency. Line synchronization is desirable when you use a low current technique, where noise reduction is critical. To activate line synchronization, simply select the function and enter a "Y".

CURRENT INTERRUPT (S): This function activates Current Interrupt IR Compensation. The number of seconds you enter is rounded up to the time it takes to collect one data point and displayed to the right of the parameter.

- 7. To enter remark, do the following:
 - (a) Select NEXT PAGE at the bottom of the SAMPLE PARAMETERSscreen. The LEGEND (Figure A-5) screen will appear.
 - (b) Select a line using the numbers in the typewriter portion of the keyboard. Type the remark and press the RETURN key. The remark will be entered as part of the setup and you can then enter a remark on another line, using the same procedure.
- 8. When finished entering parameter values and remarks, you are ready to run the experiment.
- 9. The above completes the procedure for setting up an experiment.
- 10. To run the desired experiment, select (R) RUN EXPERIMENT from any of the parameter pages.
- 11. The Model 342 software will direct you to make the cell connections. If you have not done so, set up the cell apparatus and make sure the cell

connections have been properly made. At this point, or at any point during the measurement, you can abort the experiment by holding the "Ctrl" (CONTROL) key down and pressing the "A" key.

- 12. When the cell connections are completed, set the cell switch on the front panel of the potentiostat to CELL ENABLE 0N.
- 13. Press RETURN to begin the experiment. The experiment will begin and run to completion without further manual intervention. The software will use the parameter values specified during setup to control the experiment. The conditioning and delay steps, if any, will be performed first, followed by the measurement. The status of the experiment will be displayed throughout the experiment.
- 14. You can halt any step of the experiment and advance to the next step by holding the "Ctrl" key down and pressing the "P" key. The step in progress will end immediately and the experiment will proceed to the next step. Among other things, this is useful when you want to bypass the programmed delay or conditioning step and proceed directly to the measurement.
- 15. You end an experiment at any time by holding the "Ctrl" key down and pressing the "A" key. This executes an ABORT command. If you abort an experiment during data acquisition, you are given the option of saving the data acquired to that point.
- 16. If the experiment is not interrupted by an error or an ABORT command, it will run to completion, the data will automatically be saved under the name you entered during setup, and the software will display the Main

Menu on the screen. The data scaling values (E_{CORR} , millivolts per data point, the data maximum and minimum, and the absolute data maximum and minimum) will be added to the experimental parameters. At this point, you can display or manipulate the data and perform calculations, or you can go on to another experiment, leaving these data operations for another time.

- 17. For the Tafel Plot experiment, Figure A-6 is a typical result of the experiment.
- 18. To do calculations after the experiment is over, select the (R) RESULTS MENU on the MAIN MENU. The screen will turn to RESULT CALCU-LATION MENU (Figure A-7).
- Respond the screen by selecting (6) PARCALC TAFEL ANALYSIS. The PARCALC TAFEL MENU (Figure A-8) will replace the screen.
- 20. Type (2) CALCULATION RESULT. The software begins to calculate the results based on the data obtained. Figure A-9 will be the next screen and it shows the results.
- 21. Hit (RTN) to continue, the PARCALC TAFEL MENU will be displayed again. Select (1) PLOT DATA, the software begins to plot the TAFEL PLOT according to the experimental data. Figure A-10 is the consequence of this step.
- 22. Hit (R) to return to PARCALC TAFEL MENU. Select (4) to save results and then (7) to print the plot.
- 23. From the PARCALC TAFEL MENU, select (R) to return to RESULT CALCULATION MENU.

- 24. Select (4) to do the Polarization Resistance Analysis. The software begins to calculate the polarization resistance and Figure A-11 will display the results, including the corrosion rate in mpy. Also, the software will plot the Polarization Resistance Data Plot (Figure A-12). This completes the Polarization Resistance Analysis.
- 25. Finally, return to the RESULT CALCULATION MENU by hitting (R) on the POLARIZATION RESISTANCE MENU. At this point, operator can select either (2) or (3) to list results or data on the screen or to have a printout (Figures A-13 & A-14) from the printer. This concludes the descriptions of both the PARCalc Tafel Plot and Polarization Resistance Experiments.

EG&G PRINCETON APPLIED RESEARCH MODEL 342 SOFTCORR CORROSION SOFTWARE MAIN MENU EXP. NAME:NONE DATA: Ø TECHNIQUE: NONE <S> SETUP/RUN MENÚ <P>> PLOT DATA MENU <R> RESULTS MENU <E> EDIT DATA MENU <F> FILE MGMT MENU <Q> QUIT PROGRAM <?> HELP _____ ------CHOOSE AN ENTRY Figure A-1: Main Menu SET-UP AND RUN MENU EXP. NAME: NONE DATA: Ø TECHNIQUE: NONE -----<1> POTENTIODYNAMIC <2> POLARIZATION RESISTANCE <3> REACTIVATION <4> CYCLIC POLARIZATION <5> TAFEL PLOT <6> ECORR VS TIME <7> GALVANOSTATIC <8> POTENTIOSTATIC <9> GALVANIC CORROSION < 🛛 > VIEW LAST PLOT <F> FILE MANAGEMENT MENU <M> MAIN MENU <?> HELP _____ CHOOSE AN ENTRY

Figure A-2: Set-Up and Run Menu

RUN	PARAMETERS		PAGE 1
<Ø> <1> <2> <3> <4> <5> <6> <7>	TECHNIQUE EXP NAME INITIAL E (MV) FINAL E (MV) SCAN RATE (MV/S) CONDITION E (MV) CONDITION T (S) INIT DELAY (MV/S C PLOT MAX I RANGE	TAFEL >	-250 VS E 250 VS E .2 PASS PASS PASS 1 AMP
	<pre><r> RUN EXE <s> SETUP/E <m> MAIN ME <n> NEXT PA</n></m></s></r></pre>	PERIMENT RUN MENU ENU AGE	

INPUT REQUIRED

Figure A-3:	Run	Parameters	Screen

SAMPLE PARAMETERS	PAGE 2
<0> AREA (CM^2) <1> EQ WT (G) <2> DENSITY (G/CM^3) <3> CATHODIC TAFEL (MV) <4> ANODIC TAFEL (MV) <5> LINE SYNC (Y/N) <6> CURRENT INTERRUPT (S)	1 PASS PASS PASS PASS PASS PASS
<pre><r> RUN EXPERIMENT <s> SETUP/RUN MENU <m> MAIN MENU <n> NEXT PAGE</n></m></s></r></pre>	

.

CHOOSE AN ENTRY

Figure A-4: Parameter Screen Page 2 (Sample Parameters)

و سے کہ جبہ ہیں جب عبد کے اس آبنا جنہ ہیں ہے جو بار ہے ہے جو جب وہ جو خوا کہ من جات کا سے اس	ه احد هم من حي حي حي حك حي حل حل حد حي حال ا	-
LEGEND	PAGE 3	3
و های اللہ اللہ اللہ اللہ اللہ اللہ اللہ ال		_

< 🛛 >	SS316 IN 30% WT H2S04		
$\leq 1 >$	INHIBITOR: THIOUREA	0.3%	WT
$\langle 2 \rangle$	AERATED STAGNANT		
<3>	TEMP. 30 C		
<4>	FEB 21		
<5>	BY SHANG-YINN CHIOU		
<6>			
<7>			
<8>			

	الله هي الى الى الى عن الى الى جي الله الي الله الي الله الله الله الله
<r></r>	RUN EXFERIMENT
< S >	SETUP/RUN MENU
< M>	MAIN MENU
<n></n>	NEXT PAGE



Figure A-5: Parameter Screen Page 3 (Legend)

•



Figure A-6: A Typical Tafel Plot

EEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEE	CALCULATION MENU
EXP. NAME: NONE TECHNIQUE: NONE	DATA: Ø
<1> RECAL <2> LIST <3> LIST <4> POLAL <5> REAC <6> PARC <7> SAVE	LL EXP RESULTS DATA RIZATION RESISTANCE FIVATION (COULOMETRY) ALC TAFEL ANALYSIS RESULTS
<c> CATAI <e> EDIT <m> MAIN <? > HELP</m></e></c>	LOG MENU MENU
CHOO	OSE AN ENTRY
Figure A-7	: Result Calculation Menu
PARCAL	LC TAFEL MENU
EXP. NAME: QWERT TECHNIQUE: POTENT	DATA: 847 IDDYNAMIC LE VS IJ
<1> 8 <2> 0 <3> 0 <4> 9 <5> 4 <5> 4 <5> 4 <7> 8	PLOT DATA CALCULATE RESULTS DVERLAY RESULTS SAVE RESULTS VIEW LAST PLOT PLOT WRITER PRINT PLOT
$\langle R \rangle = 1$	RESULT MENU

CHOOSE AN ENTRY

Figure A-8: Parcalc Tafel Menu

PARCALC TAFEL MENU		
EXP. NAME: TAFEL SAMPL. TECHNIQUE: TAFEL .	E 1 DATA:250 LE VS IJ	
RESULTS		
E(I=0) (MV)	-532.24	
CATHODIC TAFEL (HV)	183.18	
ANODIC TAFEL (AV)	94.28	
I-CORR (UA/CH^2)	572.2	
CORR RATE (MPY)	264.19	
CHI SQUARE	43.56	

(RTN) TO CONTINUE

Figure A-9: Typical Parcalc Results



Figure A-10: A Typical Data Plot

	***********	********
POLARIZATIO	N RESISTANCE	MENU
EXP. NAME: TAFEL S	AMPLE 1	DATA: 250
TECHNIQUE: TAFEL		CE VS II

RESULTS

E(I=0) (MV)	-532.13
POL RESIST. (K-OHMS)	.0368
I-CORR (UA/CM^2)	733.93
CORR RATE (MPY)	338.87
CORRELATION	. 99



Figure A-11: Typical R_p Calculation Results



Figure A-12: Typical Polarization Resistance Data Plot

TAFEL TECHNIQUE ORIGINAL NAME S1025 -250 VS E INITIAL E(MV) 250 VS E FINAL E(MV) SCAN RATE(MV/S) .25 PASS CONDITION E(MV) CONDITION T(S) PASS .1 M INIT DELAY(MV/S OR S)

. . . .

SAMPLE PARAMETERS

AREA(CMS^2)	1
EQ WT(GM)	27.6
DENSITY(GM/CM^3)	7.7
CATHODIC TAFEL(MV)	PASS
ANODIC TAFEL(MV)	PASS

DATA SCALE

ECORR	-485
MV/PT	2
DATA MAX	79200
DATA MIN	-96200
ABS MIN	100
ABS MAX	96200

REBULTE

E(I=0)(MV)	-469.96
CATHODIC TAFEL(MV)	223.02
ANODIC TAFEL(MV)	104.67
I-CORR(UA/CM^2)	3310.57
CORR RATE(MPY)	1542.64
E(I=0)(MV)	-472.53
POL RES.(K-OHMS CM^2)	.0086
I-CORR(UA/CM^2)	3592.5
CORR RATE(MPY)	1674.01

LEGEND

SS410 IN 20% WT H2SO4 AIR-FREE STAGNANT TEMP. 30 C FEB 7 BY SHANG-YINN CHIOU

Figure A-13: Typical Tafel Plot and Polarization Resistance Results

DATA #	REF #	I(UA/CM^2)	E(MV)
DATA # 1 2 3 4 5 6 7 8 9 10 11 12 13 4 5 6 7 8 9 10 11 12 13 14 5 16 17 18 19 20 21 22 24 25 6 7 8 9 10 11 12 13 4 5 6 7 8 9 10 11 12 13 14 5 6 7 8 9 10 11 12 13 14 5 6 7 8 9 20 11 12 23 24 25 6 7 8 9 20 11 12 23 24 25 6 7 8 9 20 11 12 23 24 25 6 7 8 9 20 11 22 23 24 25 6 7 8 9 20 12 23 24 25 6 7 8 9 20 21 22 24 25 6 7 8 9 20 21 22 24 25 6 7 8 9 20 21 22 24 25 26 27 8 9 30 31 22 23 24 25 26 29 30 31 20 20 20 20 20 20 20 20 20 20	REF # 12345378901123453789011234537890112345378901222222222222222222222222222222222222	$I(UA/CM^2)$ -9.620E+04 -8.900E+04 -8.200E+04 -8.200E+04 -7.880E+04 -7.880E+04 -7.940E+04 -7.940E+04 -7.940E+04 -7.700E+04 -7.700E+04 -7.270E+04 -7.270E+04 -6.750E+04 -6.750E+04 -6.750E+04 -6.400E+04 -5.840E+04 -5.840E+04 -5.840E+04 -5.470E+04 -5.270E+04 -5.140E+04 -5.270E+04 -4.800E+04 -4.800E+04 -4.300E+04 -4.300E+04 -4.190E+04 -3.970E+04 -3.970E+04 -3.920E+04	E(MV) -7.350E+02 -7.330E+02 -7.310E+02 -7.270E+02 -7.250E+02 -7.250E+02 -7.250E+02 -7.250E+02 -7.170E+02 -7.170E+02 -7.150E+02 -7.150E+02 -7.070E+02 -7.050E+02 -7.050E+02 -7.050E+02 -7.050E+02 -7.050E+02 -6.970E+02 -6.970E+02 -6.950E+02 -6.950E+02 -6.850E+02 -6.850E+02 -6.850E+02 -6.850E+02 -6.850E+02 -6.850E+02 -6.850E+02 -6.850E+02 -6.850E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -6.750E+02 -7.750E+02 -7.750E+02 -7.750E+02 -7.750E+02 -7.750E+02 -7.750E+02 -7.750E+02 -7.750E+02 -7.750E+02 -7.750E+02 -7.750E+02 -7.750E+02
29 30 31 32	29 30 31 32	-4.110E+04 -3.970E+04 -3.920E+04 -3.800E+04	-6.790E+02 -6.770E+02 -6.750E+02 -6.750E+02 -6.730E+02
83 34 35 36 37 38	394 34 35 36 37 0	-3.880E+04 -3.550E+04 -3.420E+04 -3.350E+04 -3.280E+04 -3.180E+04	-6.210E+02 -6.670E+02 -6.670E+02 -6.650E+02 -6.630E+02
39 40 41 42 43	20 39 40 41 42 43	-3.1302+04 -3.030E+04 -2.930E+04 -2.870E+04 -2.770E+04 -2.4805+04	-6.570E+02 -6.570E+02 -6.570E+02 -6.550E+02 -6.530E+02
44 45 43 47	44 45 46 47	-2.610E+04 -2.520E+04 -2.430E+04 -2.360E+04	-6.310E+02 -6.470E+02 -6.470E+02 -6.450E+02 -6.430E+02

.

Figure A-14: Typical Experimental Data Set

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