

ELECTROCHEMICAL CHARACTERISATION OF MILD STEEL IN ACIDIC ENVIRONMENTS

Submitted in partial fulfillment of the requirements for the award of
Bachelor of Science in Chemistry

by

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**DEPARTMENT OF CHEMISTRY
SCHOOL OF SCIENCE AND HUMANITIES**

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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **JASHWANTH N (38030006)** and **PHILOMINAL MARY A (38030010)** who carried out the project entitled **"ELECTROCHEMICAL CHARACTERISATION OF MILD STEEL IN ACIDIC ENVIRONMENTS"** under my supervision from 01/11/2020 to 31/03/2021.

Dr. A. Sheik Mideen, M.Sc., Ph.D.

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Internal Examiner

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with Signature)

External Examiner

(Name in Capital Letters
with Signature)

DECLARATION

We, **JASHWANTH N and PHILOMINAL MARY A**, hereby declare that the Project Report entitled “Electrochemical Characterisation of Mild Steel in Acidic Environments” done by us under the guidance of **Dr. A. SHEIK MIDEEN, M.Sc., Ph.D.** Professor, Department of Chemistry, Sathyabama Institute of Science and Technology, Chennai – 600119, India is submitted in partial fulfillment of the requirements for the award of **Bachelor of Science in Chemistry** in April 2021.

DATE:
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ABSTRACT

Corrosion of a material by reaction with a corrosive environment is a common problem across many industries. Mild steel (MS) is the most common type of metal used in large industries due to its acceptable material properties and low cost. The present work is focused on the corrosion behaviour of mild steel in various concentrations (0.1 M, 0.5 M and 1.0 M) of hydrochloric acid (HCl), sulphuric acid (H₂SO₄) and nitric acid (HNO₃) has been investigated by the weight loss method at different temperatures 303K, 313K and 333 K.

It was observed that nitric acid environment was most corrosive to MS because of its oxidizing nature, followed by sulphuric acid, and lastly, hydrochloric acid. The rate of metal dissolution increased with increasing concentration of the corrosion media. Further, the corrosion rate of MS exposed to all the concentrations acid increased with the increase in temperature.

The mechanism of MS corrosion in HCl is attributed to the combined effect of anodic dissolution of iron with the adsorption and liberation of Cl⁻ ions and cathodic hydrogen evolution reactions. The mechanism of MS corrosion in H₂SO₄ can be explained based on the role of sulphate anions, which contribute directly in anodic dissolution and cathodic reaction during corrosion. The mechanism of MS corrosion in HNO₃ is caused by the formation of NO₂, NO, N₂O and N₂ (emission of a brown gas) due to the cathodic reaction.

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CHAPTER 1

INTRODUCTION

1.1 CORROSION

Corrosion is a general term applied to the process in which uncombined state of metals change in to their respective stable compounds. It may be considered as the destruction of materials under the action of the environment (Akhmetov et al, 1989). In a broad sense, corrosion is a process of destructive alteration of a metal or an alloy by chemical reaction with any substance: solid, liquid or gas. The pattern of attack is largely governed by the combined influences of several factors relating to metal or alloy, condition of service and the chemical nature of the environment.

1.2 EFFECTS OF CORROSION ON MATERIALS

The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment and structures are often more serious than the simple loss of mass of a metal. Failures of various kinds and the need for expensive replacements may occur even though amount of metal destroyed may be quite small. Some of the harmful effects of corrosion are as follows [Talbot, 1998]:

1. Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown. When the metal is lost in localized zones so as to give a crack-like structure, very considerable weakening may result from quite a small amount of metal loss.
2. Hazards or injuries to people arising from structural failure (e.g., bridges, cars, aircrafts).
3. Loss of time in availability of profile-making industrial equipment.
4. Reduced value of goods due to deterioration of appearance.

5. Contamination of fluids in vessels and pipes (e.g., beer goes cloudy when small quantities of heavy metals are released by corrosion).
6. Perforation of vessels and pipes, thus allowing escape of their contents and possible harm to the surroundings. For instance, a leaky domestic radiator can cause expensive damage to carpets and decorations, while corrosive sea water may enter the boilers of a power station if the condenser tube perforates.
7. Loss of technically important surface properties of a metallic component. These could include frictional and bearing properties, ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.
8. Mechanical damage to valves, pumps, etc. or blockage of pipes by solid corrosion products.

1.3 DIFFERENT FORMS OF CORROSION [Uhlig, 1985]

1. Galvanic corrosion

When two dissimilar metals are in contact with each other in presence of aqueous solution, the more active metal (metal with high negative electrode potential) acts as anode and undergoes corrosion. *Galvanic corrosion can be prevented by making use of electrical insulator between the two metals.*

2 Pitting corrosion

Pitting is a localized attack, which results in the formation of a hole around which the metal is relatively un-attacked. The mechanism of a pitting involves setting up of differential aeration cell. *Inhibitors are used to repair the pitting type corrosion.*

3 Erosion

It is the destruction of a metal by abrasive action of the flow of liquid or gases. *The use of harder materials and changes in velocity of liquid or gas are the methods employed to prevent erosion corrosion.*

4 Intergranular corrosion

This type of corrosion occurs when metal alloys are exposed to specific corrosive environment. In alloys grain boundaries are chemically more active than grain matrix. Under certain conditions corrosion occurs along the grain boundaries. *Proper heat treatment is the remedy for this type of corrosion.*

5 Fretting corrosion

This type of corrosion occurs when two surfaces of materials under load slide over each other. Here frictional heat oxidizes the metal and this oxide then wears away. *It is minimized by using harder materials, minimizing friction (via lubricants) or by designing the equipment.*

6 Stress corrosion cracking

The cracking of metal alloy by simultaneous action of tensile stress and corrosive environment is known as stress corrosion cracking. It occurs in certain metal-environment combinations only. *Cathodic protection can be applied to delay or stop the failure.*

7 Dezincification

Preferential dissolution of zinc in brass (Cu-Zn alloys) is known as dezincification. It is believed that dissolution of brass (both Zn and Cu) occurs, however copper gets deposited back. *Addition of 1% tin to brass improves the resistance to dezincification.*

8 Biological corrosion

Sulphate reducing bacteria (SRB) promotes corrosion in pipelines extensively. The sulphates present in slightly acid to alkaline (pH 6 to 9) soils are reduced by these bacteria to form calcium sulphide and hydrogen sulphide. When these compounds come in contact with underground iron pipes, conversion of iron into iron sulphide

occurs. *The soils rich in bacteria can be modified by surrounding the pipeline structure with chalk. This type of alteration of soil prevents corrosion.*

1.4 MILD STEEL CORROSION

Mild steel is an alloy of iron, containing iron, carbon, manganese, phosphorous etc. It is fairly malleable and ductile. It can be forged (shaped by hammering and pressing while hot) but cannot be hardened by heat treatment (Talbot and Talbot, 1998).

Mild steel is used in making boiler plates, girders, bars, tubes, rivets nuts and bolts. Pipelines are typically made of mild steel, and it is known that under common operating conditions an oxide film forms on the iron surface. This oxide film mostly presents a hematite ($\alpha\text{-Fe}_2\text{O}_3$) structure.

When mild steel corrodes, there is usually a loss of the metal to a solution in some form, by a product – favoured oxidation-reduction reaction. For mild steel to corrode, anodic sites must be available for the metal to be oxidized to metal ions as electrons are produced. Anodic areas occur at cracks in the oxide coating, at boundaries between phases, or around impurities (Ita and Offiong, 1997).

1.5 ACIDIC SOLUTIONS

Material is used in various environments including mild acidic environments and can undergo electrochemical oxidation resulting in destruction of metal. This corrosion induced in the material, besides loss in weight and cross section, can lead to hostile effects on the material properties [Umoren et al., 2008]. Corrosion of MS is an important problem in industrial processes having acid environment. In the construction of oil, gas or water wells, pickling acid washing, matrix acidizing and acid fracturing are operations performed during the production stimulation processes [Ramesh et al., 2014]. Generally, acid solutions are used at room temperature for removing soil and light rust

[Mauro et al., 2014]. For example, in acid pickling, these are widely used as it is more economical and trouble free. The main advantage of these acids over other acids in cleaning and pickling operations lies in their ability to form metal chloride and metal sulphates which are fairly soluble in aqueous medium, compared to phosphate, nitrate and sulphamate ions [Sathyanarayanan et al., 2005]. But extreme care has to be taken in handling it even in small concentration as it is corrosive to many metals including MS. Hence, the destruction in acid environment is more crucial to be addressed as huge amount of material loss occurs worldwide due to acid wash every year.

In industries, acidic solutions are largely used for acidizing, de-scaling, chemical cleaning and acid pickling for steel, the most frequently used is hydrochloric acid. Naturally, these occur in corrosive environment resulting into intense corrosion complications experienced in industrial processes.

1. Hydrochloric Acid

One of the most commonly used acids in today's industrialized world is Hydrochloric acid HCl, where some of its applications include chemical cleaning and processing, acid treatment of oil wells and other applications. The wide use of this acid has led to the concentration of this study on the corrosive effects of this acid on carbon steel, which is a versatile component in many industrial structures. The main advantage of this acid over other acids in cleaning and pickling operations lies in its ability to form metal chloride, which is extremely soluble in aqueous medium, compared to sulphate phosphate and nitrate. The higher solubility of chloride salt causes the least polarizing effect and does not hinder the rate of corrosion (Singh et al., 1995).

2. Sulphuric Acid

Sulfuric acid, H_2SO_4 is a major ingredient in the chemical industry. Its common use in fertilizer manufacturing; although it plays a major role also in mineral processing, oil refining, wastewater processing, chemical synthesis, steel pickling, and other

hydrometallurgical applications. Its vast end applications include as an ingredient in domestic acidic drain cleaners, as an electrolyte in lead-acid batteries, and in various cleaning agents [Müller, 2000]. On the other hand, the aggressive nature of this acid makes it attack the metallic materials used for storage tanks and pipes construction. Consequently, a wide range of metallic materials are used for constructing tanks and pipes depending on the concentration range of sulfuric acid [Panossian et al., 2012]. Sulfuric acid has the unusual behavior that, while it acts as a non-oxidizing acid at low to rather high concentrations, it acts as a strong oxidizing acid when it becomes highly concentrated. Iron corrodes rapidly in low concentration of sulfuric acid, but passivates by forming a protective oxide layer in high concentrations [Rengstorff et al., 1984; Najjar, 2014].

3. Nitric Acid

Nitric acid is an oxidizing agent, in which the anion is more involved in oxidation than the cation [Brady et al., 2009]. It has high oxidation power, characterized by low pH values and high potential values [Davis, 2012]. Wattanaphan, 2012 showed that exposure of carbon steel to nitric acid solution gave iron (II) nitrate as the reaction product. Iron (II) nitrate is highly soluble, so it would redissolve, leaving a bare steel surface that would again react with the oxidizing agent to continue the same reaction. This was the reason why there was no nitrate content observed in the corrosion product.

CHAPTER 2

LITERATURE SURVEY

2.1 CORROSION OF MILD STEEL IN ACIDIC ENVIRONMENTS

Corrosion by sulfuric acid has received widespread interest by researchers, especially in the oil and gas industry, due to policies regarding the transformation of hydrogen sulfide and sulfur oxides that are produced during oil extraction and refining to sulfuric acid. such policies have been adopted to reduce the negative effects of aforementioned gases in the atmosphere as a result of fuel combustion, and thus to reduce global warming [Panossian, 2012; Ferhat, 2014].

Aisha H. Al-Moubaraki et al (2020) investigated the corrosion behaviour and mechanism of mild steel/H₂SO₄ systems using hydrogen gas evolution, and weight loss, electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization PDP at 30°C. EIS results showed that the R_p value decreases while the C_{dl} value increases along with increasing acid concentration. PDP results clearly revealed that the dissolution of mild steel undergoes anodic control.

Noor and Al-Moubaraki (2008) studied the corrosion behaviour and mechanism for mild steel in hydrochloric acid solutions by hydrogen evolution and mass loss methods and by electrochemical impedance spectroscopy and potentiodynamic polarization methods at 25°C. They predicted that mild steel after immersion in HCl solutions of different concentrations showed general and pitting corrosion and the latter becomes more pronounced at higher level of HCl concentration. Potentiodynamic polarization data indicated that mild steel dissolution occurs via multistep mechanism.

Anees A. Khadom et al. (2009; 2014) addressed the effect of different temperatures and acid concentrations on the corrosion of low carbon steel in hydrochloric acid. The effect of temperature was explained by application of Arrhenius

equation and transition state theory, while the acid concentration effect was explained using reaction kinetic equations. The combined effect of temperature and acid concentration then modelled using a nonlinear regression method.

Osarolubes et al. (2008) examined the corrosion behaviour of mild steel and high carbon steel in various concentrations of nitric acid (HNO_3), hydrochloric acid (HCl), and perchloric acid (HClO_4) by weight loss method. It was observed that nitric acid environment was most corrosive to both steels because of its oxidizing nature followed by perchloric acid and hydrochloric acid.

Shalini Srivastava (2015) examined the corrosion behaviour of mild steel in binary mixtures of dilute (IN) acids (H_2SO_4 , HCl , HNO_3 , H_3PO_4 , H_2CrO_4). It was observed that in $\text{HCl}:\text{HNO}_3$ and $\text{H}_3\text{PO}_4:\text{HNO}_3$ mixtures when small amount of HCl or H_3PO_4 was added to HNO_3 reduced the weight loss of mild steel considerably.

Bambang and Sakina (2019) investigated corrosion behaviour of ASTM A1008 ultralow carbon steel in mixtures of HNO_3 , H_2SO_4 and HCl using immersion and polarization methods. The results showed that the uniform and pitting corrosion damage occurred, caused by the combined activity nitric and sulfuric acid and by hydrochloric acid, respectively.

2.2 SCOPE AND OBJECTIVES OF PRESENT INVESTIGATION

The scope of present research work is that the weight loss method was applied to monitor the corrosion rate of mild steel in various mineral acids with different concentrations at different temperatures. The weight loss technique has, indeed, been acclaimed as the best and simplest of all corrosion monitoring techniques [McCafferty, 2010].

The main objectives of this work include:

- To measure the corrosion rate of mild steel in acids like HCl, H₂SO₄ and HNO₃ of concentrations 0.1 M, 0.5 M and 1M.
- To measure the corrosion rate of mild steel in acids like HCl, H₂SO₄ and HNO₃ of concentrations 0.1 M, 0.5 M and 1M at different temperatures: 30°C (303K), 40°C (313K) and 60°C (333K).

CHAPTER 3

EXPERIMENTAL

3.1 MATERIALS

The following materials were used for the PRESENT study: mild steel of composition (%W) [Mn (0.41), P (0.06), C (0.27), Si (0.16), S (0.02) and the rest iron], hydrochloric acid (Sd Fine), sulphuric acid (BDH), nitric acid (SD Fine) ethanol (BDH), acetone (BDH), electronic weighing balance (Shimadzu), thermostated water-bath thermometer, beakers, thread, emery paper and retort stands. All chemicals used were of analytical grades and applied without further purification. Solutions were all made using doubly distilled water.

3.2 MATERIALS PREPARATION

The mild steel sheet was mechanically press-cut into the rectangular dimensions and used as working specimens. The mild steel samples were mechanically polished using 1/0, 2/0, 3/0, and 4/0 emery papers and finally degreased with the organic solvent trichloroethylene and dried before use. HCl , HNO_3 and H_2SO_4 solutions of concentrations 0.1 M, 0.5 M, 1.0 M were prepared by the dilution of analytical grade HCl , HNO_3 and H_2SO_4 with double-distilled water, respectively.

3.3 WEIGHT LOSS METHOD

The immersion procedure was followed for present investigation as per the ASTM G 31-729 standard method. A predetermined volume of the experimental solution comprising 200 ml of the appropriate concentration of each acid was measured and placed in 250 ml beaker. The mild steel sample was suspended in the solution and the beaker was stoppered to avoid evaporation. Each immersion test was carried out for 24 hours at 30°C. But, at higher temperatures (40°C and 60°), the samples were kept

exposed to corrosive acids for 2 hours duration. After the prescribed duration of immersion, the samples were removed and rinsed thoroughly with plenty of tap water followed by double distilled water. Then the final mass of the samples was determined.

The corrosion rate of mild steel in various acids at different temperatures was determined using the expression:

$$\text{Corrosion Rate, } mg \text{ cm}^{-2} \text{ min}^{-1} = \frac{W}{A \times t}$$

where W is the loss in weight of the mild steel sample in milligram, A represent the area in cm^2 , t is the immersion time in minutes.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 EFFECT OF ACID CONCENTRATION ON THE CORROSION OF MILD STEEL

The corrosion rates of mild steel (MS) in hydrochloric acid, sulphuric acid and nitric acid of concentrations (0.1 m, 0.5 M and 1.0 M) at different temperatures (303K, 313K and 333K) are shown in Table 4.1, Table 4.2 and Table 4.3. The corrosion rate increased with all increases in acid concentration. Figure 4.1, Figure 4.2 and Figure 4.3 graphically depict the increase in corrosion rate with hydrochloric acid, sulphuric acid and nitric acid concentrations. At all the temperatures, the corrosion rate of mild steel was higher in nitric acid followed by sulphuric acid and hydrochloric acid. The corrosion of MS in various acids is attributed to the presence of water, air and H^+ , Cl^- , SO_4^{2-} , NO_2^- ions which accelerate the corrosion process.

Table 4.1: Corrosion rate of Mild Steel in Acidic Media at Temperature, 303K

Duration of Exposure: 24 Hours

Name of the Acid	Concentration (M)	Area (cm ²)	Initial Weight, (g)	Final Weight (g)	Weight Loss (mg)	Duration (Min)	Corrosion Rate (mg/cm ² /min)
HCl	0.1	60.70	110.5670	110.4080	159	1440	0.0018
	0.5	54.78	99.7742	99.3521	422	1440	0.0053
	1.0	52.56	92.3217	91.7424	579	1440	0.0077
H ₂ SO ₄	0.1	54.78	100.35	99.99	360	1440	0.0045
	0.5	64.80	117.33	116.39	940	1440	0.0100
	1.0	58.48	108.55	106.54	2010	1440	0.0238
HNO ₃	0.1	60.70	111.26	110.69	570	1440	0.0071
	0.5	51.08	94.44	92.75	1690	1440	0.0229
	1.0	57.00	106.4454	102.1698	4276	1440	0.0521

Table 4.2: Corrosion rate of Mild Carbon Steel in Acidic Media at 313K**Duration of Exposure: 2 Hours**

Name of the Acid	Concentration (M)	Area (cm ²)	Initial Wight, (g)	Final Weight (g)	Weight Loss (mg)	Duration (Min)	Corrosion Rate (mg/cm ² /min)
HCl	0.1	51.08	86.8880	86.6670	221	120	0.036
	0.5	57	95.3233	95.0033	320	120	0.0467
	1	54.04	83.8025	83.3545	448	120	0.0690
H ₂ SO ₄	0.1	51.08	88.9226	88.6021	321	120	0.0523
	0.5	51.08	88.4588	87.5284	930.4	120	0.1517
	1.0	57	97.6653	96.0205	1644.8	120	0.2404
HNO ₃	0.1	57	98.3413	97.7210	620.3	120	0.0906
	0.5	58.48	101.3964	98.5513	2845	120	0.4054
	1.0	51.08	91.6320	89.0235	2608	120	0.4255

Table 4.3: Corrosion rate of Mild Carbon Steel in Acidic Media at 333K**Duration of Exposure: 2 Hours**

Name of the Acid	Concentration (M)	Area (cm ²)	Initial Wight, (g)	Final Weight (g)	Weight Loss (mg)	Duration (Min)	Corrosion Rate (mg/cm ² /min)
HCl	0.1N	51.08	86.6111	86.3167	294.4	120	0.0480
	0.5N	57	95.9225	95.3704	552.1	120	0.0807
	1N	54.04	84.8357	83.8347	1001	120	0.1543
H ₂ SO ₄	0.1	51.08	87.5238	86.9672	556.6	120	0.0908
	0.5	54.04	86.0620	84.9660	1096	120	0.1690
	1	54.04	88.1655	86.1374	2028.1	120	0.3127
HNO ₃	0.1	58.48	101.9074	101.4760	431	120	0.0614
	0.5	54.04	93.8570	88.3415	5515	120	0.8504
	1.0	32.58	99.2814	94.0484	5233	120	1.3387

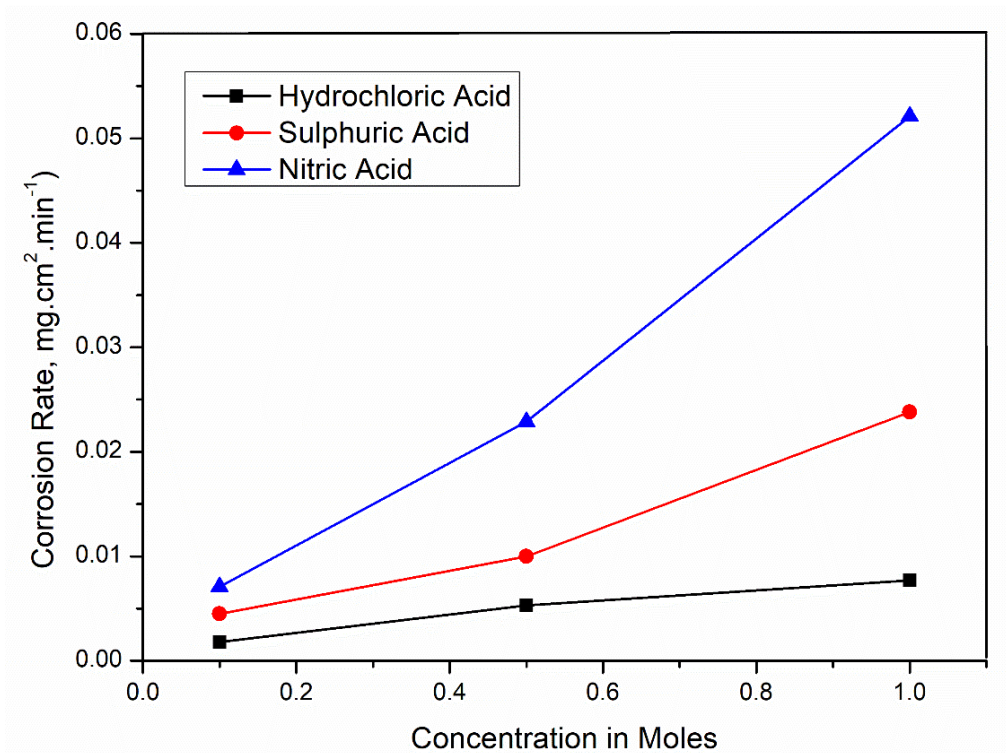


Figure 4.1: Corrosion Rate of Mild Steel in Various Acids at 303K

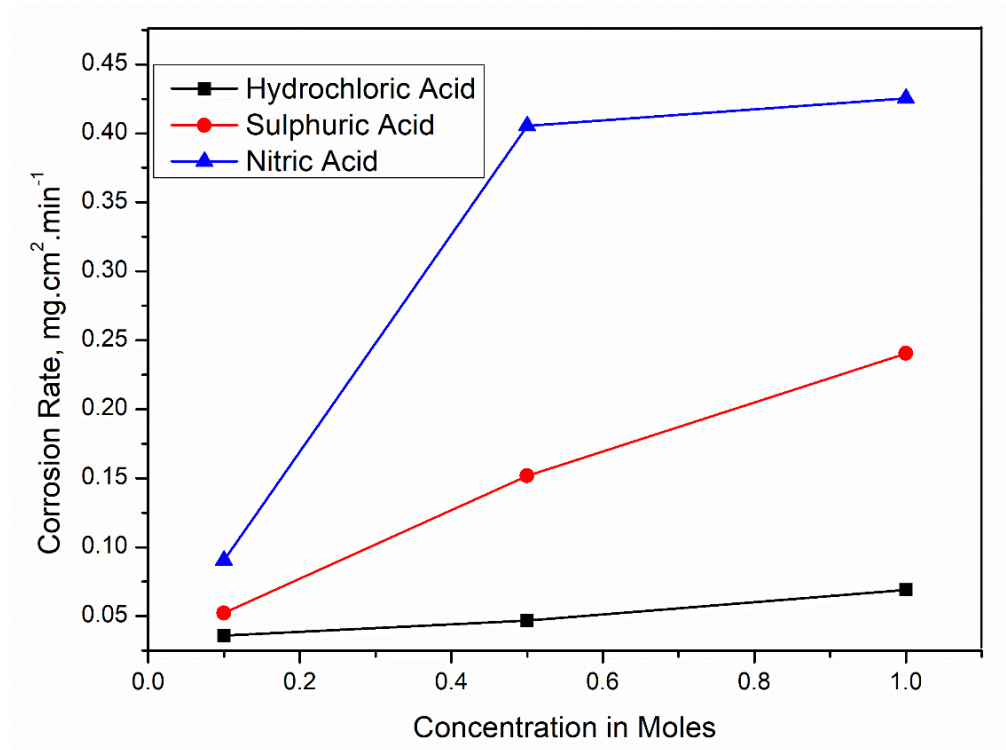


Figure 4.2: Corrosion rate of Mild Steel in Various Acids at 313K

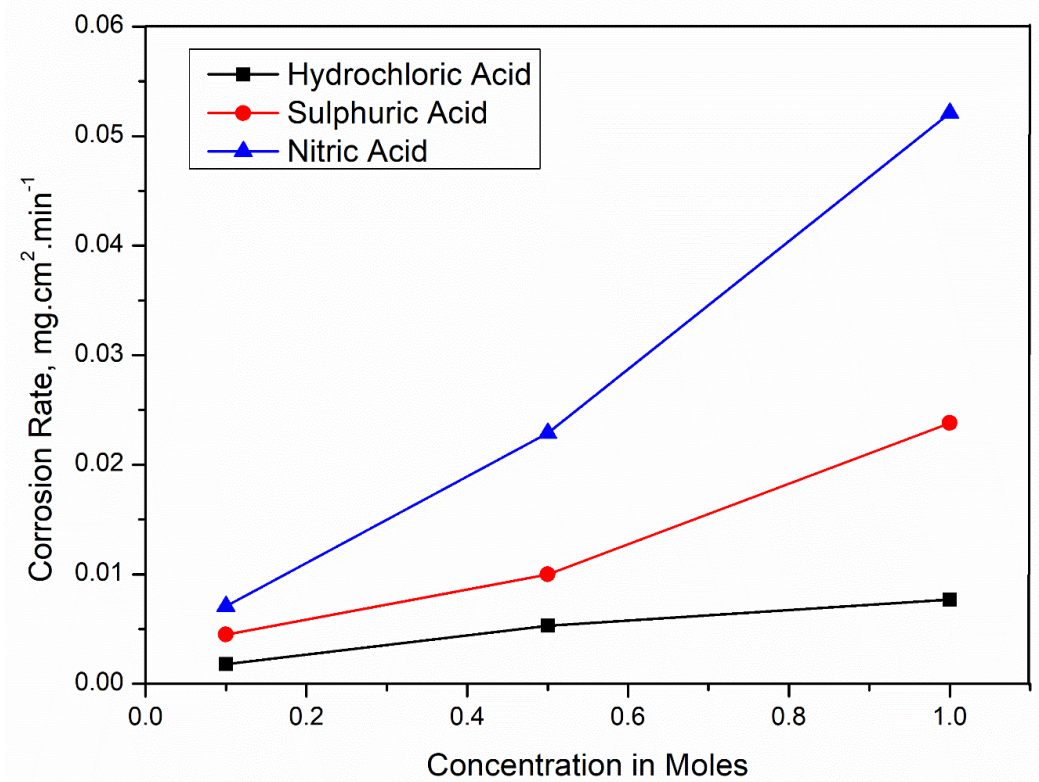


Figure 4.3: Corrosion rate of Mild Steel in Various Acids at 333K

4.2 EFFECT OF TEMPERATURE ON THE CORROSION OF MILD STEEL

The effect of temperature on the corrosion behaviour of MS in various acids of different concentrations clearly indicates that the corrosion rate increases with increasing temperature. There is a progressive increase in weight loss as the temperature is increased from 303K to 333K (Figure 4.4, Figure 4.5 and Figure 4.6). This signifies that the dissolution of the metals increased at higher temperatures. This observation is attributed to the general rule guiding the rate of chemical reaction, which says that chemical reaction increases with increasing temperatures. Also, an increased temperature favors the formation of activated molecules, which may be doubled in number, with 10°C rise in temperature, thereby increasing the reaction rate. This is because the reactant molecules gain more energy and are able to overcome the energy barrier more rapidly [Ita and Offiong, 1997]. An increase in temperature may also increase the solubility of the protective films on the metals, thus increasing the

susceptibility of the metal to corrosion [Okafor et al., 2004]. The solubility of oxygen gas decreases with increase in temperature. Thus, oxygen concentration is expected to be more at higher temperature which in this case is higher at 323K than at 313 and 303K.

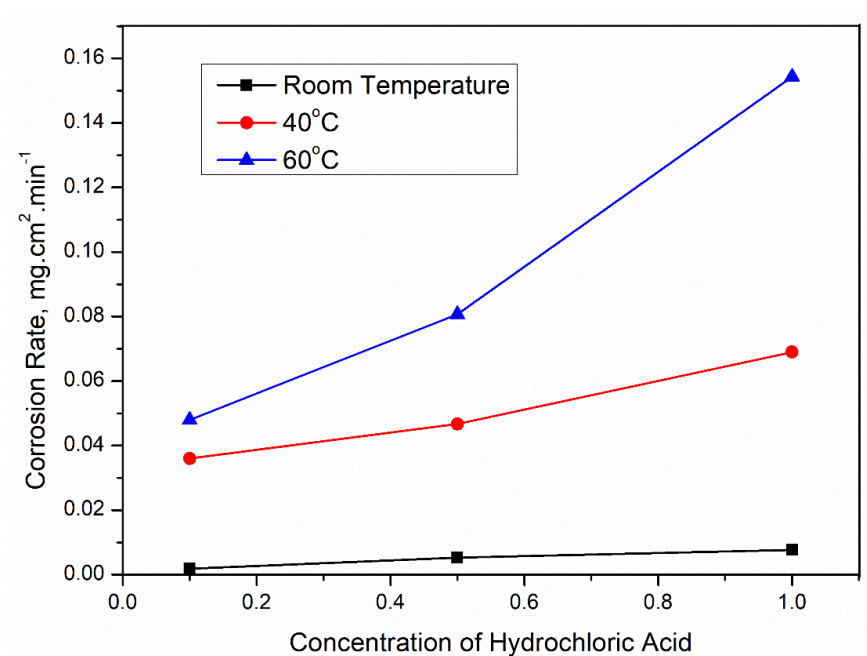


Figure 4.4: Effect of Temperature on the Corrosion rate of Mild Steel in Hydrochloric Acid

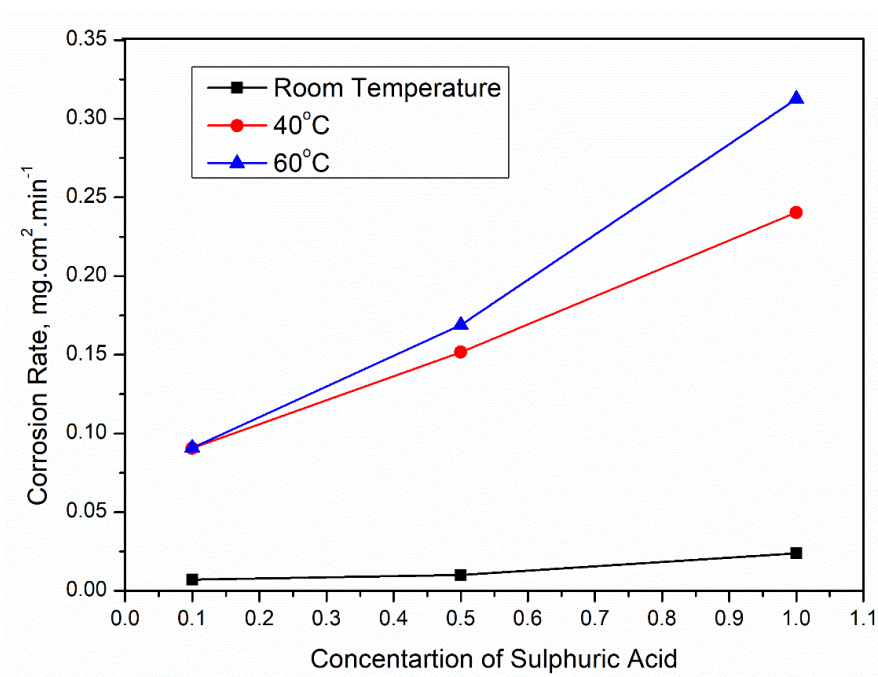


Figure 4.5: Effect of Temperature on the Corrosion rate of Mild Steel in Sulphuric Acid

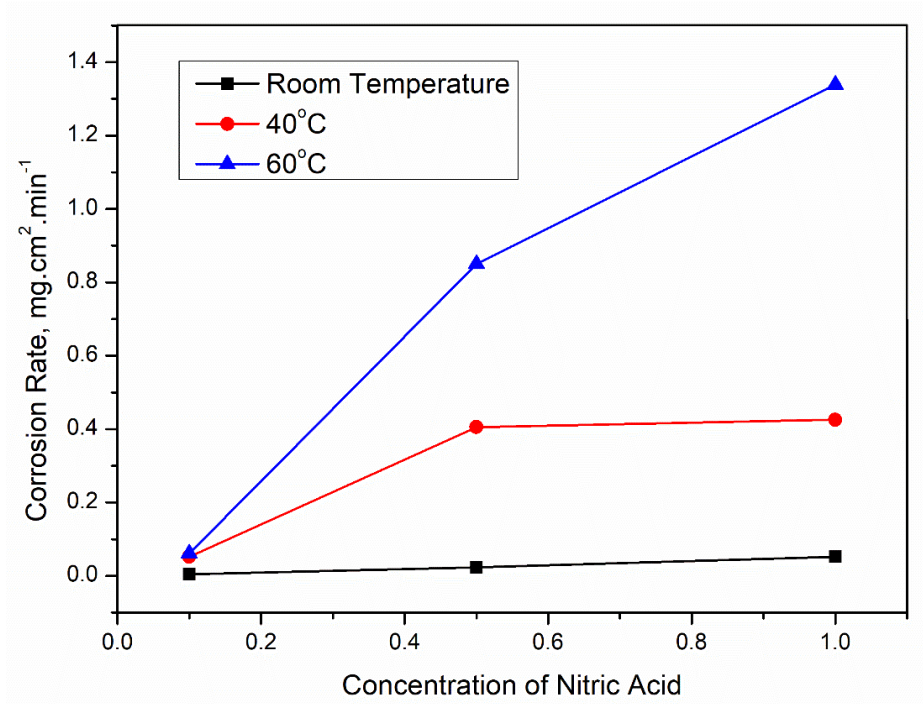
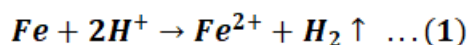


Figure 4.6: Effect of Temperature on the Corrosion rate of Mild Steel in Nitric Acid

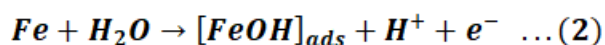
4.3 MECHANISM OF MILD STEEL CORROSION IN HCl

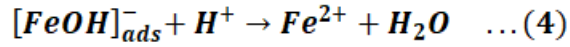
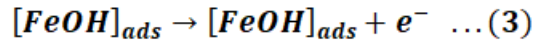
Gad Allah et al., 1992 and Noor et al., 2008 pointed out that iron dissolution in HCl solutions depends on H^+ ion more than the Cl^- ion. The hydrogen evolution and mass loss is produced by the same reaction:



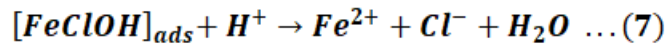
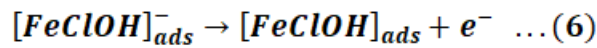
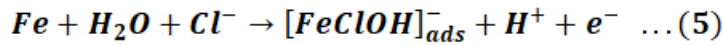
If we assume that the electrochemical reaction of iron corrosion involves transfer of two electrons, then there are two steps, each one represents transfer of one electron and one of them may be considered the rate determining step. This result is in good agreement with the mechanisms that are suggested for iron dissolution [Chin and Nobe, 1972; Macfarlane and Smedley, 1986].

(i) Aqueous solutions:





(ii) Aqueous solutions containing Cl^{-} ions:



Where $[FeOH]_{ads}$ and $[FeClOH]_{ads}^{-}$ are the adsorbed intermediates which each of them is involved in the rate determining step (Equations 3 and 6 respectively) of mild steel dissolution according to mechanism (i) and (ii) respectively. It must be pointed out that the presence of Cl^{-} ions does not exclude dissolution through the $[FeOH]_{ads}$ intermediate in chloride free acid media, as the two mechanisms can proceed simultaneously [Meszaros, et al, 1990].

4.4 MECHANISM OF MILD STEEL CORROSION IN H_2SO_4

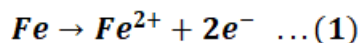
The behavior of mild steel corrosion in H_2SO_4 solution has established significant interest in the literature [Gan et al., 1987; Ellison, 2006; Panossian et al., 2012]. The role of the SO_4^{2-} anions and other components in mild steel corrosion in H_2SO_4 solution must be considered. Accordingly, the corrosivity of H_2SO_4 solutions are determined by two main factors. The first is the concentration of SO_4^{2-} anions which determines the main corrosion phenomena progress, i.e., ions and electrons move from the metal to the solution. The second is the intensity of dissolution rate of the corrosion products, i.e., salt films formed on the steel surface, which count on the acid concentration. The

minor corrosion processes, i.e., the removal of the surface salt films after damaged by water molecules, comprise the hydration, diffusion, and migration of their compounds into the solution. Dehydration of SO_4^{2-} anions is accompanied with electrostatic adsorption on the mild steel surface.

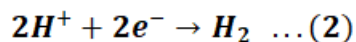
As a result of electrostatic interaction, and due to the attraction of double bonds to protons, a complex double layer of metal surface-anions-hydrogen ions may be developed. Both the electrostatic adsorption of SO_4^{2-} anions on the metal surface with unfilled d-levels and the creation of a complex double layer reduce the work function of the metal thus facilitating hydrogen ions discharge, i.e., reduce the excess voltage needed for hydrogen evolution. As a result of this loss of electrons, the metal turn into positively charged, anion adsorption is enhanced, and so is the process of metal ions flow into solution.

The above discussion of the role of anions on corrosion of mild steel in H_2SO_4 solutions can be explained according to electrons exchange by metal oxidation (anodic reaction) and hydrogen reduction (cathodic reaction) with the following reactions, separately [Lyon, 2012]:

Anodic reaction:

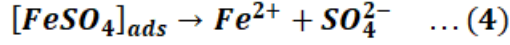
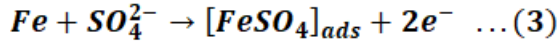


Cathodic reaction:



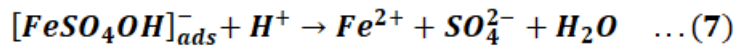
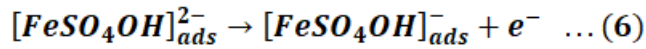
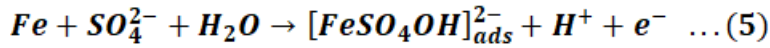
In the presence of SO_4^{2-} anions in aqueous solutions, several mechanisms on the anodic dissolution of iron have been assumed.

(i) **Primary (main) corrosion Mechanism** [MacFarlane and Smedley, 1986]:



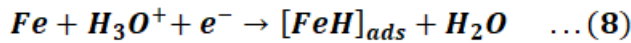
In the presence of SO_4^{2-} anions, reaction (3) progresses on the metal surface rapidly. Therefore, the dissolution of iron (anodic reaction) was main controlled by both electro-dissolution of iron and diffusion of soluble $[FeSO_4]_{ads}$ to the bulk solution. The anodic dissolution of iron in aqueous solutions including SO_4^{2-} anions may also involve the formation of adsorbed intermediate $[FeSO_4OH]_{ads}^{2-}$. Therefore, the below reactions contribute to iron dissolution.

(ii) **Secondary (minor) corrosion mechanism** [Zhou et al., 2017]:

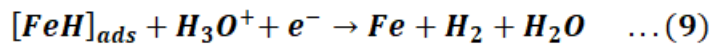


The cathodic hydrogen gas evolution (HE) reaction might be described as follows [Atta et al., 2011]:

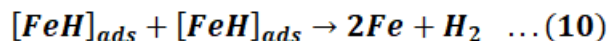
- Principal discharge stage (Volmer reaction)



- An electrochemical-desorption stage (Heyrovsky reaction)



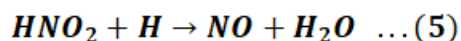
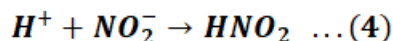
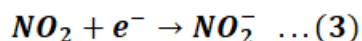
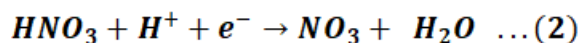
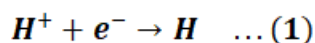
- A recombination stage (Tafel reaction)



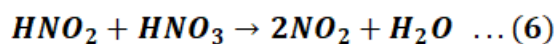
In acidic media, the hydrogen atoms that are absorbed $[FeH]_{ads}$ will recombine to form hydrogen molecules, which rise as bubbles on the metal surface. This process is the second stage of the cathodic reaction (HE). This stage can happen via an atom-atom combination as suggested by the chemical recombination mechanism (Tafel-Volmer) or an ion-atom reaction as suggested by the electrochemical recombination mechanism (Volmer-Heyrovsky) [Atta et al., 2011].

4.5 MECHANISM OF MILD STEEL CORROSION IN HNO_3

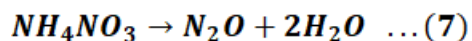
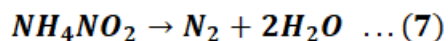
The nitric acid corrosion mechanism has been studied for many years. Although the anodic reaction is fairly simple, iron being oxidized to ferrous cation (Fe^{2+}), there are a number of cathodic reactions that occur in this process. The cathodic reduction of nitric acid likely proceeds in five steps [Evans, 1944]:



The nitrous acid (HNO_2) that is formed in step (4) regenerates NO_2 by an interaction with the nitric acid [Evans, 1944]:



Thus, the reaction becomes autocatalytic. Ammonium salts are also formed during the cathodic reaction. The ammonia salts decompose to form N_2 and NO_x compounds by the following reactions [Evans, 1944]:



Thus, the formation of NO_2 , NO , N_2O and N_2 (i.e., a brown gas should be emitted) due to the cathodic reaction is expected. Iron differs from many metals in that the corrosion rate increases with acid concentration, up to approximately 6 M, and then decreases dramatically. Uhlig reports that the corrosion rate in 1 M nitric acid at 25°C is approximately 2 inches per year [Uhlig, 1948] to a maximum of approximately 13 inches per year at 6 M nitric acid. However, at higher concentrations, a passive ferric oxide film forms on the surface and corrosion rate is reduced significantly.

CHAPTER 5

CONCLUSIONS

Based on the experimental results and discussions, we concluded that:

- ❖ It was observed that nitric acid environment was most corrosive to MS because of its oxidizing nature, followed by sulphuric acid, and hydrochloric acid.
- ❖ The rate of metal dissolution increased with increasing concentration of the corrosive media. The corrosion of MS in various acids is attributed to the presence of water, air and H^+ , Cl^- , SO_4^{2-} , NO_2^- ions, which accelerate the corrosion process.
- ❖ Further, the corrosion rate of MS exposed to all the concentrations acids increased with the increase in temperature. An increase in temperature may also increase the solubility of the protective films on the metals, thus increasing the susceptibility of the metal to corrosion.
- ❖ The mechanism of MS corrosion in HCl is attributed to the combined effect of anodic dissolution of iron with the adsorption and liberation of Cl^- ions and cathodic hydrogen gas evolution reactions.
- ❖ The mechanism of MS corrosion in H_2SO_4 could be explained based on the role of sulphate anions, which contribute directly in anodic dissolution and cathodic reaction during corrosion.
- ❖ The mechanism of MS corrosion in HNO_3 is caused by the formation of NO_2 , NO , N_2O and N_2 (emission of a brown gas) due to the cathodic reaction.

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