

**SYNERGISTIC EFFECTS OF INHIBITORS AND
HEAT TREATMENT ON CORROSION
BEHAVIOUR OF MILD STEEL IN
SALINE ENVIRONMENT**

BY

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APRIL, 2009.

CERTIFICATION

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This work has not been presented elsewhere for the award of a degree, or any other purposes.

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14-05-09



DEDICATION

This project / thesis is dedicated to the memory of my Late Father, Rev. J.A. Adubuola and My Mother Mrs. Lydia Adubuola



ACKNOWLEDGEMENT

First and foremost, I am grateful to Almighty God for His goodness and tender mercies that saw me to the end of this work.

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The Almighty God will help you all.



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ABSTRACT

The synergistic effects of alanine, methionine and glutamic acid inhibitors and heat treatment, as a function of weight loss on the corrosion behaviour of mild steel in the presence of 3% KCl were investigated. The corrosion rate and inhibition efficiency were determined. A microstructural examination to reveal the phases of the corroded samples was undertaken to ascertain the synergistic effect of some amino acid inhibitors and heat treatment on corrosion behaviour of mild steel. The result obtained showed that alanine was observed to be more efficient than both methionine and glutamic acid. Reduction in corrosion rate could be attributed to the adsorption of inhibitors on the steel at the initial stage of inhibition and film growth and stability of film at later stages of inhibition. The combined effect inhibitors and heat treatment resulted in better corrosion resistance. This study was carried out due to its importance in providing useful data for organic inhibitors capable of curtailing the menace of corrosion in industries where steels are used for production of structures.

CHAPTER ONE

INTRODUCTION



1.0 Background

Steel corrodes in most environments; consequently the useful life of the steel is reduced and become a major problem in most industries such as petrochemical, pharmaceutical, fertilizer, agriculture and in food processing industries. The properties of steel are related to its structural make-up. The desired mechanical properties can be obtained by altering the size, shape and distribution of various constituents which can be achieved by heat treatment processes. Corrosion which is defined as the destructive alteration of a metal by chemical or electrochemical reaction with its environment, Staniar (1962) can be controlled by modification of the environment which can either be gaseous, liquid and solid. The failure of metal systems in oil pipeline or failure of refinery equipment in service has caused Nigeria an unquantifiable loss of lives, production shut down, environmental pollution and several billions of Naira. This necessitated this research for appropriate corrosion protection system. Corrosion prevention is an essential factor in the economic utilization of steel, national economic life and development. According to Uhlig (1971) the durability of machines and structures is controlled by surface related phenomenon. Heat treatment which is a combination of heating and cooling operations is applied on mild steel in this research to produce desired properties to reduce the rate of metal dissolution. Sverdrup et al, (1942) reported that sea water is one of the most prolific natural corrosion agents (3-3.5%NaCl). Various other researchers have proposed the mechanisms of

corrosion inhibition in metal systems, among who are Oni (1997) who worked on the inhibition of stress corrosion cracking of a low carbon steel in sulphuric acid by potassium chromate-sodium nitrate mixture due to synergism, Oyetunji (2000) studied the effects of some inhibitors on the corrosion rate of low carbon steel submerged in sea water. The present drive to encourage oil industries and other related down stream industries in Nigeria has led government to make huge investment on installations of pipeline and machineries, but one of the impeding factors to achieving this laudable objectives of government is the rate at which plant break down due to corrosion. Hence, this research is designed to investigate combination of inhibitors and heat treatment capable of reducing or eliminating corrosion.

1.1 Aim and objectives

The aim of this project is to study the combined effect of heat treatment and inhibitors on corrosion behaviour of mild steel in saline environment, with the aim of reducing the rate of corrosion and examining the inhibitors properties with the purpose of improving the corrosion efficiency of metal systems.

The research is expected to proffer solution to mitigating corrosion problems of steel structures normally employed in oil and gas and industries and also to establish a suitable processing technique for steel samples prior its use in saline environment

The destructive effect of corrosion necessitated the need to find solution to combat or counteract the corrosion effect on steel owing to its industrial application.

Some organic compounds containing N, O, and functional groups have been identified as inhibitors for aqueous corrosion of metals such as Fe, Al and Cu, Oni (1992). Despite the numerous availability of materials reported on inhibitors for corrosion of steel, research still continue to identify highly efficient inhibitors for a particular application. This project is focused on the use of amino acid inhibitors to condition the corrosive environment i.e. Saline, and heat treatment operations to condition the metal in order to provide required mechanical strength when designing equipment for certain service life.

The corrosion inhibitors were limited to alanine, methionine and glutamic acid and due to their availability and enhanced deep study of each inhibitor.

Oil pipelines carrying products are made of steel and mostly offshore, therefore are exposed to sea water (3% NaCl) the corroding medium used in this project is 3%KCl just to simulate sea water conditions.

LITERATURE REVIEW

2.0 Introduction

Metal can generally be said to corrode because of their instability in the refined state. Steels would want to revert to their oxides as they occur naturally in the earth crust. Corrosion is defined as the destruction of metal by chemical or electrochemical reaction with its environments (Moody, 1971). The steel is not homogenous at the initiation of corrosion, anodic and cathodic sites are formed on the surface of the alloy(steel Fe-C). In the presence of the electrolyte, small corrosion cells are set up on the surface and at the anodic areas. Iron goes into solution as ferrous ion(Fe^{2+}) i.e. its corrodes (Anver, 1974).

2.1 Electrochemical Corrosion and its Mechanism

Electrochemical corrosion mechanism involves the corrosion of a metal which occurs at metal/liquid interface with subsequent transfer of electrons through the metal, and ions through the solution. The mechanism is of the independent position and distance of separation of anodic and cathodic sites.

It usually occurs at the surface of a metal in which particles of an impurity are present as part of the microstructure. Particles of an impurity will be cathodic towards the metallic matrix, since impurities are usually segregated at crystal boundary. This will result in a gradual inter crystalline corrosion of the materials as more particles of impurity become exposed by an electrolytic action. Figure 2.1

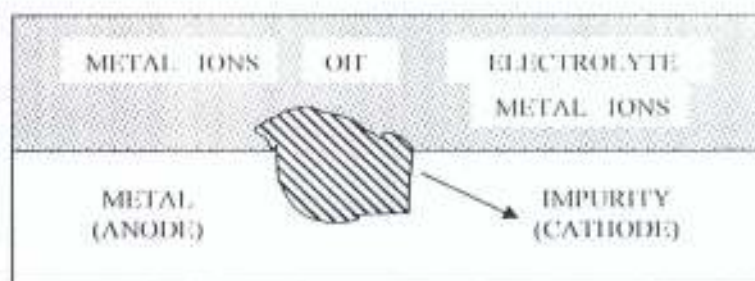
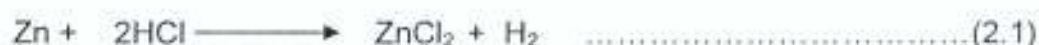


Fig 2.1 Mechanism of electrolytic corrosion

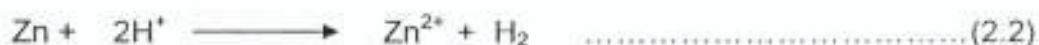
2.1.1 Electrochemical Reactions

The electrochemical nature of corrosion can be illustrated by the attack of zinc by HCl. When Zn is placed in diluted HCl, a rigorous reaction occurs, H_2 gas is evolved and the Zn dissolves forming a solution of $ZnCl_2$

This reaction is expressed as



This equation can be written in a simplified form



Hence, Zn reacts with H^+ of the acid solution to form Zn^{2+} and H_2 . Zn is oxidized to Zn^{2+} and H^+ is reduced to H_2 . This equation can be divided into two reactions, the oxidation of Zinc and reduction of hydrogen ions

Oxidation (Anodic reaction)



Reduction (cathode reaction)



The anodic reaction is the oxidation of metal to its ions. This can be written in general form:



Examples are:-



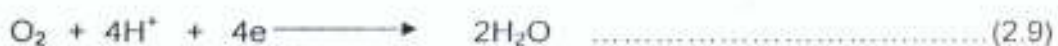
There are different cathodic reactions which are always encountered in metallic corrosion.

Cathodic reactions are

Hydrogen evolution



Oxygen reaction (acid solution)



Oxygen reaction (Neutral or basic solution)



Metal ion reaction



Metal deposition



Hydrogen evolution is a common cathodic reaction since acid or acidic media are frequently encountered. Oxygen reduction is very common, since any aqueous solution in contact with air is capable of producing this reaction.

Acidic attack often starts to form as surface defects and then spreads out. In electrochemical corrosion (mainly in aqueous solution of salts, acid and base) anodic reaction involve the destruction of the metal and causing it to dissolve as ions or to revert to a compound state as oxide. The deposition

of the reaction products plays a decisive role in controlling the rate of corrosion. They may form on either the anodic or cathodic site thereby inhibiting further corrosion.

2.1.2 Corrosion of iron and Steel

Corrosion of iron and steel, Shreir, (1976) is essentially the conversion of iron into a hydrated form of iron oxide i.e. rust. The driving force of the reaction is the tendency of iron to combine with oxygen.

Iron is not visibly corroded in the absence of either water or oxygen. The overall reaction in their presence may be written as:-

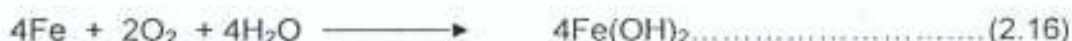


When the supply of oxygen is restricted, the corrosion product may contain ferrous ions.

The overall reaction may be divided into two reactions:



Overall reaction is therefore



In the presence of oxygen, the ferrous hydroxide is converted into rust in the reaction



Evans, (1960) established that the conversion of iron to rust is accompanied by a flow of electrons in the metal from anodic to the cathodic region and movement of ion into solution.

In order to inhibit corrosion, the flow of current is stopped by suppressing either the cathodic or the anodic reaction or by inserting a high resistance in the electrolytic path of the corrosion current.

2.1.3 Corrosion Of Steel by Fluids

Corrosion by fluid is of primary importance to the process industry and second to atmospheric corrosion in total wastage of metals. It is almost entirely electrochemical, since the metal is in contact with an electrically conducting fluid which has a tendency to go into solution in the form of ions and hydrogen is displaced from the solution.

Figure 2.2 illustrates a steel immersed in an aqueous solution, iron goes into solution by displacing hydrogen.

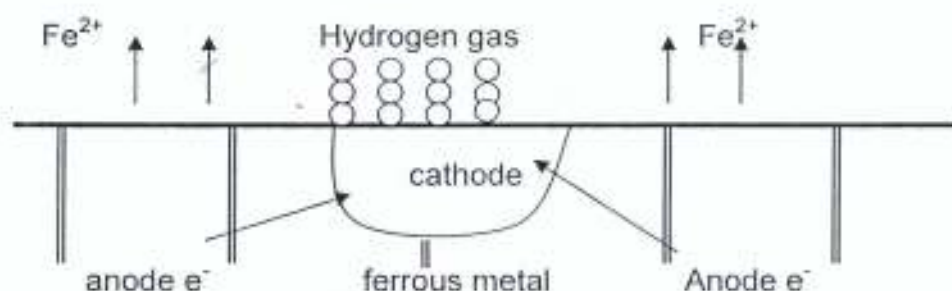
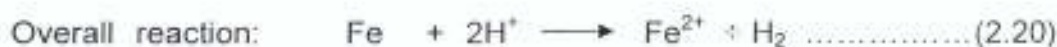
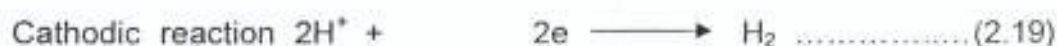


Fig 2: Typical corrosion of steel by fluid



Bockris et al, (1965) concluded from permeation experiment that in acidic as well as in alkaline solution, hydrogen evolution on ion occurred according to a coupled discharge-recombination-mechanism.

Corrosion process will continue as long as there are hydrogen ions in the solution. However, as corrosion proceed, the hydrogen formed is not immediately evolved and a gaseous layer is formed over the surface of the metal, this hydrogen gas layer interferes with the flow of electrons by preventing the electron required to produce more nascent hydrogen. This reduction in the flow of electrons slows the corrosion process. This process is known as "Polarization" and the metal is said to be polarized.

2.1.4 Types of Corrosion

Corrosion can be classified by the forms in which it manifests, the basis for this classification being the appearance of the corroded metal. Each form can be identified by mere visual observation. In most cases the naked eye is sufficient, but sometimes magnification is helpful or required. Valuable information for the solution of a corrosion problem can often be obtained through careful observation of the corroded test specimens or failed equipment. Examination before cleaning is particularly desirable.

Some of the forms of corrosion are unique, but all of them are more or less interrelated. The different forms of corrosion as classified by Fontana and Greene, (1967) are:

1. Uniform or general attack
2. galvanic or two metal corrosion

3. crevice corrosion
4. pitting corrosion
5. intergranular corrosion
6. selective leaching
7. erosion corrosion
8. stress corrosion

2.1.5 Factors Affecting The Rate of Corrosion of Steel

Generally, corrosion reactions are very slow. Some factors tend to increase the rate of corrosion while others serve to retard the corrosion processes, either by slowing the rate of surface film growth or by improving on the passivity of the surface film in the corroding media. Corrosion rates in aqueous solutions are governed by the nature of the corrosive medium and by the composition of the iron. Other common factors are:

(a) Hydrogen Ion Concentration.

Acid solutions, that is those having a large content of hydrogen ions and a low pH value, are more corrosive to unalloyed cast iron than those that are in alkaline solutions. Electrical conductivity of solutions increases with the amount of dissolved salts and gases giving increased corrosion rates. Interfering with the removal of hydrogen from solution will slow down the corrosion process, while anything that aids the removal of hydrogen from solution will speed up the corrosion process.

(b) Temperature

Rise in temperature increases the rate of most chemical reactions and corrosion rates also increase the ionization and mobility of all reacting- fluid phases. It also has an effect upon film formation and solubility. Solubility of film increases with increasing temperature.

(c) Fluid Velocity

The velocity of corrosive fluid can have an effect on the corrosion of steel used in the construction of pipelines, valves, and heat exchangers. Fluids moving at high velocity may damage protective surface and accelerate corrosion in localized areas. Therefore, the flow of corroding fluid across the surface of a metal depends on a passivating film. The corrosion resistance should be streamlined and not exceed a velocity of 1.8 – 2.4m/s, Staniar (1962)

(d) Effect of pH

In strong acids e.g. HCl, H_2SO_4 , the diffusion barrier oxide film on the surface of iron is dissolved below pH of 4 (Uhlig, 1971). In weaker acids e.g. acetic or carbonic acids, dissolution of oxide occurs at higher pH, hence the corrosion rate of iron increases which is accompanied by hydrogen evolution at pH of 5 or 6 (Uhlig, 1971). The difference is explained by the higher total acidity or neutralizing capacity of a partially dissociated acid compared with a totally dissociated acid at a given pH.

In strong acids there is more available H^+ to react with and dissolve the barrier oxide film as compared to a weak acid.



The increased corrosion rate of iron or steel as pH decreases is not caused by increased hydrogen evolution, it is the greater accessibility of oxygen to the metal surface oxide which favours oxygen depolarization (Uhlig, 1971).

(e) Nature of the Metal Surface

The nature of the metal surface has considerable effect on its corrosion resistance. A smooth surface offers greater resistance to corrosion than the rough one. A smooth surface possesses fewer crevices and indentations which might induce concentration cell corrosion and also offers less surface area on which attack may initiate.

2.2 Corrosion Testing

Corrosion testing involves the measurement of corrosion rate of a metal or an alloy in its environment either directly through the change in weight or indirectly through changes in its various physical, electrical or electrochemical properties.

Corrosion testing may be classified into two types: namely:

- (1) Laboratory test
- (2) Service tests.

Laboratory test may be further sub-divided into

- (a) Long time test without acceleration and
- (b) Short time test with acceleration

While service test may be sub-divided into:

- (a) plant test and
- (b) Field or atmospheric tests.

Corrosion tests are conducted to determine:

- (1) the mechanism of corrosion
- (2) the usefulness of new metals and alloys in various corrosion media for a possibility of substitution of cheaper and metal readily available alloy of satisfactory corrosion resistance or for more expensive and difficult to obtain.
- (3) the effect of changes in composition or treatment in developing corrosion resistant alloy
- (4) the development of new alloys for specific purposes
- (5) the effect on materials by contamination from corrosion product
- (6) the environment in which a given metal can be satisfactorily employed and to estimate its life expectancy
- (7) the use of inhibitors efficiency to select efficient method of corrosion protection in a particular environment.
- (8) the premature failure of an equipment and also quality control measures

2.2.1 Methods of Corrosion Testing

The ideal corrosion testing equipment should be designed to duplicate conditions to which the materials to be tested is exposed to under operating conditions. Such equipment would incorporate features making it possible to determine the effect of temperature, velocity, aeration, turbulence, impingement, galvanic couples, and plastic deformation, residual and applied stresses and joining fabrication method on the corrosion rate.

The most commonly used methods in the laboratory are the total-immersion test, the alternate-immersion test, the partial immersion test, and the salt-spray test

(a) Total-Immersion Test

This consist essentially of immersing prepared and weighed sample in the test solution for a number of periods of usually two or more days duration and determining the weight loss by cleaning and reweighing the sample after each period.

According to Staniar(1962) the corrosion rate per unit area or penetration rate factor can be determined from the expression.

$$R = \frac{(720 \times W)}{(A \times D \times T)} \dots\dots\dots (2.21)$$

Where

R = corrosion rate, (cm penetration per month)

W = weight loss, (grams)

A = Area, (Sq.cm)

T = Time, (hour)

D= Density (g/cm³)

The total immersion test is the most widely used method. Test data obtained by this test method are very valuable, although it is desirable to confirm results by special tests or plant exposure.

Variation in aeration, temperature and velocity have been found to affect the result from this test, thus various devices have been used for providing control of these three major factors.

(b) Alternate- Immersion Test

In this testing procedure, special mechanical equipment is required which permits automatic immersion and withdrawals of the samples from the solution. The test is designed to determine the effect of alternate exposure to the corrodent and to air, such as occurs in tanks, pipelines and on roofs. The tests are normally conducted at room temperature or slightly above. The test period is usually longer than that employed in total immersion testing.

The procedure for preparing test sample and determining the degree of deterioration is the same as that in the total immersion testing.

(c) Partial Immersion Tests

In this test, samples are only partially immersed in the test liquid. The object of this test is to determine the rate of corrosion at the liquid-vapour level. This is important in constant level tanks and in partially filled pipelines.

(d) Salt Spray Test

The most common of the spray test is the salt-spray test which was originally developed by Capp (1914) for studying the protective value of metallic coatings on steel under conditions that would simulate explosive to a sea-coast atmosphere.

Phosphate coatings are occasionally tested by continuous salt spray without sealing oil film and are expected to withstand one two hours spray without showing signs of rust.

2.3 Corrosion Prevention

By retarding either the anode or cathode reactions the rate of corrosion can be reduced. This can be achieved in several ways:

1. Conditioning the Metals

(a) Coating the metal in order to interpose a corrosion resistant coating. It may consist of:

- (i) another metal e.g. zinc or tin on steel;
- (ii) a protective coating derived from the metal itself e.g. aluminum on anodized aluminum; and
- (iii) organic coating such as plastic, resin, paints, enamel, oil and grease

(b) Alloying the metal to produce a more corrosion resistant alloy e.g. stainless steel in which ordinary steel is alloyed with chromium and nickel

2. Conditioning the Corrosive Environment

(a) Removal of oxygen: by the removal of oxygen from water systems, one of the components required for corrosion would be absent. This is achieved by the use of strong reducing agents e.g. Sulphite.

(b) Corrosion inhibitors: A corrosion inhibitor is a chemical additive, which when added to a corrosive environment reduce the rate of metal wastage. It can function in one of the ways,

- (i) anode inhibitor
- (ii) cathodic inhibitors
- (iii) adsorption type corrosion inhibitors: many organic inhibitors work by an adsorption mechanism. The resultant film of

chemisorbed inhibitor is responsible for protection either by physically blocking the surface of the metal from the environment or by retarding the electrochemical process. The functional groups are capable of forming chemisorbed bonds with the metal surface e.g. amino ($-\text{NH}_2$), ($-\text{COOH}$) and phosphonate ($-\text{PO}_3\text{H}_2$)

(iv) Mixed inhibitors: because of danger of pitting when using anodic inhibitors along, incorporating a cathodic inhibitor give a better performance by the combination of inhibitors. This is referred to as synergistic action of inhibitors.

3. Electrochemical Control

Since corrosion is an electrochemical process, its progress may be monitored by changes which occur in metal potential with time or with applied electrical current. Conversely, the rate of corrosion reactions may be controlled by fluid of anodic or cathodic currents into metal.

2.4 Electrochemical Measurement

Most of the electrochemical methods of measurement may be classified in the following group:

(a) **Electrode Potential measurement:** - This method involves the measurement of the potential of the test specimen in a suitable environment with respect to a reference electrode. The electrode potentials are followed with time from the time of immersion to the time of failure or end of the test period

(b) **Polarization Measurement:** This method involves the measurement of change in potential or changes in current when a constant external current (Galvanostatic method) or a constant external potential (potentiostatic method) is impressed on the test metal. Examples are Tafel extrapolation, linear polarization which is also known as polarization resistance method and polarization break method

(c) **Impedance Measurement:** - Electrode surface generally behave, at any given frequency, as a network of resistance and capacitance element from which electrical impedance can be measured and analyzed.

2.5 PASSIVITY

Passivity involves a strongly reduced corrosion tendency of metals due to a protecting layer of corrosion products. Passivity is of two kinds, chemical and mechanical passivity.

(a) **Chemical passivity:** - Appears on certain so-called passivating metals, many of which are so-called transition metals, characterized by an unfilled d-group of electrons in an inner electron shell. Passivating transition metals are for example, the iron and platinum group of metals, chromium, molybdenum and tungsten, titanium and zirconium, even some non-transition metals such as aluminum show chemical passivity. This type of passivity is ascribed to an invisible thin but dense and semi conducting oxide film on the metal surface displacing the electrode potential of the metal in the positive direction.

(b) **Mechanical passivity:** - May occur on practically all metals in environments where conditions are favorable to the precipitation of

solid salts on the metal surface. The cause of the strongly reduced corrosion rate is a thick but more or less porous salt layer, usually non-conducting in itself. Example of this is lead in sulphuric acid, magnesium in water or fluoride solutions

2.6 Corrosion Inhibitors

Inhibitors are chemical substances which reduces the aggressive nature of an environment towards a metal by preventing the corrosion reactions either by reducing the probability of its occurrence or by reducing the rate of attack or both when present in certain quantity.

The application of inhibitors for aqueous or partly aqueous system is concerned with three main types of environment, which are:

- (a) Natural water, supply water, industrial cooling water, in near-neutral pH range;
- (b) aqueous solutions of acids as used in metal cleaning processes such as pickling for the removal of rust or unrolling scale during the production and fabrication of metals, or in the post-service cleaning of metal surface; and
- (c) primary and secondary production of oil and subsequent refining processes.

2.6.1 Classification of Inhibitors

There are many methods of classifying inhibitors into types or groups. The protective actions of inhibitors have also been explained, but there is still

no general agreement on the allocation of an inhibitors for a particular group some of the main classification used particularly for inhibitor in near-neutral pH aqueous systems are as follows:

(a) Anodic and Cathodic Inhibitors

This classification is based on whether the inhibitors cause increase in polarization of the anodic reaction (metal dissolution) or of the cathodic reaction (oxygen reduction) in near-neutral solution or hydrogen discharge in acidic solution.

(b) Oxidizing and Non-Oxidizing Inhibitors

These are characterized by their ability to passivate metal. Non-oxidizing inhibitors require the presence of dissolved oxygen in the liquid phase for maintenance of the passive oxide film, whereas dissolved oxygen is not necessary with the oxidizing inhibitors.

In oxidizing inhibitors, the mechanism is more complex than the direct surface oxidation since passivity is favoured by conditions increasing the rate of the cathodic process or decreasing the rate of the anodic metal (active-passive) dissolution process below primary passivation potential, the oxidizing inhibitors can rationally be divided depending on mechanism, into two groups:

(i) Non-Oxidizing Anodic Inhibitors

These are inhibitors which retard the anodic process. Such inhibitors directly enhance anodic passivation. This is accomplished by shielding part of the anodic surface as a result of:

- Specific adsorption of the oxidizing ions by the metal surface (e.g. formation of chemisorbed thinner chromate film and thicker phosphate film to form protective films of the chemisorbed or phase types.
- Making conditions more favourable for adsorption of oxygen (e.g. polyphosphates, alkalis, silicates, borates) . Since all these are non-oxidizing in order to inhibit corrosion, hence oxygen is properly considered the passivating substance. Inhibition of the anodic process is promoted through a reduction of the anodic area by shielding or by limiting diffusion of the anodic products (for thicker protective film) and through an increase in the anodic over voltage by reducing the exchange current density for



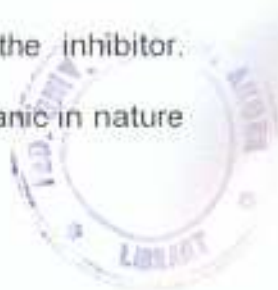
or the corresponding change of potential in the layer (film thinner chemisorbed film of oxidizer or oxygen).

(ii) Oxidizing Anodic Inhibitors (Passivators)

These are inhibitors which enhance the effectiveness of the cathodic process. These inhibitors (oxidizers) do not directly change or appreciably affect the kinetic of the anodic process, but by increasing the effectiveness of cathodic depolarization shift the overall potential of the system to more positive potential corresponding to the onset of passivity.

(C) Organic and Inorganic Inhibitors

The distinction is based on the chemical nature of the inhibitor. However, in their inhibitive action, many compounds that are organic in nature



for example, the sodium salt of carboxylic acid, often have more similarities with inorganic inhibitors.

(d) Other Types of Inhibitors

According to Antropov (1977), corrosion inhibitors may also be classified as liquid-phase and vapour-phase or volatile, depending on the conditions of their use.

(i) Liquid-Phase Inhibitors

These are subdivided according to their utilization (in neutral, alkaline or acidic media). The inhibitors most often used for neutral solutions are inorganic compounds of the anionic type. Their inhibiting effect being associated with either the oxidation of the metal surface e.g. nitrites and chromates or with the formation of a film of a different compound between metal and the given anion and possibly oxygen inhibitor effect is mainly associated with adsorption phenomenon. All corrosion inhibitors that are used for neutral solution slow down predominantly the anodic reaction.

In alkaline solutions, only high-molecular weight compounds possess some inhibitive properties. Corrosion inhibitors for acidic solutions are almost exclusively organic substances containing nitrogen, sulphur or oxygen. In the form of amino, carboxyl and carbonyl. The action of organic substances is due to their adsorption on the metal interface which retards cathodic and anodic reactions, thereby reducing the corrosion rate.

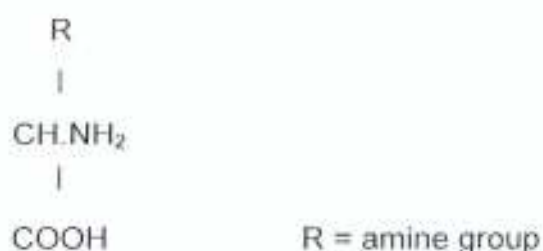
(ii) Vapour-Phase Inhibitors

These are used for corrosion protection in machines, apparatus and other materials during their service in the air medium, during transportation and storage. These inhibitors are usually sprinkled as solid in container or placed close to the surface to be protected, as a result of the sufficiently high vapour pressure, volatile inhibitors reach metal-air interface and dissolve in the moisture film covering the metal. The compound commonly used as vapour-phase inhibitors are anions of low molecular weight to which corresponding groups e.g. NO_2 or CO_2 are added

(iii) Amino Acid Inhibitors

Some organic compounds containing N, O, and or functional groups have been identified as inhibitors for aqueous corrosion of metal such as Al, Fe and Cu (Oni, 1992). The action exerted by a given derivative depends on its structure as well as the composition of the solutions.

Amino acids are carboxylic acids which also contain an amino ($-\text{NH}_2$) group in the molecule. The amino group is usually in the α -position with respect to the carboxyl (Data and Ottaway, 1976) with the general formula



All amino acids are colorless, crystalline solids and very soluble in water (except aspartic and glutamic acids, cystine and aromatic amino acids).

They are soluble in dilute acidic and alkalis from and insoluble in organic solvent, being participated from aqueous solution by alcohol (Data and Ottaway, 1976).

Amino acids may be classified into three groups:

1. Aliphatic amino acid
2. aromatic amino acid
3. heterocyclic amino acid

They may further be subdividing under this heads into:

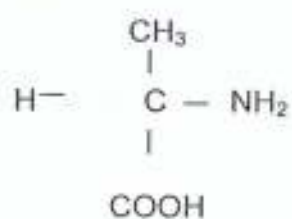
1. Neutral amino acid:- i.e. containing one-NH₂ and one-COOH in the molecule
2. Acidic amino acid:- i.e. containing one-NH₂ and two – COOH in the molecule
3. Basic amino acids: i.e. containing two-NH₂ group or one

NH₂ and some other basic group such as a imidazohyl or guanidio and one-COOH (Data and Ottaway, 1976)

Molecular structures of amino acid inhibitors used in this study are:-

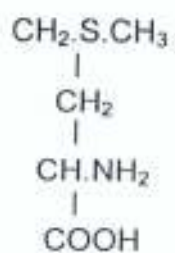
Neutral Group

1



Alanine

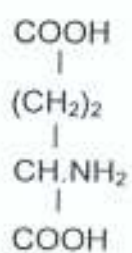
2



Methionine

Acidic Group

3



Glutamic acid



2.6.2 Mechanism of Corrosion Inhibition

The action of inhibitors may change with the corroding media. For instance, the corrosion of metals in neutral solutions differs from that in the acid solution in two important respects. In air saturated solution the main cathodic reaction in neutral solution is the reduction of oxygen, i.e.



Whereas in acid solution, it is hydrogen evolution in the reaction i.e.



Corroding metal surfaces therefore in acid solution are oxide free, whereas in neutral solution metal surface are covered with films of oxides hydroxides or salts due to the reduction solubility of these species. As a result of these difference, substance which inhibit corrosion in acid solution by absorption of oxide free surface, do not generally inhibit corrosion in neutral solution.

(a) Mechanism of Corrosion Inhibition In Acid Solution

Putilova et al(1960) and TrabANELLI and Carassiti (1970). Stated that the corrosion of metal in aqueous acid solution can be inhibited by a very wide range of substances. Primarily is the absorption of inhibitors on metal surface which usually oxide-free in acid solution. The absorbed inhibitor then act to retard the cathodic and anodic electrochemical process of corrosion.

(b) Mechanism of Corrosion Inhibition in Neutral Solutions

Inhibition in neutral solution is due to compounds which can form or stabilize protective surface films. The inhibitor may form a surface film of an insoluble salt by precipitation reaction. Inhibitor forming films other types include salts of metal such as Zn, Mg, Ni, Soluble calcium salts and

Polyphosphate. Evans(1960). Stated that, the salt films which are often quite thick and may be visible restrict diffusion particularly of dissolved oxygen to the metal surface.

Some inhibitors in near-neutral solutions act by stabilizing oxide films on metals to form thin protective passivating film. Such inhibitors are the anions of weak acids such as chromate, nitrate, benzoate and silicate, phosphate and borate. The passivating oxide film on metal ions and the anode reaction of metal dissolution is inhibited, These inhibitive anions are referred to as Anionic inhibitors.

2.6.3 Efficiency of Inhibitors.

The efficiency of an inhibitor under a given set of conditions according to Loto, (1997), is expressed by the relationship:

$$\% \text{ Inhibition efficiency} = 1 - \frac{\text{Corrosion rate with inhibitors}}{\text{Corrosion rate without inhibitor}} \times 100\% \dots\dots (2.24)$$

In general, the efficiency increases with increase in inhibitor concentration.

2.6.4 Factors Affecting the Efficiency of Inhibitors

Corrosion of iron and steel can be inhibited by the anion of most weak acids under suitable conditions (Brasher, 1969). Other anion particularly those of strong acids tend to prevent the action of inhibitive anion and stimulate breakdown of the protective oxide films. Such aggressive anions are halides of sulphate and nitrate. The inhibitive and aggressive properties of a specific anion depend on the following factors.

(a) Concentration of Anions

Inhibition of iron corrosion in distilled water occurs only when the anion concentration is below the critical value, inhibitive anions may act aggressive and stimulate breakdown of the oxide film.

(b) pH Value of Corrosion Media.

Inhibitive anions are effective in preventing iron corrosion only at pH value more alkaline than a critical pH value.

(c) Temperature of Corroding Media.

The critical concentrations of anions required for the protection of steel increases as the temperature of the corroding media increases. Studies by Omar (1987) showed that effect of temperature on the percentage inhibition efficiency depends largely on the concentration of inhibitors. He concluded that at lower concentration of inhibitor, the efficiency of the inhibitor decreases with temperature whereas at higher concentration the efficiency of inhibition increases with temperature.

2.7 Heat Treatment of Steels.

This is the process by which metals and alloys in the solid state are subjected to one or more temperature cycles, to confer certain desired properties by changing the size and shape of the grains and by altering the micro constituents suitable for a particular application (Kamma, 2001)

There are several heat treatment methods. Such methods include but not limited to annealing, normalizing, hardening and tempering.

2.7.1 Heat Treatment Types

(a) Treatment Producing Equilibrium Condition

- (i) **Stress Relief:** Stress relief or (Stabilizing) treatment is usually applied to stressed and hardened components to relieve them of quenching (internal) stress. This does not seriously affects the hardness if the temperature of treatment is about 150°C . It involves heating to a temperature below that of recrystallization and then cooled freely in air.
- (ii) **Annealing:** is the process of heating to and holding to a suitable temperature, followed by cooling at a suitable rate for the purpose of inducing softness, improving cold-work properties, obtaining a desired structure and removing stress. It is done by heating to or below the recrystallization temperature and held at the high temperature to produce slight grain growth and an austenitic structure and then cool very slowly to produce pearlitic structure.
- (iii) **Normalizing:** It is the process of heating steel and holding at a suitable temperature above the upper critical temperature, followed by cooling freely in air in order to modify the grain size, and mechanical properties. The steel is heated to δ -range, soaked and then cooled freely in air. Free cooling will produce a finer structure than that produced by annealing and a better surface can be produced by machining. Normalizing is done before hardening to produce uniformity.

(b) Treatment Producing Non-Equilibrium Conditions

- (i) **Hardening:-** When steel is heated to a high temperature the α -Fe changes to the δ -Fe arrangement, where all the carbon present in the steel are dispersed throughout the structure, constituting the solid solution (austenite). When steel is cooled, the δ -Fe reverts to the α -Fe which can accommodate only a small amount of the carbon. The precipitation of the excess carbon from the δ requires slow cooling through the transformation range. If the δ -Fe is quenched (cooled very rapidly), the excess carbon will not be precipitated but trapped within the lattice to form a super-saturated solid solution of carbon in α -Fe called Martensite. It is a fine needle-like structure, which due to enormous super-saturation that causes a distortion of the Bcc-lattice. It is very strong and hard but very brittle. It is the process of heating iron to produce δ -Fe and then quenched to produce the martensitic structure.

- (ii) **Tempering:** - It involves re-heating of steel to a sub-critical temperature after hardening, to improve toughness and ductility at the expense of hardness and strength and so make the materials more suitable for service requirements.

Tempering temperature depends on properties required and usually between $180-650^{\circ}\text{C}$. Duration of heating also depends on the material thickness. (Rajan, et al, 1988)



CHAPTER THREE



3.0 EXPERIMENTAL TECHNIQUES

3.1 Materials Preparation

(a) Mild Steel

The mild steel sample used in this study was obtained from the Universal Steel Limited, Ogba-Ikeja Lagos in as-rolled state. The chemical composition of the mild steel sample was determined using spectrometric analyzer. The results obtained are presented in Table 3.1

Table 3.1: Chemical Composition of Mild Steel Sample

Elements	C	Si	S	P	Mn	Ni	Cr	Cu	Sn	Pb	Fe
Composition	0.1581	0.0804	0.0306	0.0044	0.4392	0.0162	0.0122	0.01223	0.00022	0.0014	99.236

The as-received sample was cut and machined into test specimens in readiness for heat treatment and corrosion studies. Typical dimension of test specimen is as shown in Fig.3.1

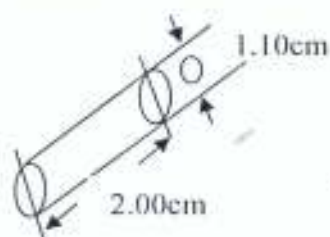


Fig 3.1: Test specimen

(b) Inhibitors and preparation

The inhibitors used in this work are amino acid derivatives such as Alanine ($\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$), Methionine ($\text{CH}_2\text{S}(\text{CH}_2)_2\text{CH}(\text{NH}_2)\text{COOH}$) and Glutamic acid $\text{C}_5\text{H}_9\text{NO}_4$.

They were purchased from local vendor, different concentrations of 0.1M, 0.2M, 0.3M, and for inhibitors were prepared by dissolving appropriate weight of the sample into the measured amount of distilled water.

(c) Preparation of Corroding Medium

The corroding medium used in this work is 3% potassium chloride

The solution of potassium chloride (KCl) was prepared by dissolving 3g of (KCl) in distilled water and making up to 100ml mark

3.1 Heat Treatment Procedure

Prior to corrosion studies, all samples were heat treated and different heat treatment procedures were carried out. These are schematically presented in Figures 3.2-3.5

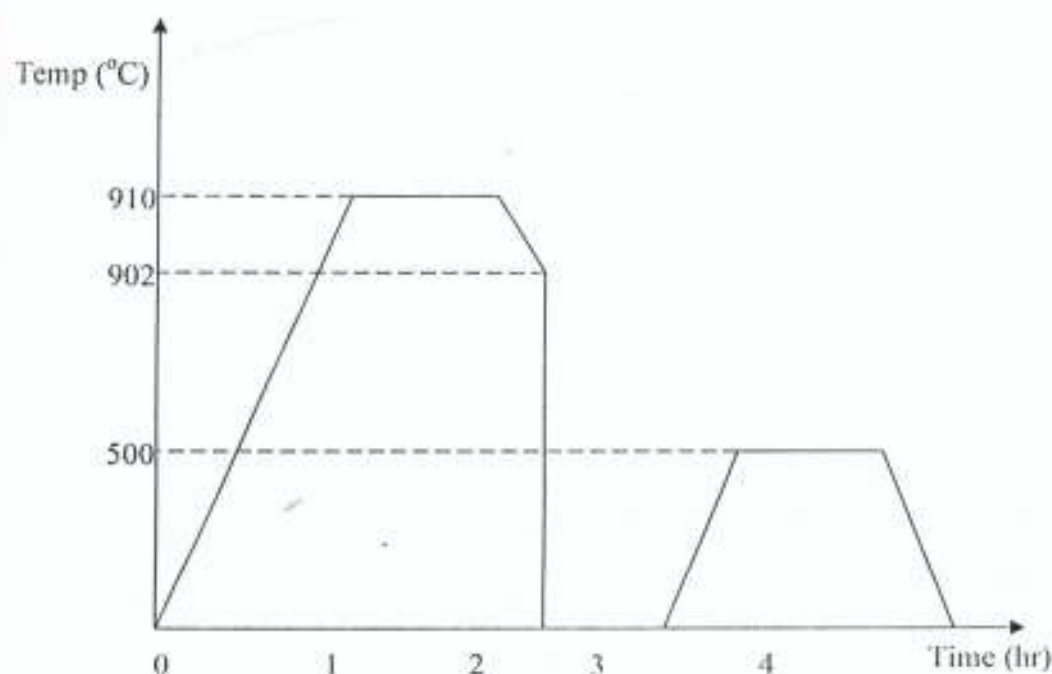


Fig. 3.2 process 1 Heat Treatment Procedure

In Fig. 3.2 samples were first austenised to temperature of 910°C , soaked at this temperature for 30 minutes and allowed to cool in the furnace to 902°C

and then quenched. These quenched samples were thereafter tempered at 500°C

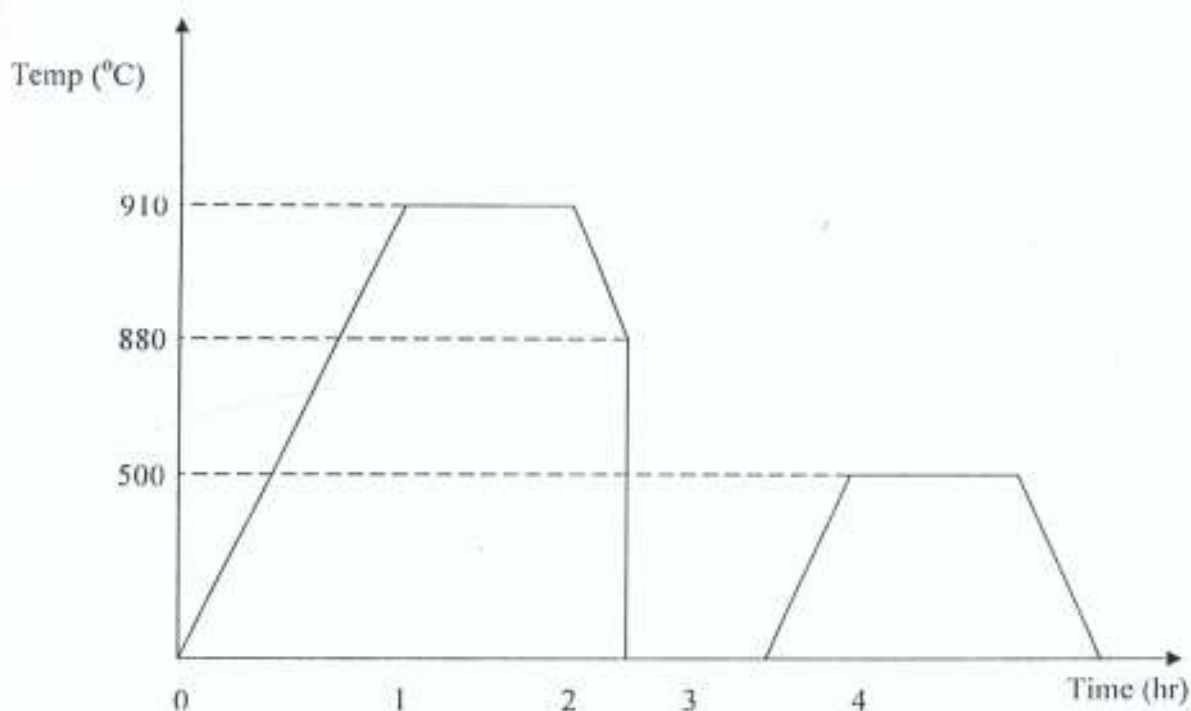


Fig. 3.3 process 2 Heat Treatment Procedure

In figure 3.3, samples were first austenitised to temperature of 910°C soaked at this temperature for 30 minutes, cooled in the furnace to 880°C and then quenched. The quenched samples were thereafter tempered at 500°C .

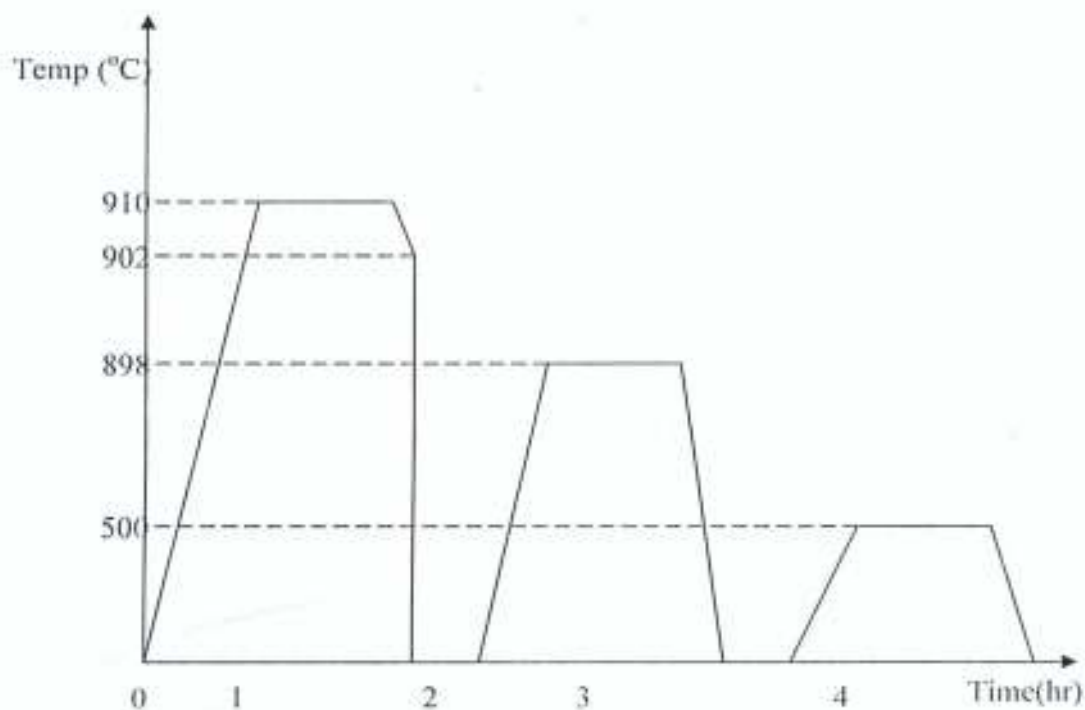


Fig. 3.4 process 3 Heat Treatment Procedure

In Fig. 3.4 the samples were first austenised to temperature of 910°C , soaked at this temperature for 30 minutes, cooled in the furnace to 902°C and then quenched. The quenched samples were reheated to temperature to 898°C , soaked again for 30 minutes and then quenched. The quenched samples were thereafter tempered at 500°C .

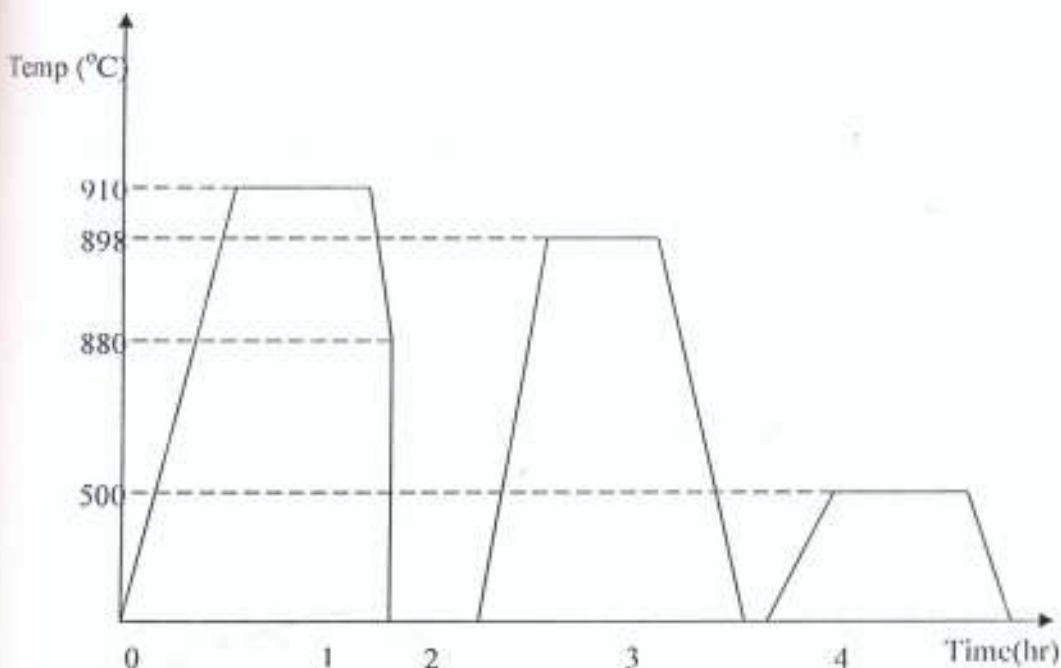


Fig. 3.5 process 4 Heat Treatment procedure

In Fig. 3.5 the samples were first austenitised to temperature of 910°C . Soaked at this temperature for 30 minutes, cooled in the furnace to 880°C and the quenched. The quenched samples were reheated to temperature of 898°C and quenched again. The quenched samples were later tempered at 500°C

3.2 Experimental Procedures

The total immersion test method was adopted in this work. The experimental set up is as shown in Fig 3.6

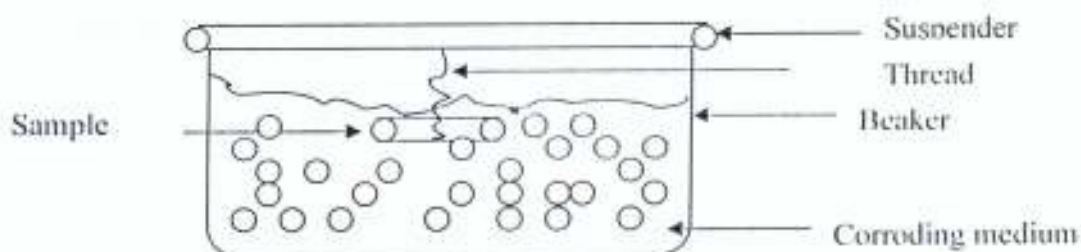


Fig 3.6 Experimental set up

At the onset of the experiment the weight of test specimen was taken and noted using sensitive Electronic weighing balanced. Similarly, the surface area of samples were also determined and recorded. The test specimen was then immersed in 200ml of the corroding medium. The set up was replicated for samples containing different molar concentrations of inhibitors i.e. 0.1M, 0.2M, 0.3M, of alanine, methionine and glutamic acid respectively and independently. A set up of without an inhibitor served as control experiment. Measurement of weight loss was carried out at 15 days interval for 105 days. On removal from the corroding medium the samples was washed in distilled water and then in acetone to aid the drying process and to avoid water deposited film on the samples. The sample was thereafter weighed and its weight recorded. The Electrochemical potential was also measured using ELE digital potentiometer equipped with a reference platinum electrode. The measurement was repeated at every 15 days interval for 105 days.

The above procedure was carried out for all heat treated samples. The results of weight loss measurements were used to determine the corrosion rate using the expression by Fontana (1985), given as

$$\text{Corrosion rate (cm/hr)} = \frac{0.9538W}{T} \dots\dots\dots(3.1)$$

W = weight loss of sample immersed in corrosion medium

T = exposure time (hr)

Similarly the inhibitors efficiency was also determined from the expression suggested by Loto (1997)



$$\% \text{ inhibition efficiency} = 1 - \frac{\text{corrosion rate with inhibitors}}{\text{corrosion rate without inhibitors}} \times 100\% \dots\dots\dots (3.2)$$

The results of corrosion rates and inhibition efficiency are presented in various Figures and discussed in Chapter Four.

3.3 Metallographic Investigations

The test samples were first mounted with bakelite molding compound for easy holding during grinding and polishing operations. Thereafter, the samples were subjected to grinding on silicon carbide abrasive papers of successful finer grades of 60, 120, 320, 400 and 600 grits under running water. The grinding operations involved forward and backward movement of the samples on the emery papers in direction perpendicular to that of preceding grinding paper.

This was followed by polishing on velvet cloth impregnated with 0.3µ choromic oxide emulsion until a mirror like surface was obtained. The samples were washed under running tap water and swabbed with methylated spirit, etched in 2% Nital and observed under optical microscope using Olympus optical microscope with digital camera. The micrographs obtained are also presented in Plates 4.1 to 4.11

CHAPTER FOUR

RESULTS AND DISCUSSION



4.0 Results

Experimental measurements were made to determine the combined effect of heat treatment and inhibitors on the corrosion of mild steel in chloride environment. Four sequences of heat treatment processes were carried out on the mild steel samples prior to corrosion studies. The samples were thereafter immersed in the corroding media with and without inhibitors. The inhibitors concentration varied from 0.1M to 0.3M. Corrosion of mild steel samples in the chloride medium was monitored by taken weight loss at regular intervals over a period of 105days. The result obtained were presented in various plots and discussed. Micrographic examination of samples were also carried out and discussed along with observation on the corrosion studies.

4.1 Discussion

4.1.1 Effect of inhibitors concentration on corrosion of heat treated mild steel.

From the results shown in Figures 4.1 to 4.16 which are representative plots of variation of weight loss ($\text{g}/\text{cm}^2/\text{days}$) with immersion time of samples in inhibitors of different concentrations and without inhibitors. The weight loss of samples in 3%KCl was found to generally increase sharply with immersion time for the few days after which the rate of corrosion (weight loss per unit surface area) starts to decrease, this may be attributed to non-stability of the film formed on the samples while the inhibitors later enhance the formation

and stability of the passivating film and consequently inhibit the anodic reaction i.e. metal dissolution.

The results in Figures 4.1 to 4.16 and 4.41 to 4.40 showed that corrosion rate decreases with the addition of inhibitors. This was due to adsorption of the inhibitors molecules on the metal surface (Rawat and Udayaghanu, 1985). It can be also by mechanism of passivation exhibited by inhibitors. Inhibitors were able to displace the existing adsorbed species on the surface of the metal, after which it forms surface compounds which are immune to the environment and thereby effect the inhibition. Another reason is the ability of cation to form soluble metals complexes, which activate the corrosion process when the adsorption is strong enough to resist the hydrolysis that causes inhibition. It is seen in Figures 4.1 to 4.16 that there is progressive decrease in weight loss as the concentration of inhibitors increases for all the samples. This may be due to greater proportion of surface areas covered by the inhibitors which reduced the corrosion rate (Scully, 1990)

Examination of these curves showed that the inhibitive power of the inhibitors declines from Alanine through Methionine and to Glutamic acid in that order. The reason for this is probably because glutamic acid contains two carboxyl groups and only one amino group, their aqueous solutions are therefore acidic (Data and Ottaway, 1976). This may be ascribed to the dissolution of the film formed on the surface of the metal.

Alanine and Methionine are more inhibitive than glutamic acid and because they also belong to neutral group of the amino acid derivatives which contain one-NH₂ and one -COOH in the molecule, as different from glutamic

acid which belong to acidic group that contains one -NH_2 and two -COOH in the molecule.

Process 1 (Hardening at 910°C , Quench at 902°C and Tempered at 500°C)

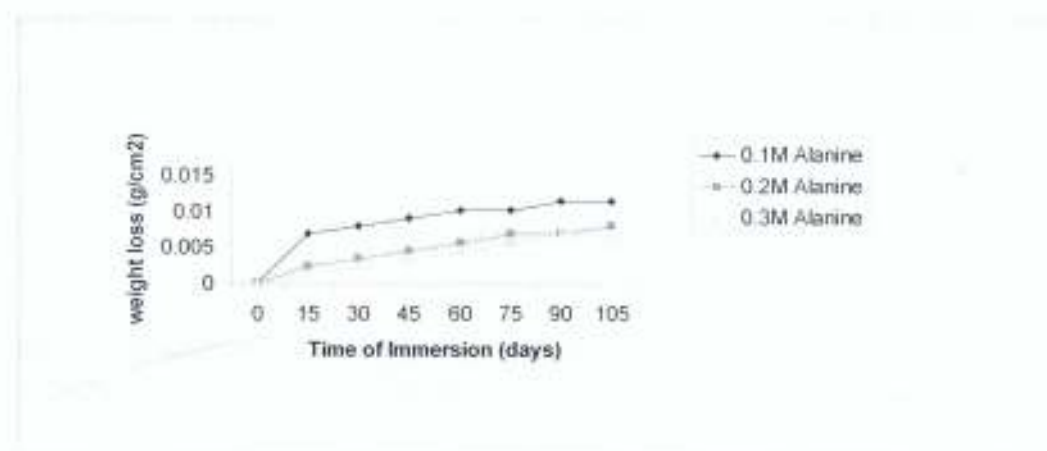


Fig. 4.1 Variation of Weight Loss of Mild Steel with Immersion Time in KCL Solution Containing Different Concentrations of Alanine

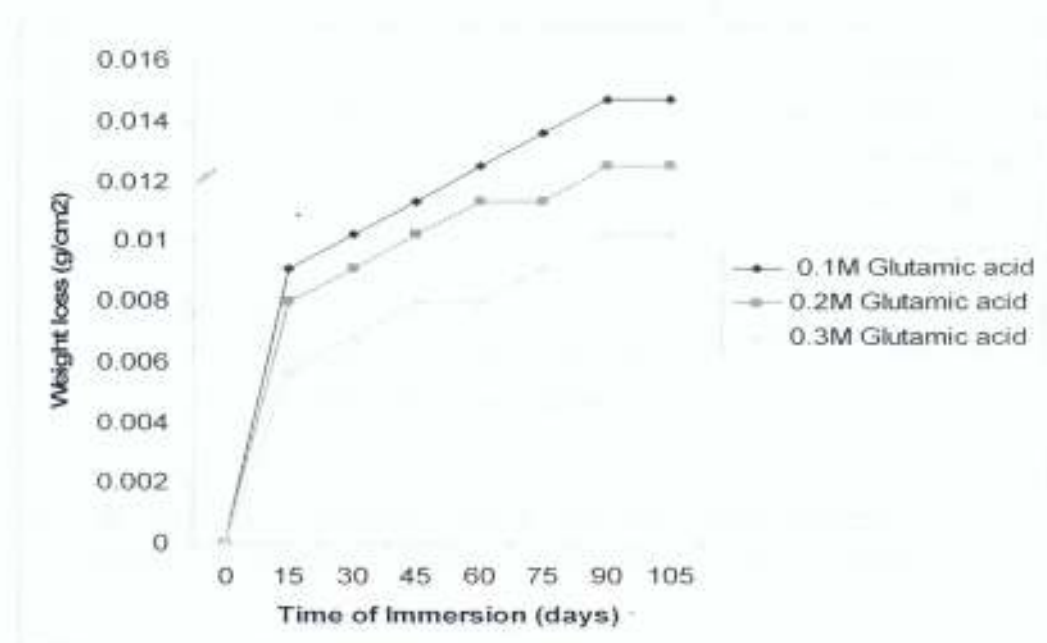


Fig. 4.2 Variation of Weight Loss of Mild Steel with Immersion Time in KCL Solution Containing Different concentrations of Glutamic acid

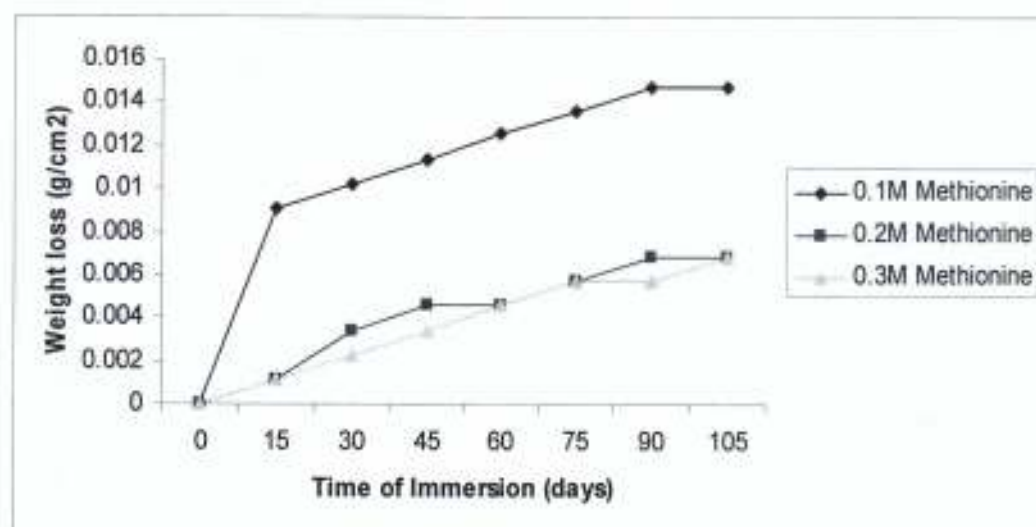


Fig. 4.3 Variation of Weight Loss of Mild Steel with Immersion Time in KCL Solution Containing Different Concentrations of Methionine

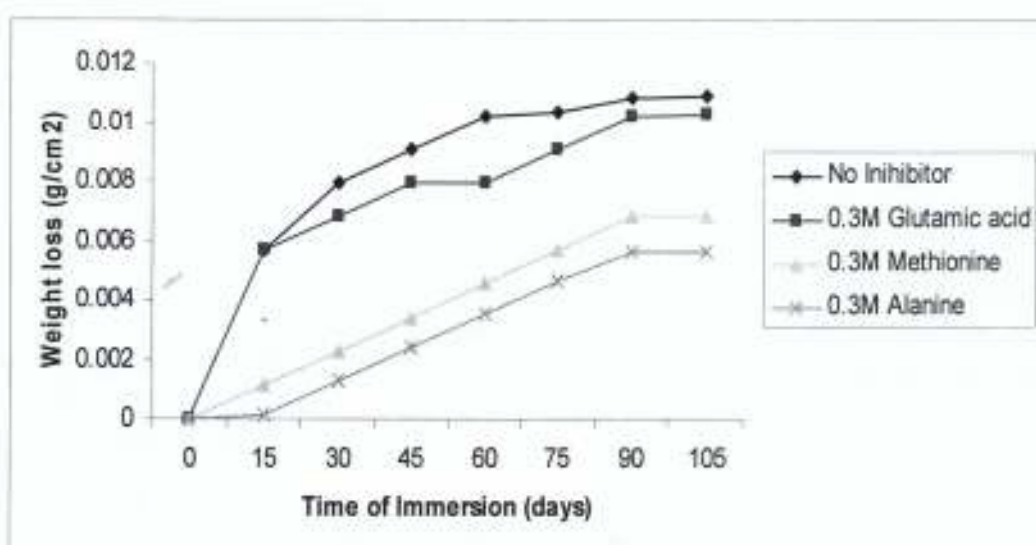


Fig. 4.4 Variation of Weight Loss of Mild Steel with Immersion Time In KCL Solution Containing Different Inhibitors of 0.3m Concentrations

Process 2 (Hardening at 910⁰ C, Quench at 880⁰C and Tempered at 500⁰C)

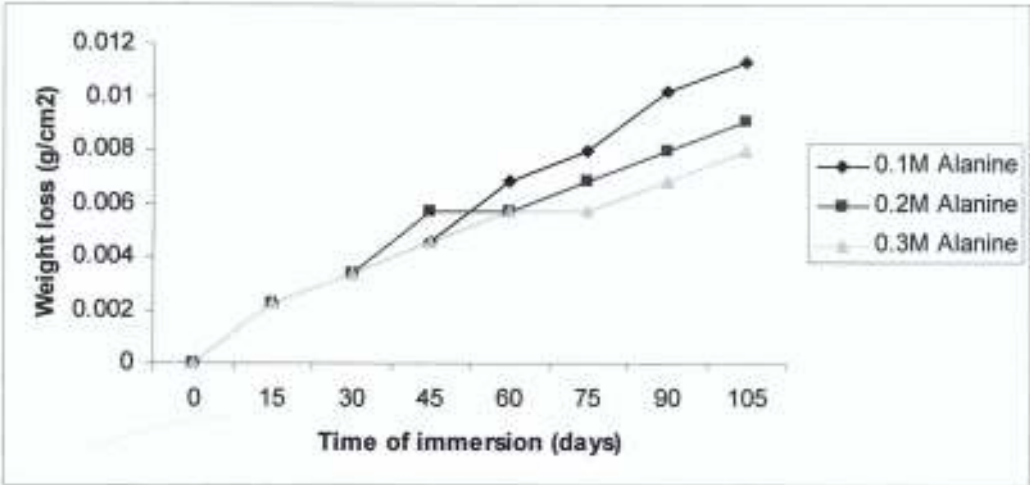


Fig. 4.5 Variation of Weight Loss of Mild Steel with Immersion Time In KCL Solution Containing Different Concentrations of Alanine

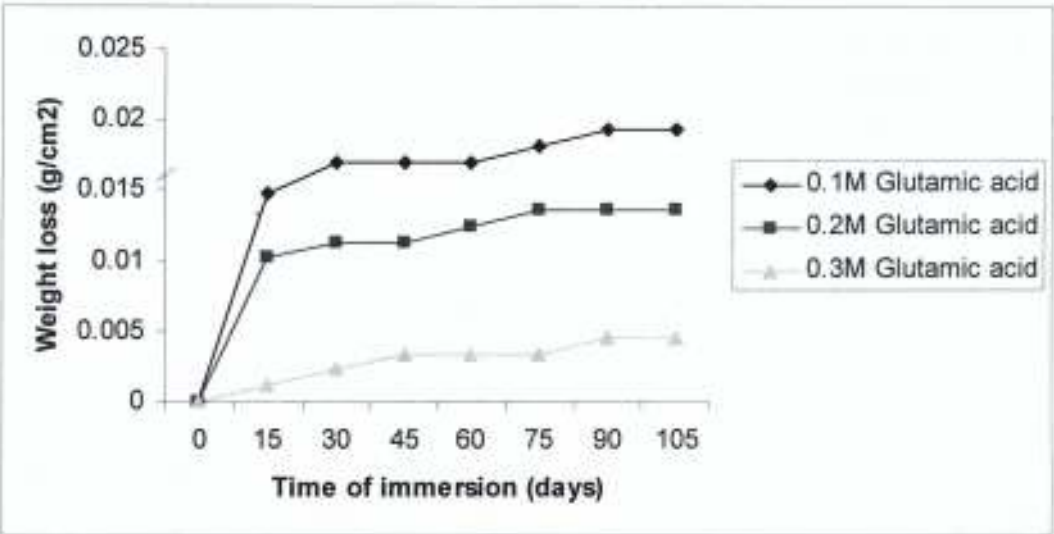


Fig. 4.6 Variation of Weight Loss of Mild Steel With Immersion Time In KCL Solution Containing Different Concentrations of Glutamic Acid

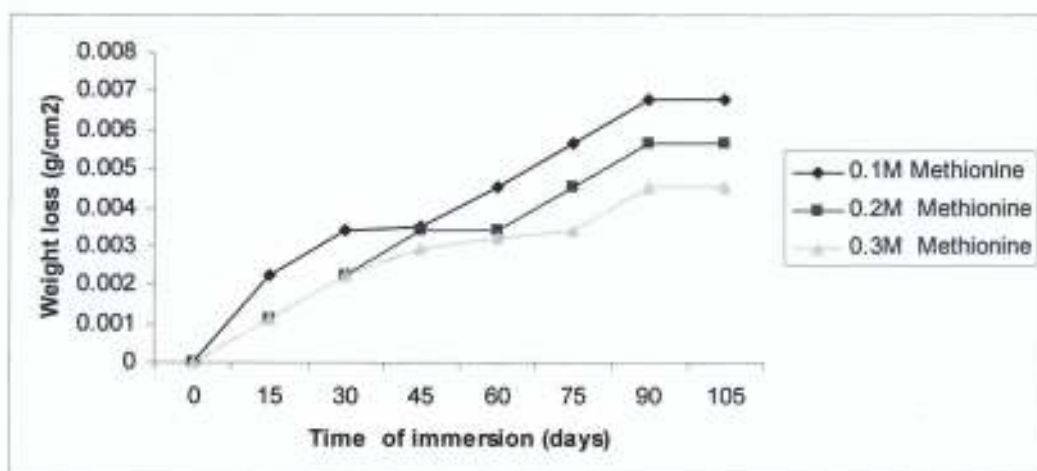


Fig. 4.7 Variation of Weight Loss of Mild Steel with Immersion Time In KCL Solution Containing Different Concentrations of Methionine

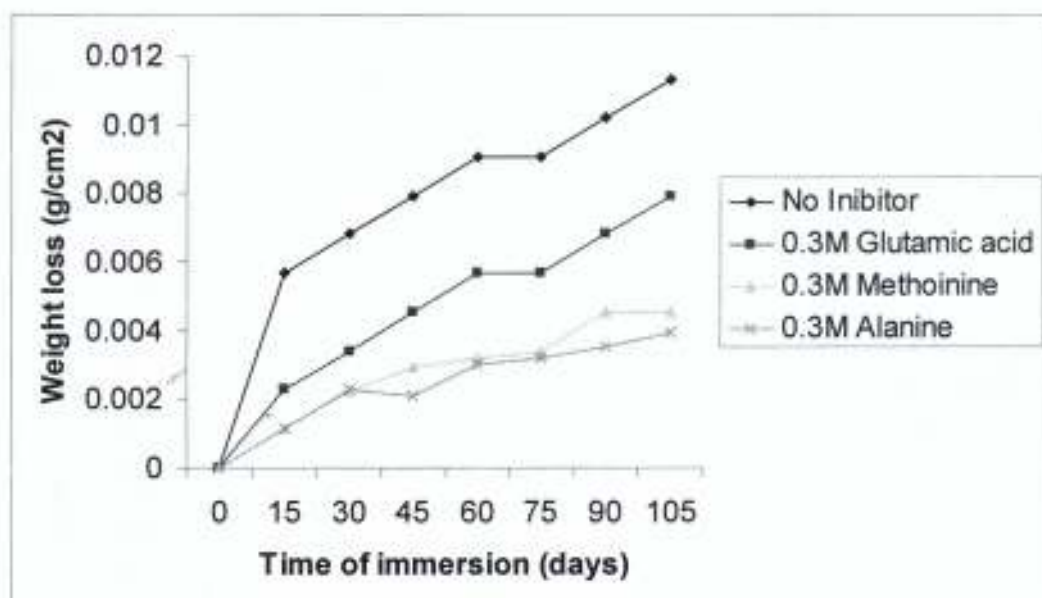


Fig. 4.8 Variation of Weight Loss of Mild Steel with Immersion Time In KCL Solution Containing Different Concentrations of Inhibitors of 0.3M



Process 3 (Hardening at 910°C , Quench at 902°C , Reheated to 898°C and Tempered at 500°C)

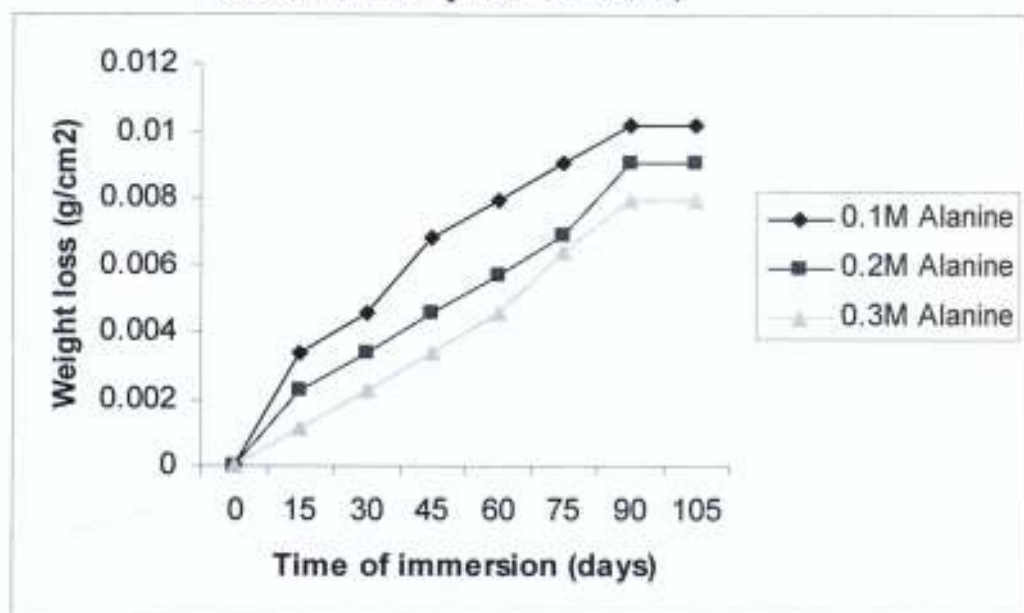


Fig. 4.9 Variation of Weight Loss of Mild Steel with Immersion Time In KCL Solution Containing Different Concentrations of Alanine

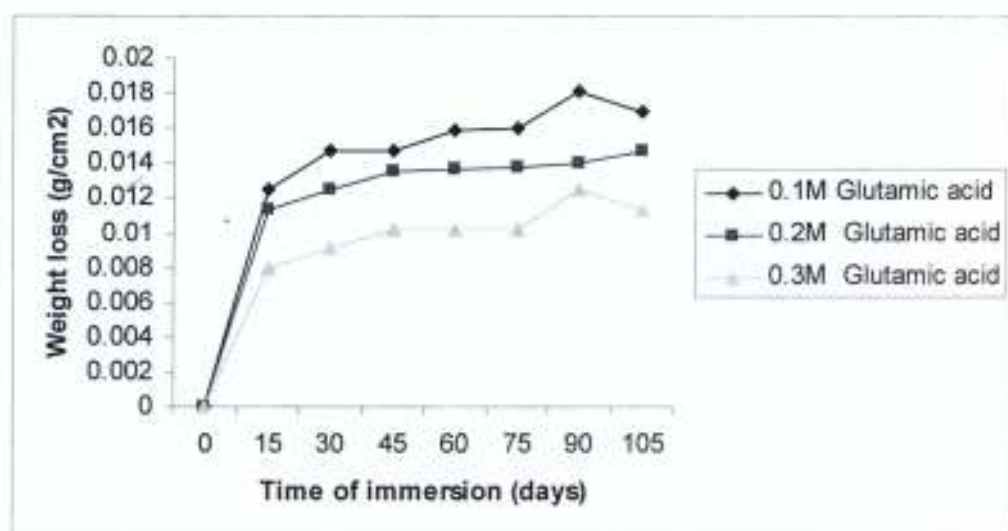


Fig. 4.10 Variation of Weight Loss of Mild Steel with Immersion Time In KCL Solution Containing Different Concentrations of Glutamic Acid

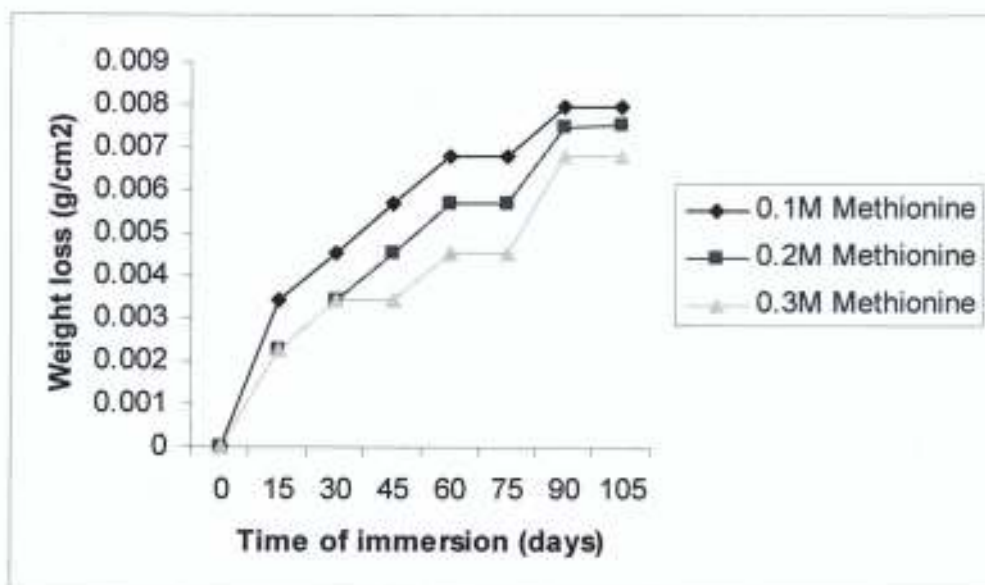


Fig. 4.11 Variation of Weight Loss of Mild Steel with Immersion Time In KCL Solution Containing Different Concentrations of Methionine

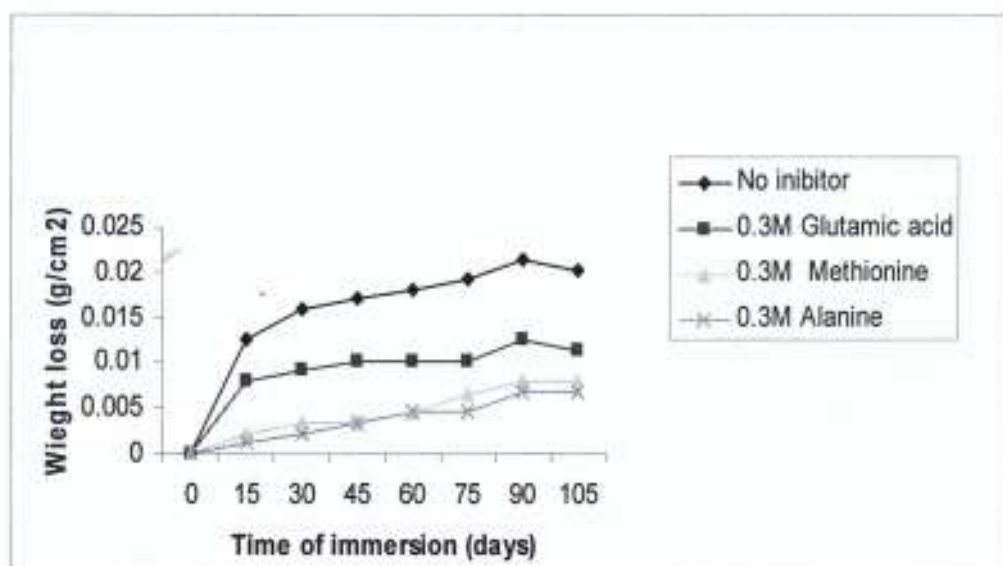


Fig. 4.12 Variation of Weight Loss of Mild Steel with Immersion Time In KCL Solution Containing Different Concentrations of Inhibitors of 0.3M

Process 4 (Hardening at 910°C , Quench at 880°C , Reheated to 898°C and Tempered at 500°C)

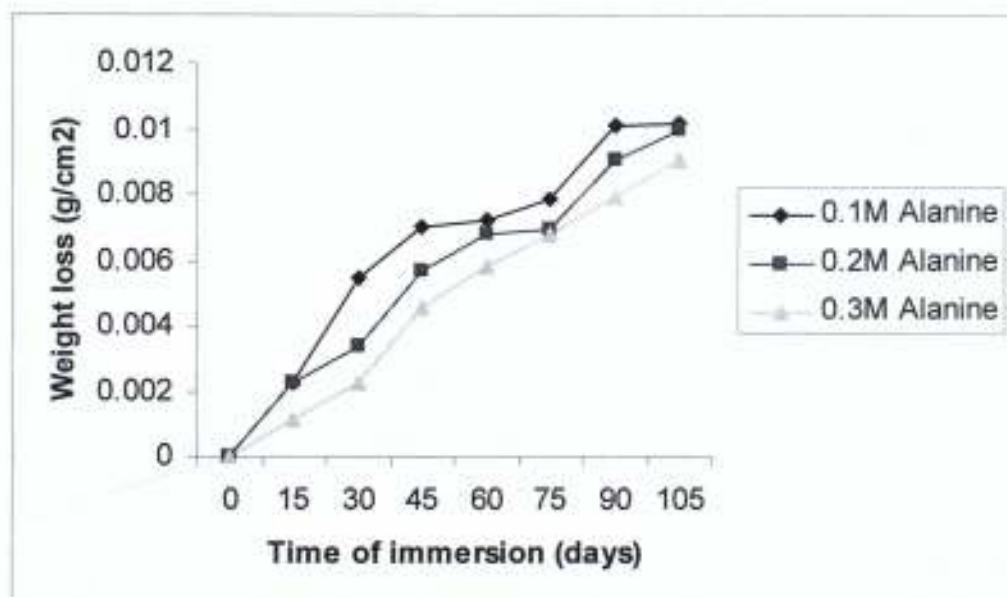


Fig. 4.13 Variation of Weight Loss of Mild Steel with Immersion Time In KCL Solution Containing Different Concentrations of Alanine

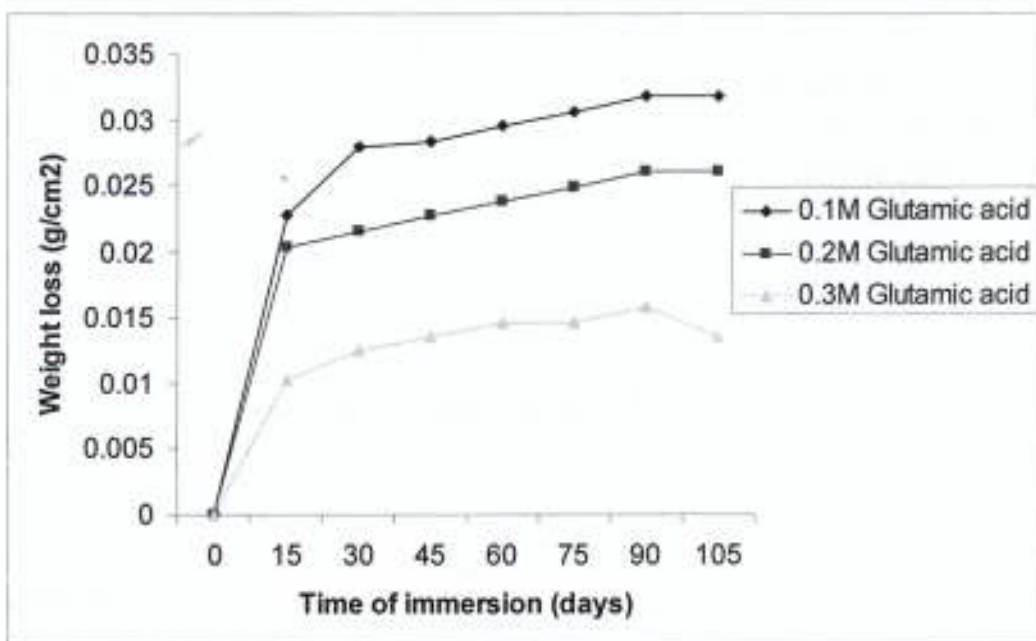


Fig. 4.14 Variation of Weight Loss of Mild Steel with Immersion Time In KCL Solution Containing Different Concentrations of Glutamic Acid

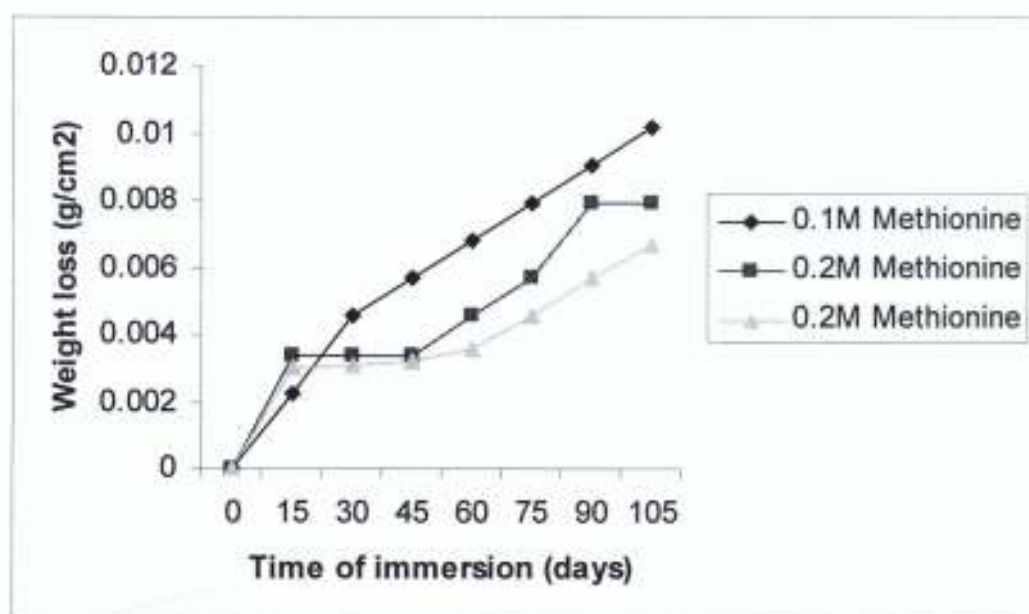


Fig. 4.15. Variation of Weight Loss of Mild Steel with Immersion Time In KCL Solution Containing Different Concentrations of Methionine

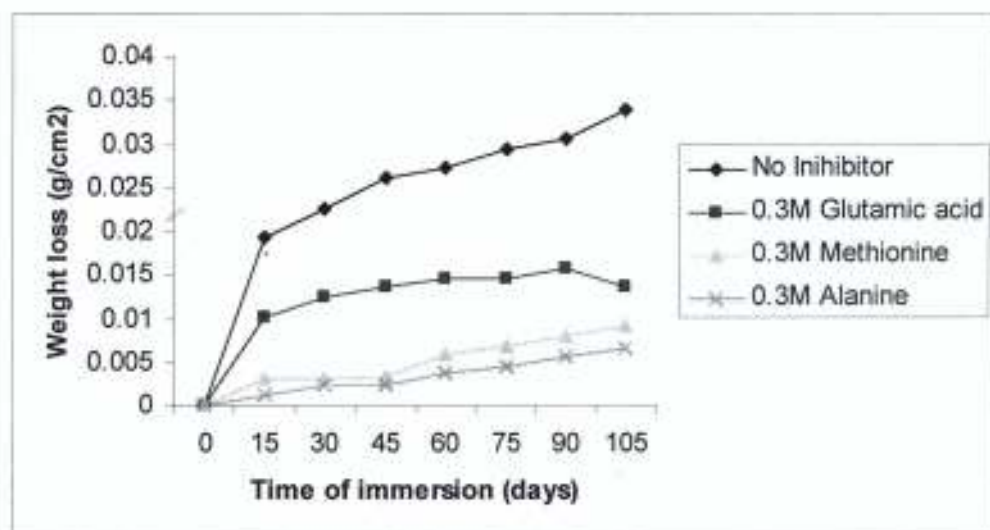


Fig. 4.16 Variation of Weight Loss of Mild Steel with Immersion Time In KCL Solution Containing Different Inhibitors of 0.3M Concentrations

4.1.2 Effects of Potential Variation with Immersion Time

In figures 4.17 to 4.32, it can be seen from the plots that the potential generally increases with time towards noble direction. This behaviour can be attributed to an overall thickening of the passivating oxide film and the fluctuation in the potential is essentially related to the break down of the passivation due to large concentration of chloride ions in the corroding media. The solution having no inhibitors recorded the highest corrosive potential value which confirms that the solution without inhibitors will be more susceptible to corrosion attack.

Process 1 (Hardening at 910⁰ C, Quench at 902⁰C and Tempered at 500⁰C)

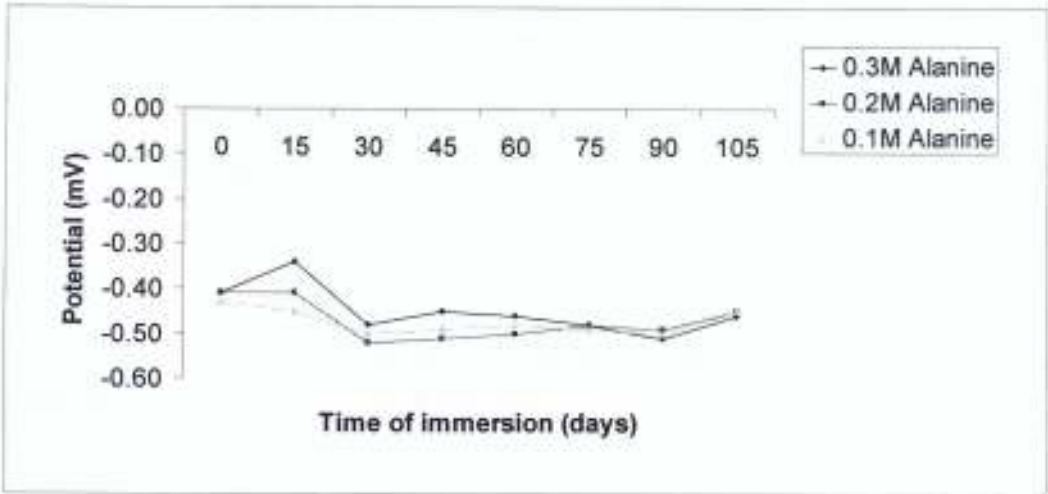


Fig. 4.17 Variation of Potential of Mild Steel with Immersion Time In Different Concentrations of Alaninine

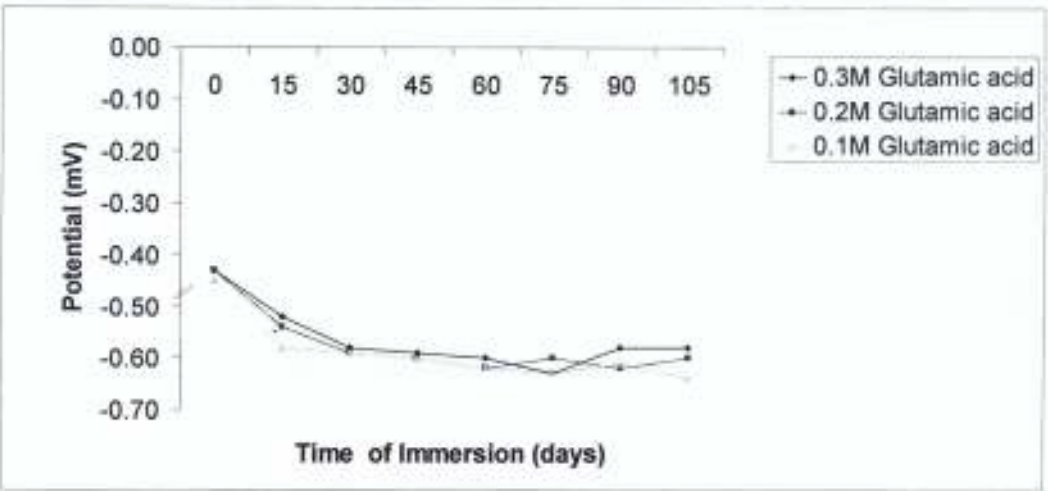


Fig. 4.18 Variation of Potential of Mild Steel with Immersion Time In Different Concentrations of Glutamic Acid

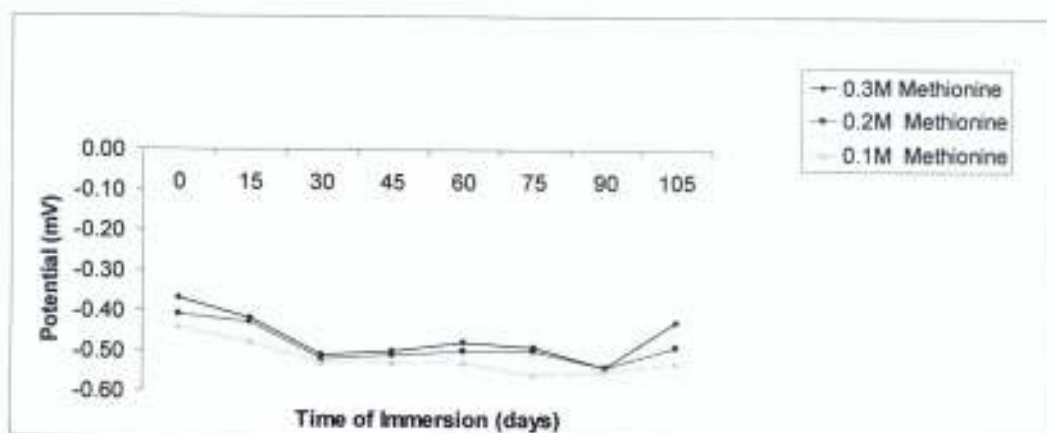


Fig. 4.19 Variation of Potential of Mild Steel with Immersion Time In Different Concentrations of Methionine

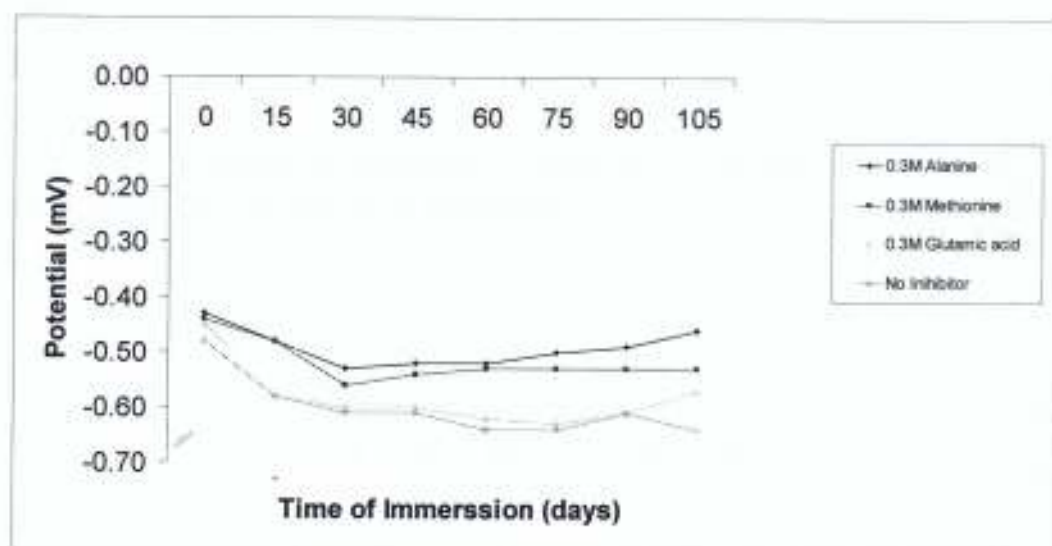


Fig. 4.20 Variation of Potential of Mild Steel with Immersion Time In Different Concentrations of Inhibitors

Process 2 (Hardening at 910°C , Quench at 880°C and Tempered at 500°C)

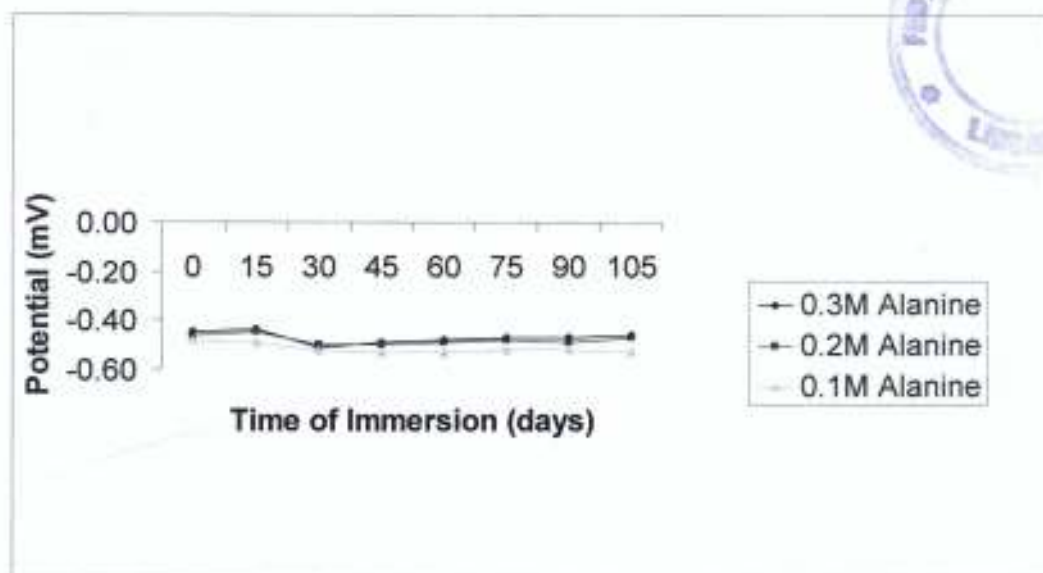


Fig. 4.21 Variation of Potential of Mild Steel with Immersion Time In Different Concentrations of Alanine

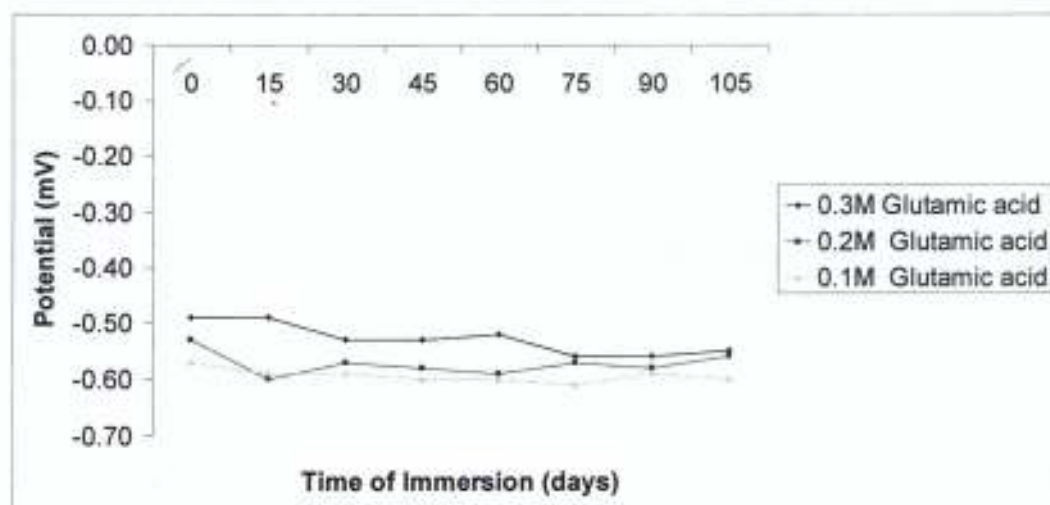


Fig. 4.22 Variation of Potential of Mild Steel with Immersion Time In Different Concentrations of Glutamic Acid

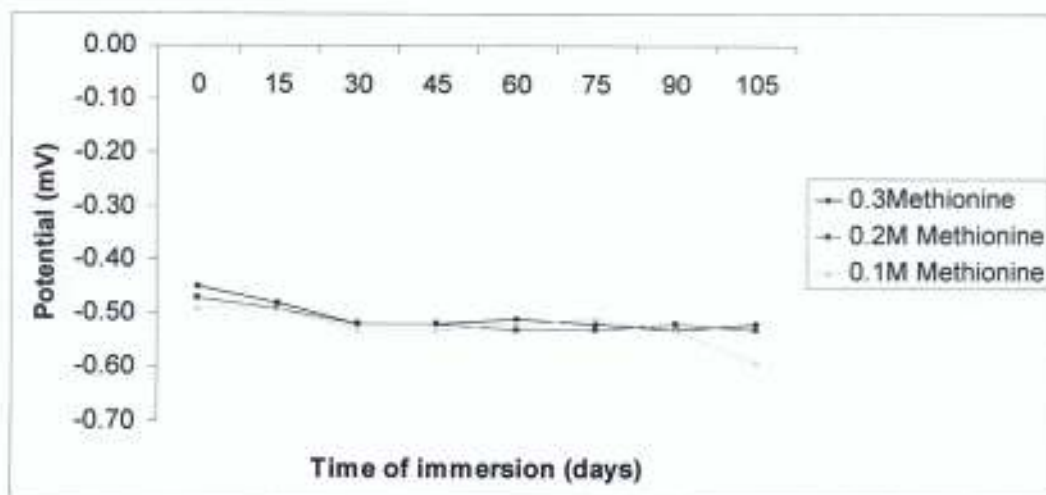


Fig. 4.23 Variation of Potential of Mild Steel with Immersion Time In Different Concentrations of Methionine

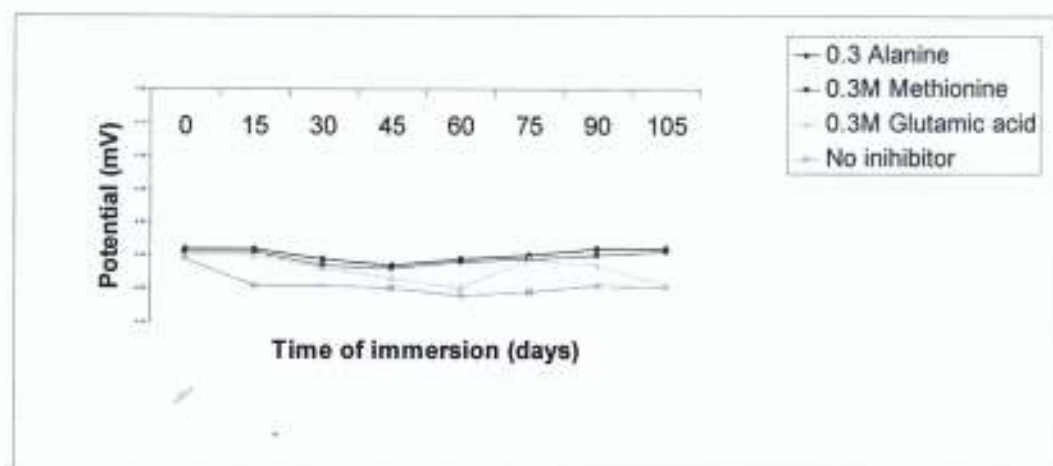


Fig. 4.24 Variation of Potential of Mild Steel with Immersion Time In Different Concentrations of Inhibitors

Process 3 (Hardening at 910°C , Quench at 902°C , Reheated to 898°C and Tempered at 500°C)

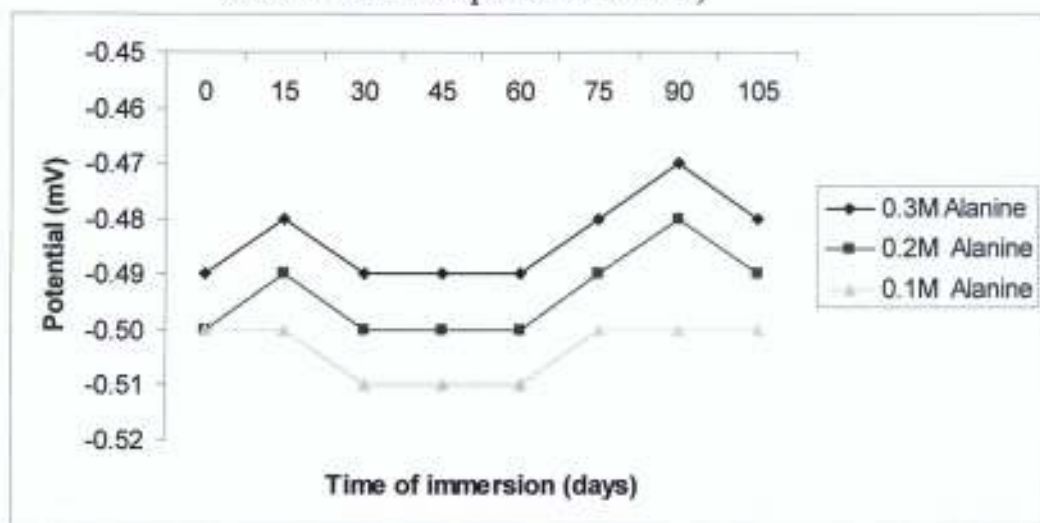


Fig. 4.25. Variation of Potential of Mild Steel with Immersion Time In Different Concentrations of Alanine

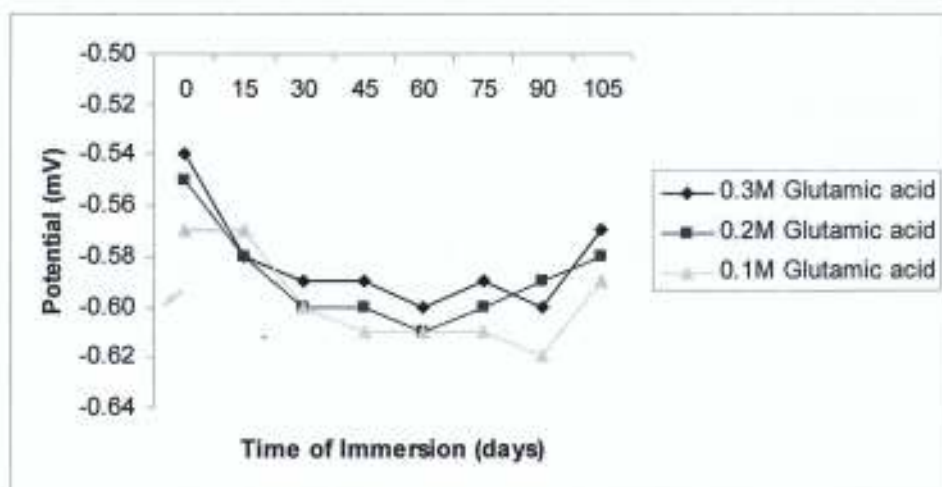


Fig. 4.26 Variation of Potential of Mild Steel with Immersion Time In Different Concentrations of Glutamic Acid

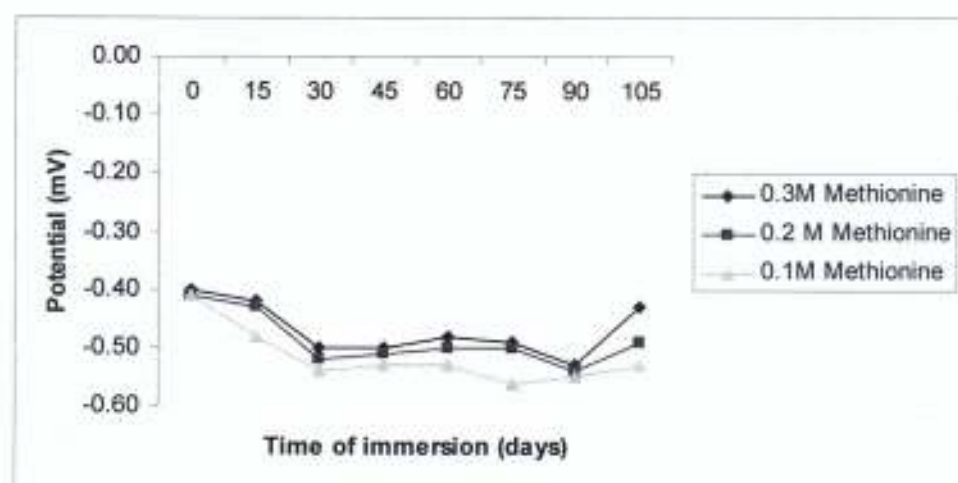


Fig. 4.27. Variation of Potential of Mild Steel with Immersion Time In Different Concentrations of Methionine

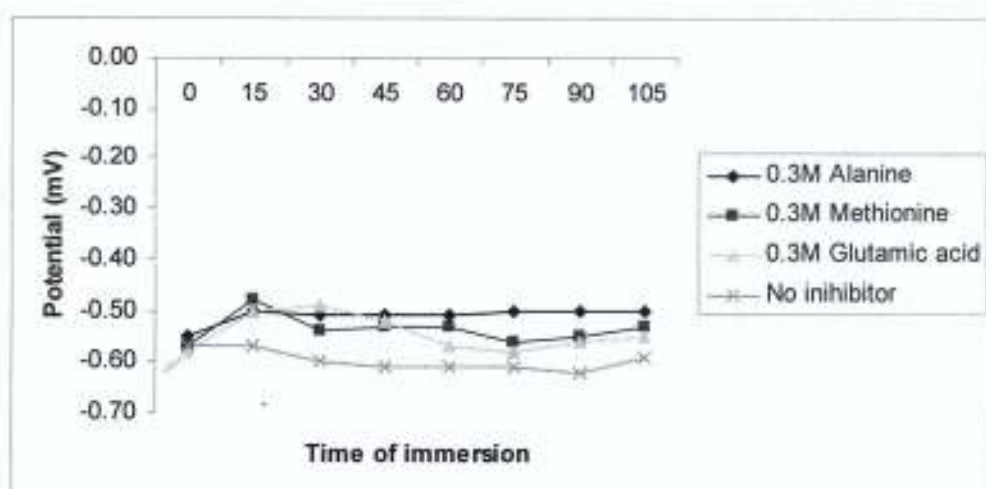


Fig. 4.28 Variation of Potential of Mild Steel with Immersion Time In Different Concentrations of Inhibitors

Process 4 (Hardening at 910°C, Quench at 880°C, Reheated to 898°C and Tempered at 500°C)

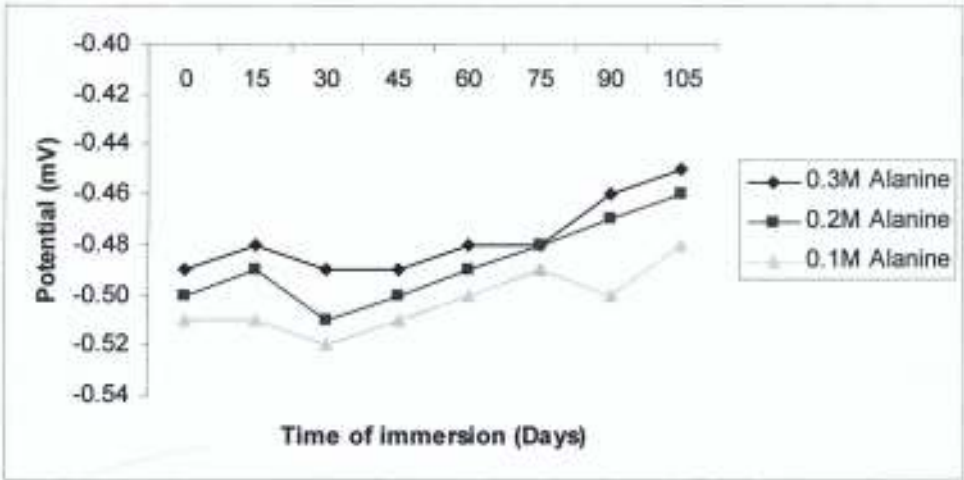


Fig. 4.29 Variation of Potential of Mild Steel with Immersion Time In Different Concentrations of Alanine

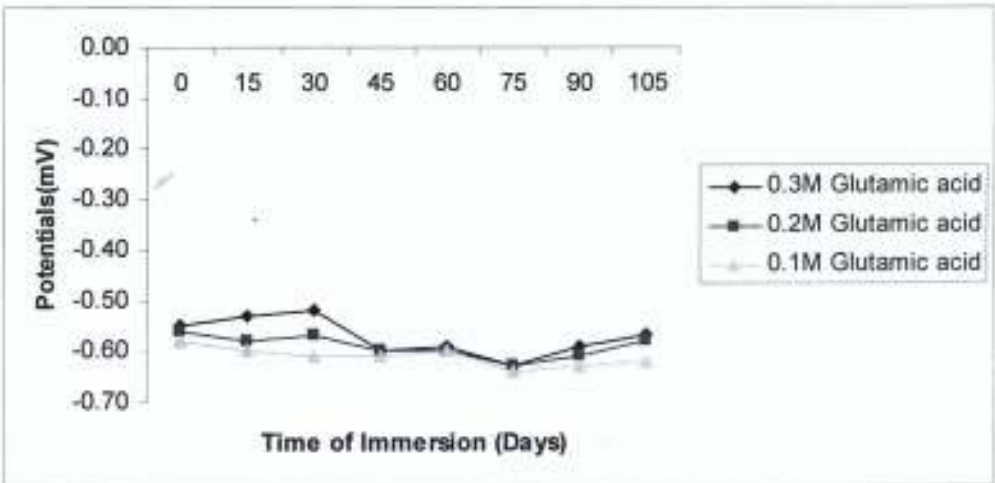


Fig. 4.30 Variation of Potential of Mild Steel with Immersion Time In Different Concentrations of Glutamic Acid

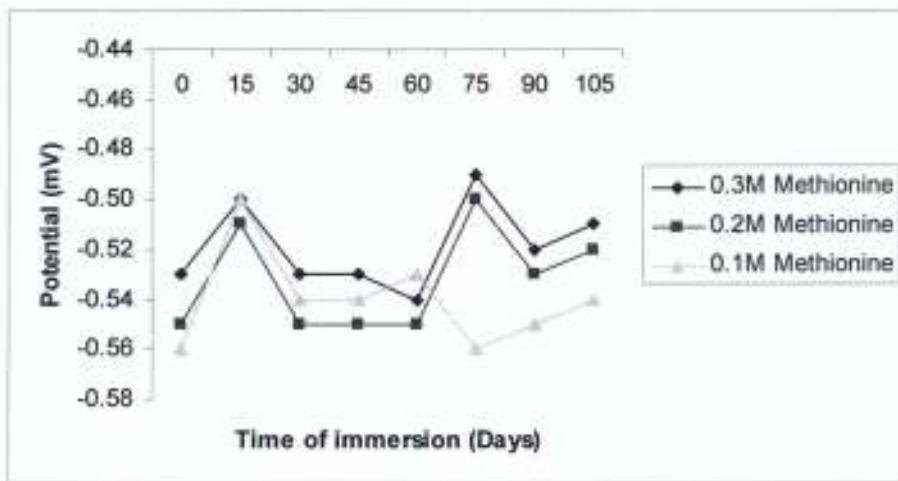


Fig. 4.31 Variation of Potential of Mild Steel with Immersion Time In Different Concentrations of Methionine

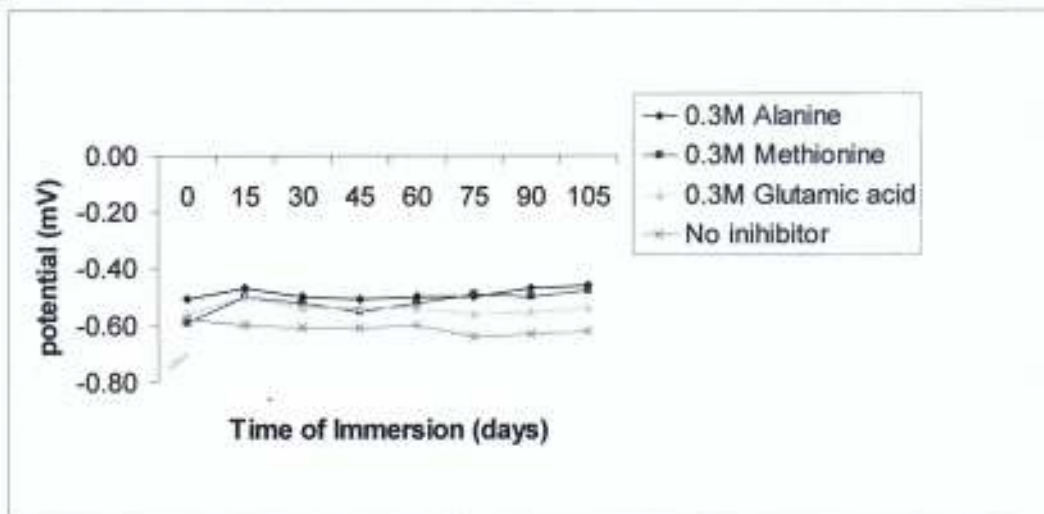


Fig. 4.32 Variation of Potential of Mild Steel with Immersion Time In Different Concentrations of Inhibitors

4.1.3 Effect of Inhibitors Concentration on Inhibition Efficiency

Figures 4.33 to 4.40 revealed that there is progressive increase in inhibition efficiency for the entire sample for some days and later showed slight decrease in inhibition efficiency for the rest of immersion period with a remarkable reduction in corrosion rate. The inhibition efficiency also increases with increase in inhibitor concentration. From the figures, the most effective inhibitor is alanine and the order of effectiveness of inhibitors are, alanine > methione > glutamic acid.

Process 1 (Hardening at 910°C , Quench at 902°C , and Tempered at 500°C)

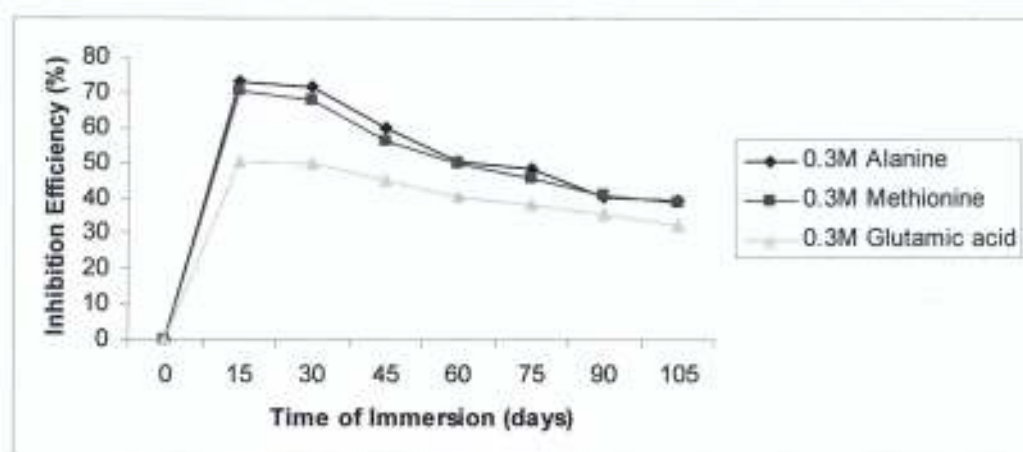


Fig. 4.33 Effect of Inhibitors Concentration on Inhibition Efficiency

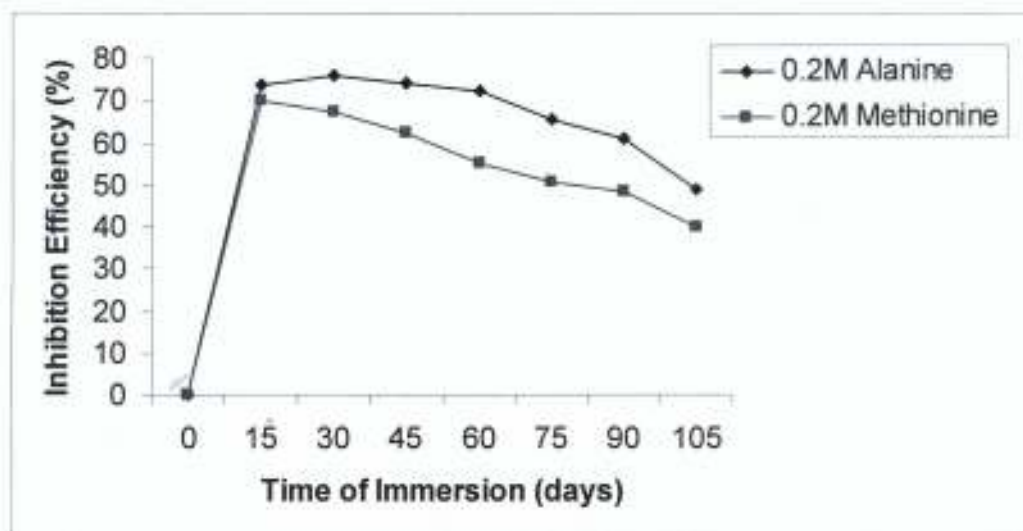


Fig. 4.34 Effect of Inhibitors Concentration on Inhibition Efficiency



Process 2 (Hardening at 910°C , Quench at 880°C , and Tempered at 500°C)

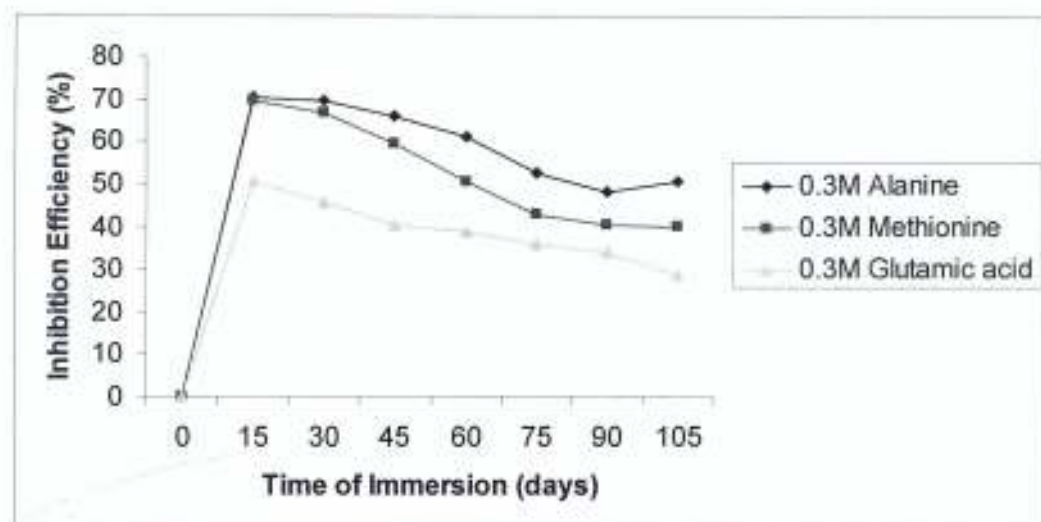


Fig. 4.35 Effect of Inhibitors Concentration On Inhibition Efficiency

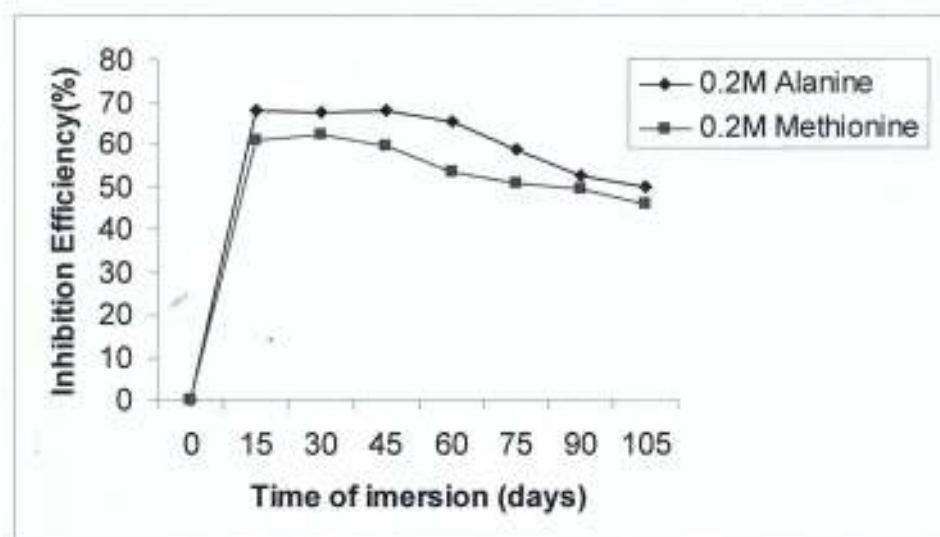


Fig. 4.36 Effect of Inhibitors Concentration on Inhibition Efficiency

Process 3 (Hardening at 910⁰ C, Quench at 902⁰ C, Reheated to 898⁰ C and Tempered at 500⁰ C)

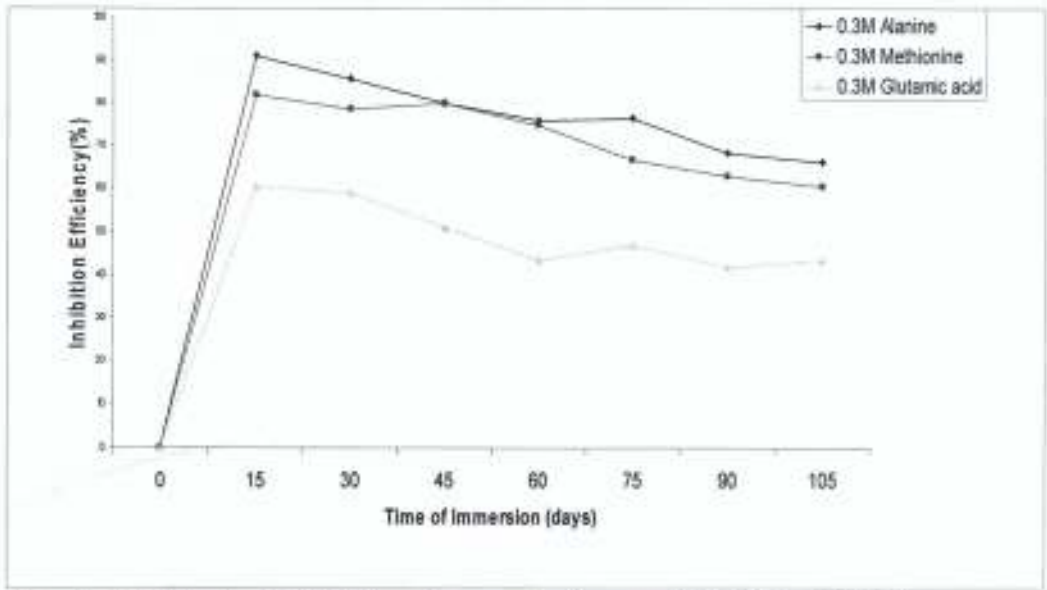


Fig. 4.37 Effect of Inhibitors Concentration on Inhibition Efficiency

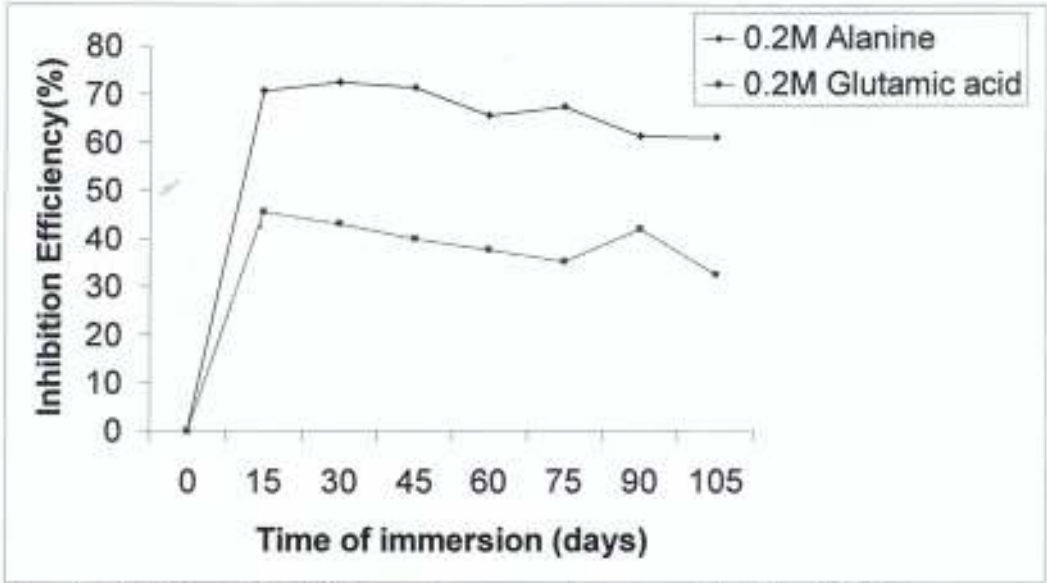


Fig. 4.38 Effect of Inhibitors Concentration on Inhibition Efficiency

Process 4 (Hardening at 910°C , Quench at 880°C , Reheated to 898°C and Tempered at 500°C)

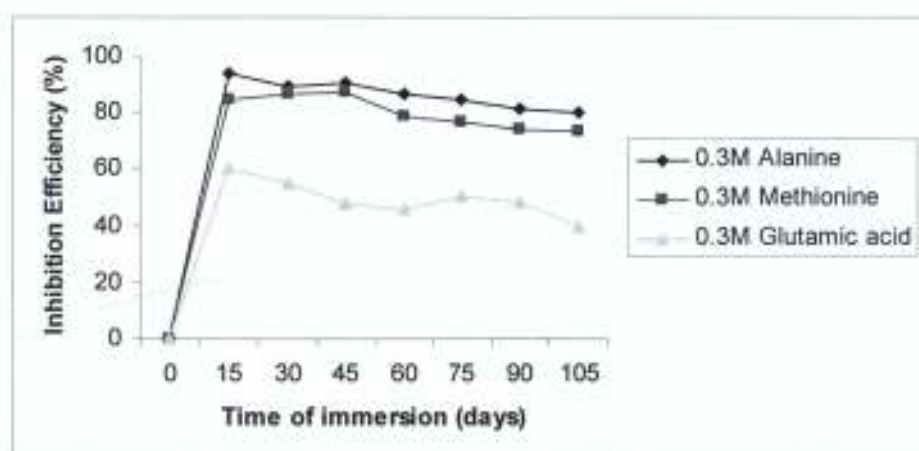


Fig. 4.39 Effect of Inhibitors Concentration on Inhibition Efficiency

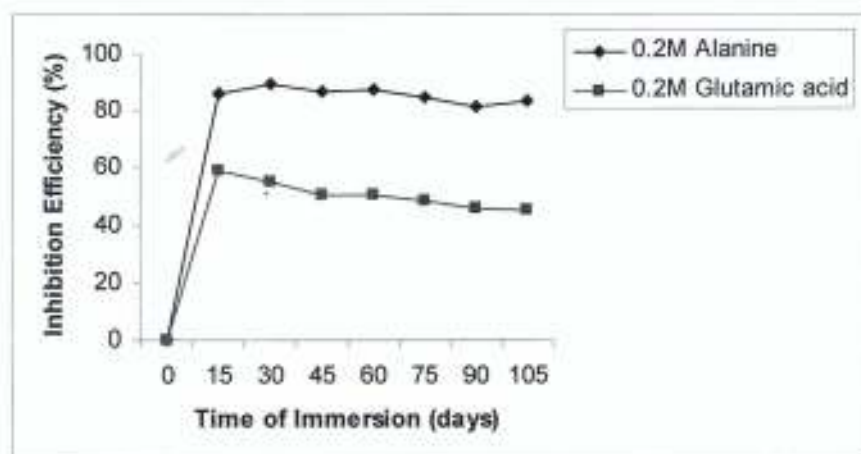


Fig. 4.40 Effect of Inhibitors Concentration on Inhibition Efficiency

4.1.4 Effects of Corrosion Rate on Inhibitors and Heat Treated Mild Steel

From figure 4.41 to 4.48, it was observed that there was a rapid increase in rate of corrosion on the first few days followed by a continuous decrease in the corrosion rate, this result was due to the adsorption of the inhibitor molecules on the metal surface and passivation exhibited by the organic inhibitors, closer observation of the graphs show that alanine has the highest inhibitive power follow by methionine and glutamic acid in that order.

Process 1 (Hardening at 910°C , Quench at 902°C and Tempered at 500°C)

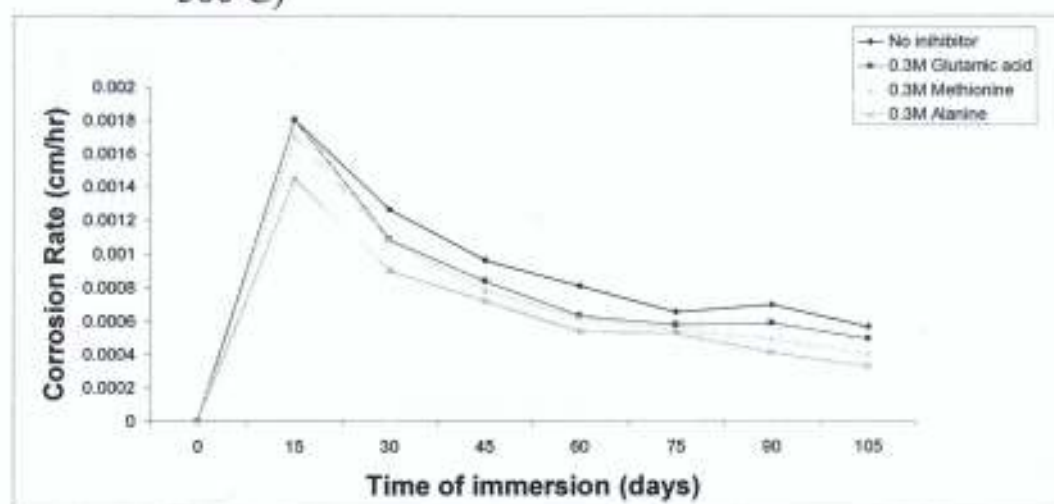


Fig. 4.41 Variation Of Corrosion Rate With Immersion Time Of Mild Steel Without/With 0.3M Inhibitors Concentration

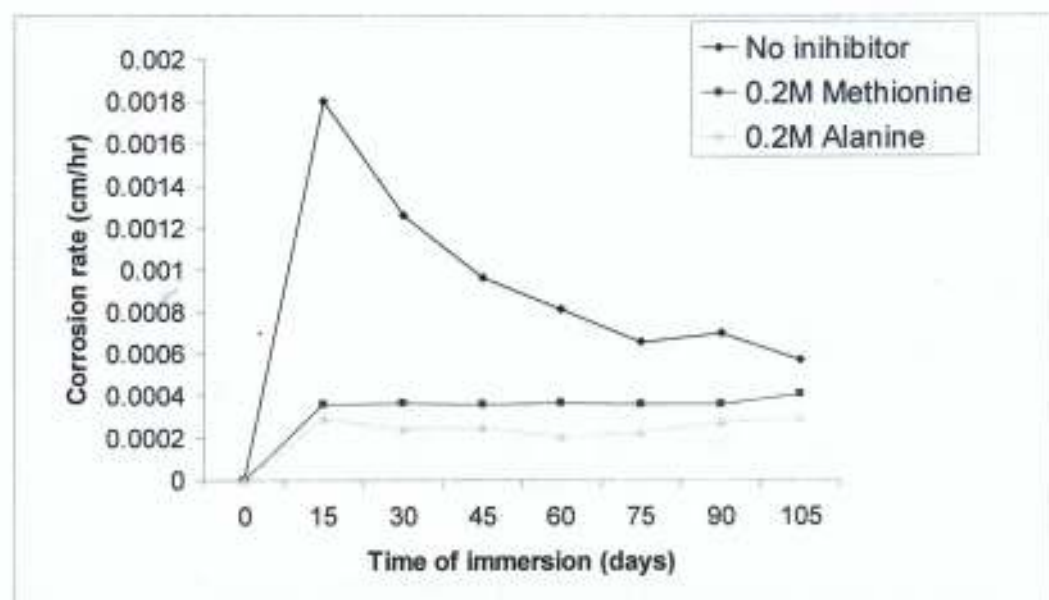


Fig. 4.42 Variation of Corrosion Rate with Immersion Time of Mild Steel In Different Concentration of Inhibitors



Process 2 (Hardening at 910°C , Quench at 880°C and Tempered at 500°C)

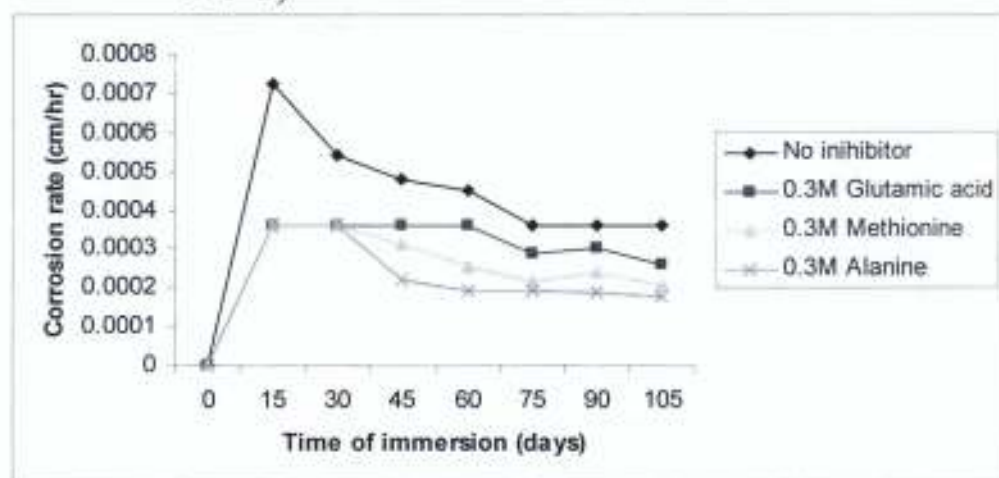


Fig. 4.43 Variation of Corrosion Rate with Immersion Time of Mild Steel Without /With 0.3M Inhibitors Concentration

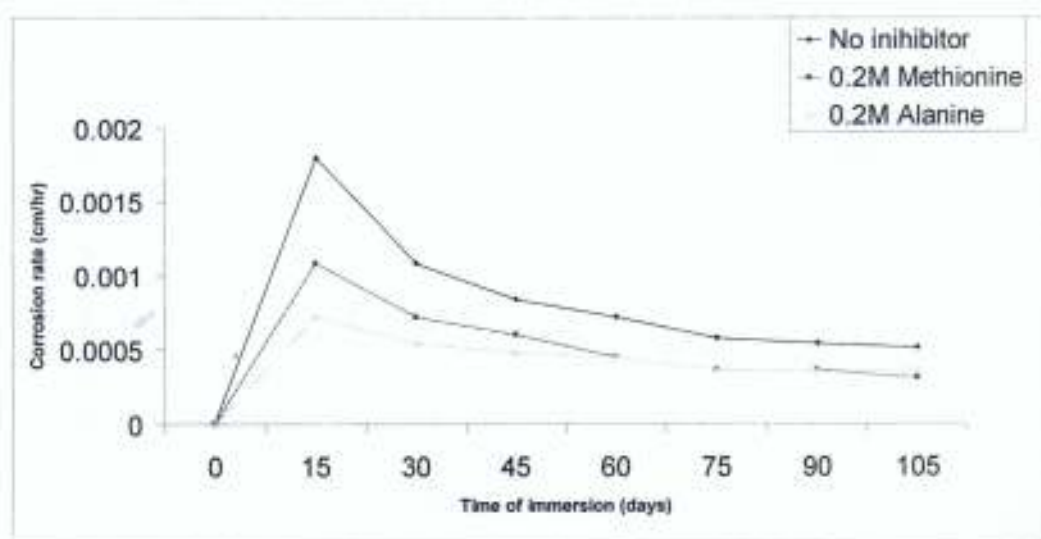


Fig. 4.44 Variation of Corrosion Rate with Immersion Time of Mild Steel In Different Concentrations of Inhibitors

Process 3 (Hardening at 910°C , Quench at 902°C , Reheated to 898°C and Tempered at 500°C)

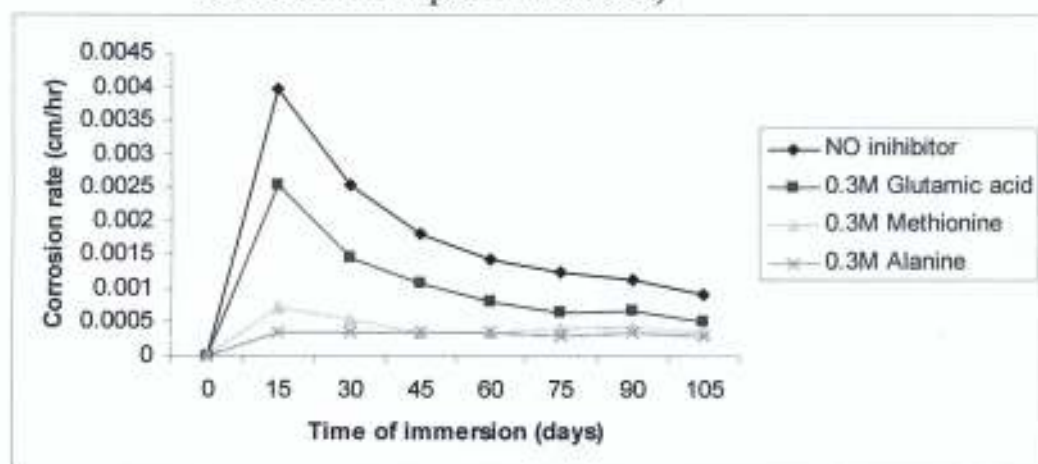


Fig. 4.45 Variation of Corrosion Rate with Immersion Time of Mild Steel Without/ With 0.3M Inhibitors Concentration

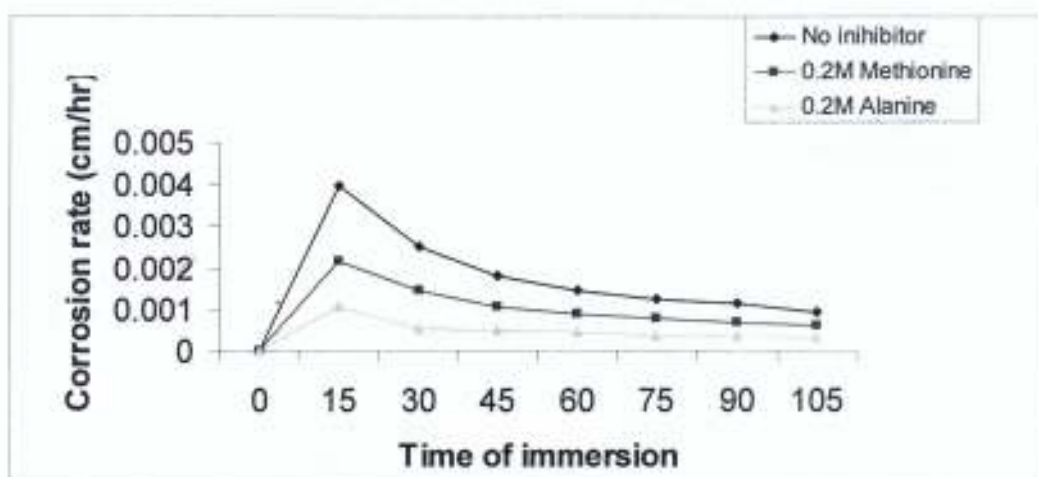


Fig. 4.46 Variation of Corrosion Rate with Immersion Time of Mild Steel In Different Concentrations of inhibitors

Process 4 (Hardening at 910°C , Quench at 880°C , Reheated to 898°C and Tempered at 500°C)

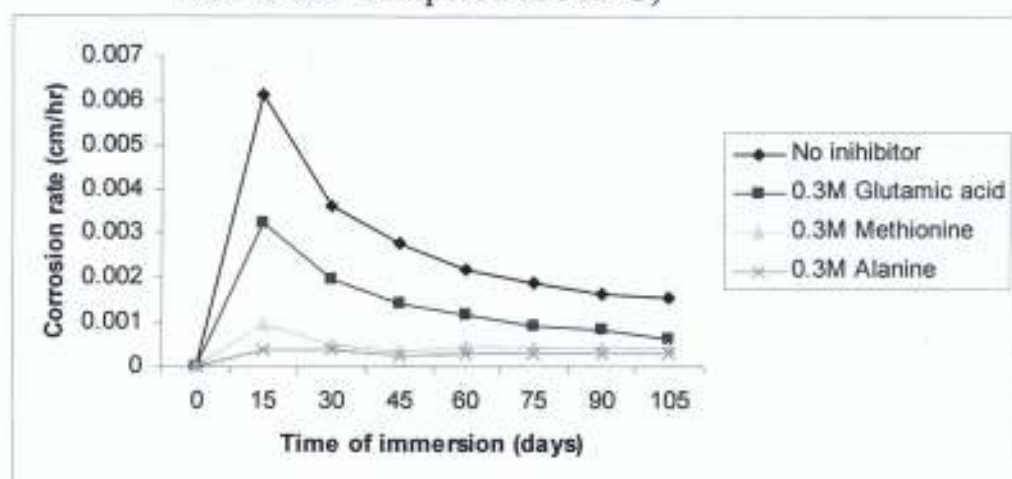


Fig. 4.47 Variation of Corrosion Rate with Immersion Time of Mild Steel Without/With 0.3M Inhibitors Concentration

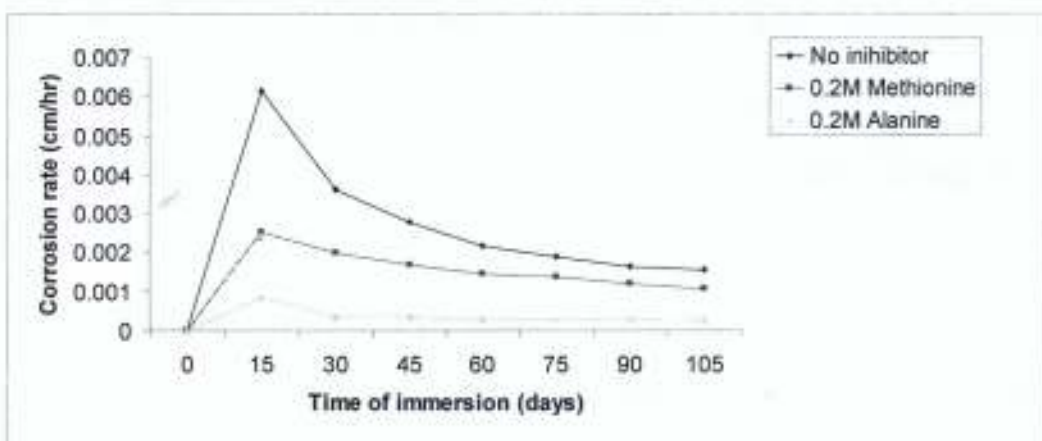


Fig. 4.48 Variation of Corrosion Rate with Immersion Time of Mild Steel In Different Concentrations of Inhibitors

4.1.5 Microstructural Investigation

(a) Effect of Heat Treatment

This is the process of metal conditioning to provide the required material properties such as mechanical strength to withstand the electrochemical wearing away of materials due to chemical or physical process. In this research work heat treatment was conducted to aid preferential precipitation of ferrite phase i.e. effects of process conditions on mechanical properties.

(b) Effect of Microstructure on Corrosion Resistance

The results are shown of Plate 4.1 to 4.11. The microstructures revealed the mixture of ferritic and pearlitic phases. At low concentration of inhibitors i.e 0.1M, the pitting attack showed a little reduction which was caused by the inability of the inhibitors to effectively plug all corrosion sites. At high concentration of inhibitors i.e 0.3M the rate of corrosion was low, the cavities created are much reduced as a result of effective coverage of inhibitors on the surface of the samples.

Plate 4.1 represents the microstructure of the as received samples. In process 1, plates 4.2 to 4.4 represent the microstructure of heat treated samples, plate 4.2 revealed that ferritic phase has completely oxidized to iron-oxide, while plate 4.3 and 4.4 revealed that ferrite surface (light areas) and pearlite surface (dark areas) were well pronounced which indicate that the inhibitors used are very effective, but work best on plate 4.4.

In process 2, Plates 4.5 to 4.7 also revealed ferritic and pearlitic phases while Plate 4.7 showed that ferritic phase is more pronounced when compared to plates 4.5 and 4.6.

In process 3, Plate 4.8 to 4.10 represents the microstructure of sample in glutamic acid. The synergistic effect is well pronounced on plate 4.10 when compared to plates 4.8 and 4.9.

In process 4, Plate 4.11 represents the microstructure of 0.3M in glutamic acid.



Plate 4.1: As received sample



Plate4, 2: Process 1 micrograph of mild steel immersed in 3% KCl solution without inhibitors for 105 days, etched in 2% Nital, showing the effect of corrosion in the microstructure (X160)



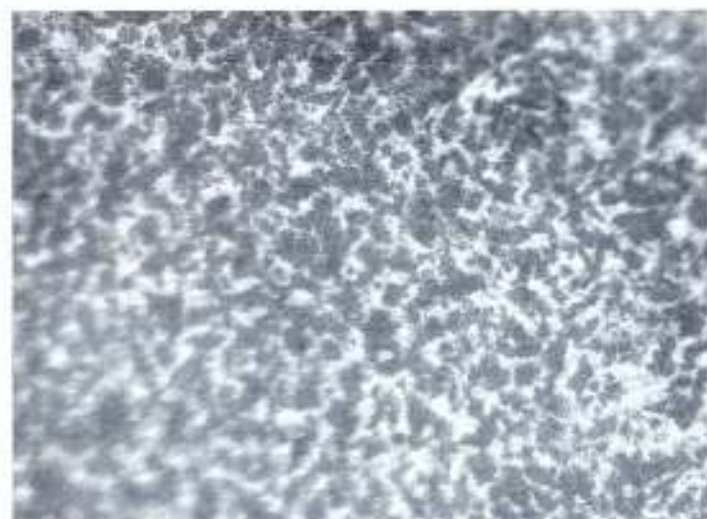


Plate 4. 3: Process 1 micrograph of mild steel immersed in 3% KCl solution with 0.2M of alanine concentration for 105 days, etched in 2% Nital, showing the effect of corrosion in the microstructure (X160)

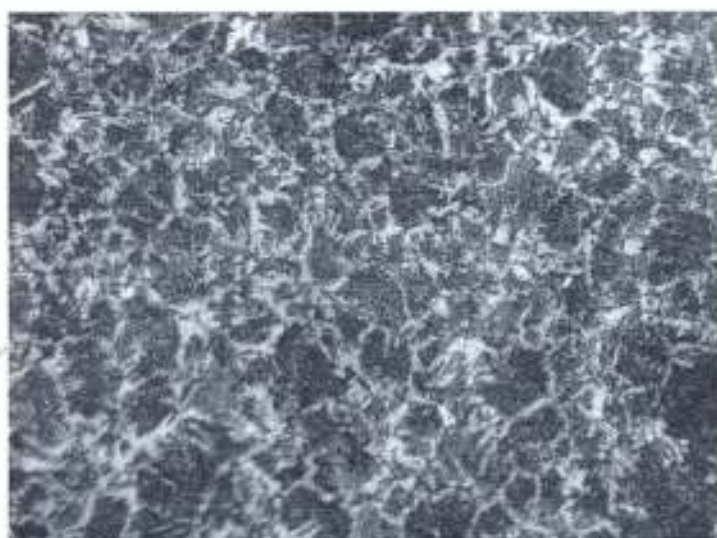


Plate 4. 4: Process 1 micrograph of mild steel immersed in 3% KCl solution with 0.3M of alanine concentration for 105 days, etched in 2% Nital, showing the effect of corrosion in the microstructure (X160)



Plate 4. 5: Process 2 micrograph of mild steel immersed in 3% KCl solution with 0.1M of Methionine concentration for 105 days, etched in 2% Nital, showing the effect of corrosion in the microstructure (X160)

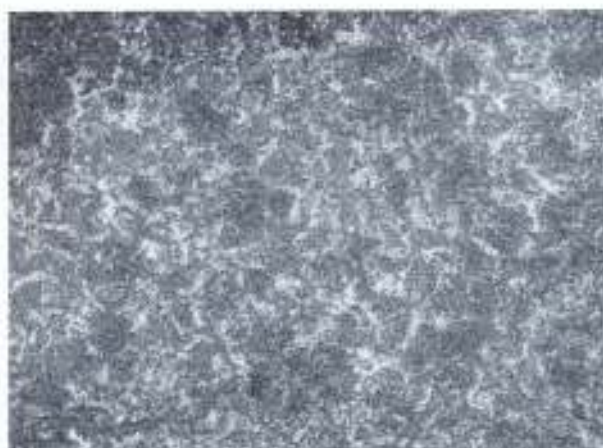


Plate 4. 6 :Process 2 micrograph of mild steel immersed in 3% KCl solution with 0.2M of methionine concentration for 105 days, etched in 2% Nital, showing the effect of corrosion in the microstructure (X160)

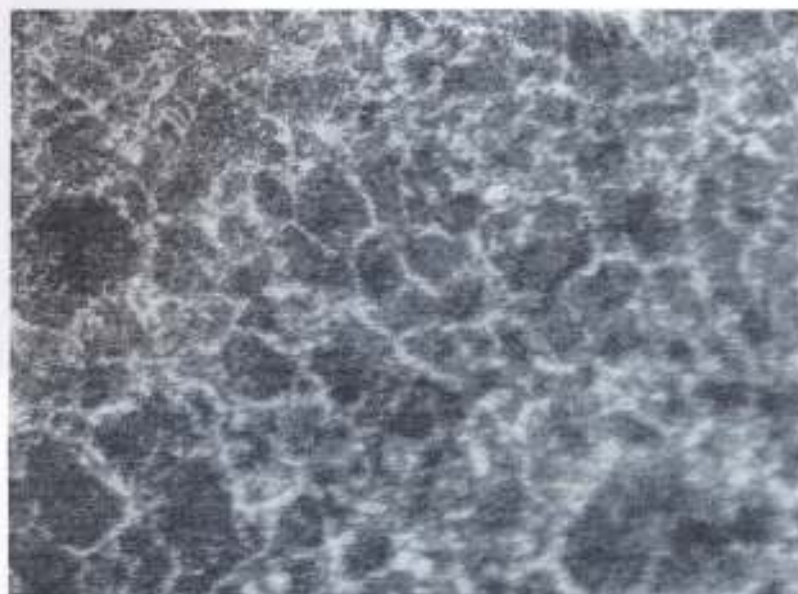


Plate 4. 7: Process 2 micrograph of mild steel immersed in 3% KCl solution with 0.3M of methionine Inhibitors concentration for 105 days, etched in 2% Nital, showing the effect of corrosion in the microstructure (X160)

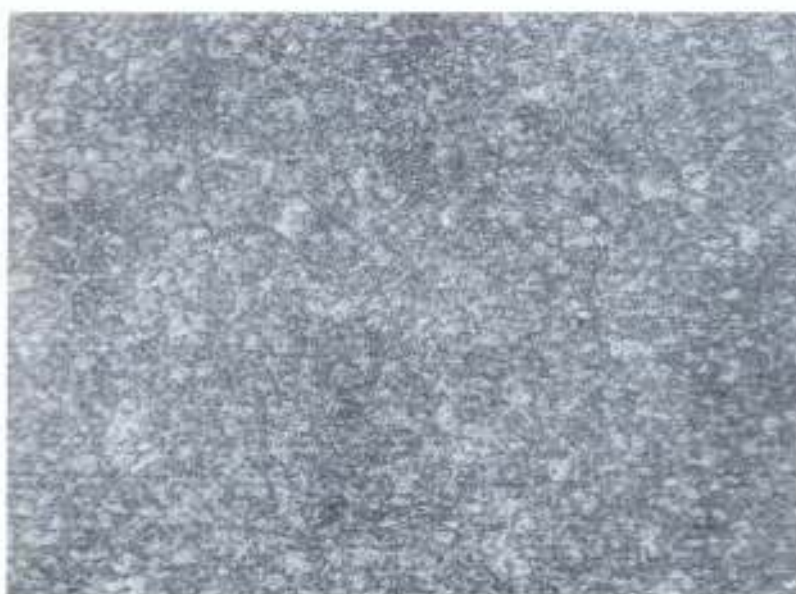


Plate 4.8 :Process 3 micrograph of mild steel immersed in 3% KCl solution without inhibitor for 105 days, etched in 2% Nital, showing the effect of corrosion in the microstructure (X160)



Plate 4.9: Process 3 micrograph of mild steel immersed in 3% KCl solution with 0.2M of glutamic acid concentration for 105 days, etched in 2% Nital, showing the effect of corrosion in the microstructure (X160)



Plate 4.10: Process 3 micrograph of mild steel immersed in 3% KCl solution with 0.3M of glutamic acid concentration for 105 days, etched in 2% Nital, showing the effect of corrosion in the microstructure (X160)



Plate 4.11 :Process 4 micrograph of mild steel immersed in 3% KCl solution with 0.3M of glutamic acid concentration for 105 days, etched in 2% Nital, showing the effect of corrosion in the microstructure (X160)



5.1 Conclusions

- 1 The synergistic effects on inhibitors and heat treatment led to an increase in inhibition efficiency and reduced the rate of corrosion.
- 2 The amino acid inhibitors enhance the formation of passivating oxide film and their inhibitive power in 3% KCl solution has been in order Alanine > Methionine > Glutamic acid.
- 3 The corrosion behaviour of mild steel in 3% KCl was determined by the reaction taken place on the metal-oxide layer interface through competitive adsorption of either the inhibitive ions or aggressive ions taken place.
- 4 The electrode potential of mild steel which rises towards active direction initially later moves generally in the noble direction with increasing time of immersion.
- 5 The inhibition efficiency of inhibitors in 3% KCl on corrosion of mild steel increases as the concentration of the inhibitors increases.

5.2 Recommendations

The following recommendations are proposed

- 1 More inhibitors in the neutral, basic and acidic group should be used in order to have a very good comparison of the effect of corrosion on mild steel in saline environment.

2. Various heat treatment methods should be applied on the inhibitors to determine suitable method to combat corrosion of mild steel in saline environment



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