CORROSION UNDER TWO – PHASE FLOW KEROSENE / WATER SIMULATED BY TURBLENTLY AGITATED SYSTEMS

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Submitted to the College of Engineering

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of the Requirement for the degree of

Master of Science in

Chemical Engineering

by

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Abstract

The corrosion of carbon steel in agitation systems of single phase (1% wt. NaCl solutions) and two phases (1% wt. NaCl solutions / Kerosene) were investigated by weight loss and polarization techniques. In single aqueous phase the weight loss experiments were carried out at different rotational velocities (262, 349, 438, 525, 600, 612, 800, 1000, 1200 and 1400) rpm using circle disk turbine agitator of 8 cm diameter. The average corrosion rate increased with increasing rotational speed. The Polarization experiments were carried out at the same rotational velocities as in weight loss. The limiting currents (i.e. average corrosion rate) were found to support the results obtained by weight loss technique, i.e., limiting current increased as rotational velocity increased too.

In two-phase system (1%wt. NaCl solution / Kerosene) investigation was performed by weight loss technique only due to the high electric resistance of agitated solutions. These test runs were carried out in aqueous phase concentrations 1% vol., 5 % vol., 8% vol., and 16.4% vol. of 1% wt. NaCl solutions mixed with kerosene at rotational velocities of 600, 800, 1000, 1200, and 1400 rpm. The average corrosion rate increased with increasing speed of rotation in all aqueous concentrations. Furthermore, the average corrosion rate can be stated to increase with Reynolds number, Weber number and inversely with Sauter mean diameter.

The effect of phase concentration was noted to be dependent on aqueous phase concentration as follows: In low range aqueous phase (1%wt. NaCl solution) concentrations of 1% vol., and 5% vol., the average corrosion rate increased as aqueous phase concentration increased at Reynolds number of 38428, 51238, 64047, 76856, and 89666. Furthermore these average corrosion rates were lower than those in single aqueous phase (1% wt. NaCl

solution) at equivalent Reynolds numbers. Using high range aqueous phase (1% wt. NaCl solutions) concentrations of 8% vol., and 16.4% vol., the average corrosion rate increased as phase concentration increased, and they were higher than those in single aqueous phase of 1% wt. NaCl solutions at equivalent Reynolds number.

Effect of inhibitor**:** Test runs were carried out using two types of inhibitors (sodium nitrite, and sodium hexapolyphosphate) in 8% vol. aqueous phase mixed with kerosene only. In presence of these two types of inhibitors when speed of rotation was increased the percent protection decreased, while the average corrosion rates decreased when the concentration of inhibitors increased.

Sodium hexapolyphosphate is found more efficient as inhibitor than sodium nitrite. At 20, 40, and 60 ppm sodium hexapolyphosphate, the inhibition efficiency was found to be 67.43 to 58.71%, 84.79 to 48.8%, and 93.46 to 58.75% respectively as the speed of rotation (i.e., Re) was changed from 600 to 1400 rpm. Under similar conditions, sodium nitrite at 485, 970, and 1940 ppm, the percent protection was 57.53 to 36.41%, 69.32 to 49.78%, and 86.4 to 94.58% respectively.

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List of Symbols

Symbols	Definition	Unit(SI)
A	The area of specimen	m^2
a	The total area of drops or bubbles at this volume	=
C_b	Bulk concentration	$mole/m^3$
C_s	Surface concentration	$mole/m^3$
c	Constant	
D	Diffusivity coefficient	$m^2/s.$
D_a	Diameter of impeller	m
D_P	The drops or bubbles were sphere in dia.	
Ds	The volume surface mean diameter	=
D_t	Diameter of tank	=
d	Diameter of pipe	=
E	Distance from center of impeller to bottom Of tank	=
F	Faradays constant (96487)	Col./equiv.
f	Friction factor	
H	Height of tank	m
h	Height of two specimens from bottom of agitation	=
I	Total current	A/m^2
i	Current density	=
i_c	Corrosion current density	=
i_L	Limiting current density	=
i_o	Exchange current density	=
J	Width of baffles	m
L	Length of impeller	=
M	Distance between two specimens	cm
N	is the mass of (Fe) reacted due to corrosion).	$gmol/m^2.s.$
NA	Rate of flux	$mol/m^2.s.$
N_I	Rotational speed of impeller	rev./s.
n	The number of drops	
R	Universal gas constant	8.314j/mol.K
Re	Reynolds impeller No.	
R_F	The resistance produces by surface of site	Ω.cm

R_{Sol}	The electrical resistance	Ω.cm
T	Thickness of wall of agitation	m
t	Exposure time	day
V	Average velocity	m/s.
ν	kinematics viscosity	m^2/s.
W	Width of impeller	m
ΔW	Average Weight loss	g
We.	Weber Number	
Z	The no. of electrons involve one act	

Abbreviations

DRAS	Drag Reducing Agents
gmd	gram per square meter day
HVL	Highly Volatile Liquid
LNG	Liquefied Natural Gas
LPG	Liquefied Petroleum Gas
rpm	revolution per minutes
rps	revolution per second
%vol.	Percentage volume
%wt.	Percentage weight

Greek Symbols

Symbols	Definition	Unit(SI)
$\alpha_{a,c}$	Transfer coefficient for anodic or cathodic reaction	
β	Tafel slope	mV/decade.
δ_d	Diffusion layer thickness	µm
µ	Viscosity	Kg/m.s.

η	**Polarization overpotential**	**mV**
η^A	**Activation overpotential**	**=**
η^c	**Concentration overpotential**	**=**
η^R	**Resistance overpotential**	**mV**
η^T	**total overpotential**	
ρ	**Density**	**Kg/m^2**
Ψ	**Volume fraction of dispersed phase-in system**	
σ	**Interfacial tensile**	**N/m^2**

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Chapter One

Introduction

1.1 Mixing of Immiscible Liquid Phases:

The mixing of immiscible liquid phases is among the most important chemical engineering operation, yet quantitative information on the mixing process is rather lacking. Most available information is applicable only to specilized equipment or to particular liquid system. In mixing two immscible fluids in a stirred system energy is transferred to the fluid by the stirrer and the energy serves to suspend the dispersed phase to create turbulence in the fluid. If the intensity of the turbulence is uniform throughout the tank the suspended droplets would be subdivided until they were of size that was no longer affected by the turbulence. In the usual case the intensity of the turbulence is not uniform throughout the tank and regions of varying intensity exist. In region of lower intensity colliding droplets may coalesce, the larger droplets thus formed on passing to regions of higher intensity will again be sheared and broken up. The end state of this sequence of dispersion is a dynamic equilibrium where distribution of droplet size is established throughout the tank. In present study the corrosion rate is determined under two phase flow (water /oil) for various values of Reynolds numbers at different compositions of water/oil. Also various types of corrosion inhibitors are used, and investigation of the effect of emulsion droplet size on corrosion of carbon steel has been studied in a wide range of dispersed phase fraction. Agitation systems give good similarity for emulsion type that occurs in the equipment under actual production in oil and gas deposit. Metal surface comes in contact with emulsion of oil in water or water in oil types. The first type is normally encouuntered in wells with high water content. Also in oil refineries these two types of emulsion are encountered. Because of considerable experrimental difficulties involved, it is only recently that the corrosion of metals in emulsion systems has begun to be studied and the mechansim of this process remains unclear for along time.

1.2 Cost of Corrosion:

A) Corrosion Inhibitor

A corrosion inhibitor may be defined, in general terms, as a substance that when added in a small concentration to an environment effectively reduces the corrosion rate of a metal exposed to that environment(1). Inhibition is used internally with carbon steel pipes and vessels as an economic corrosion control alternative to stainless steels and alloys, coatings, or non-metallic composites. A particular advantage of corrosion inhibition is that it often can be implemented or changed in situ without disrupting a process. The major industries using corrosion inhibitors are oil and gas exploration and production, petroleum refining, chemical manufacturing, heavy manufacturing, water treatment, and the product refining. The total consumption of corrosion inhibitors in the United States has doubled from approximately $600 million in 1982 to nearly $1.1 billion in 1998(2, 3).

B) Gas and Liquid Transmission Pipelines:

There are more than 528,000 km (328,000 miles) of natural gas transmission and gathering pipelines in United States, 119,000 km (74,000 miles) of crude oil transmission and gathering pipelines, and 132,000 km (82,000 miles) of hazardous liquid transmission pipelines. For all natural gas pipeline companies, the total investment in 1998 was $63.1 billion, from which total revenue of $13.6 billion was generated. For liquid pipeline companies, the investment was $30.2 billion, from which revenue of $6.9 billion was generated. At an estimated replacement cost of $643,800 per km ($1,117,000 per miles), the asset replacement value of the transmission pipeline system in the United States is $541 billion; therefore, a significant investment is at risk, with corrosion being the primary factor in controlling the life of the asset. The average annual corrosion-related cost is estimated at $70 billion, which can be divided into the cost of capital (38 percent), operation and maintenance (52 percent), and failures (10 percent) (4).

C) Petroleum Refining:

The U.S. refineries represent approximately 23 percent of the world's petroleum production, and the United States has the largest refining capacity in the world, with 163 refineries. In 1996, U.S. refineries supplied more than 18 million barrels per day of refined petroleum products. The total annual direct cost of corrosion is estimated at $3.7 billion. Of this total, maintenance-related expenses are estimated at $1.8 billion, vessel turnaround expenses at $1.4 billion, and fouling costs are approximately $0.5 billion annually(3).

1.3 The Scope of Present Work:

1) To study the corrosion in single phase of 1% wt NaCl solutions to assess the effect of changing velocity (262, 349, 438, 525, 600, 612, 800, 1000, 1200 and 1400 rpm) under turbulent flow conditions on corrosion rate by using weight loss and polarization techniques. (i.e. limiting current).

2) To study the corrosion in two--phase (kerosene / water), i.e., the effect of percent of aqueous phase solutions (1%vol., 5%vol., 8%vol. and

16.4%vol.) based on Reynolds number, Weber number and Sauter diameter using weight loss technique .

3) To study the effect of inhibitors(Sodium hexapolyphosphate and Sodium nitrite at difference concentrations on corrosion rate at different rotational velocities in a mixture of (8%vol.) aqueous phase (1%wt.NaCl) / 92%vol. kerosene.

Chapter Two

Corrosion in Petroleum Industry

2.1Corrosion:

The word corrosion comes from Latin "corrodere-to gnaw away". It is the gradual deterioration of a material caused by chemical or electrochemical reaction with environment, gradual destruction of material by physical cause like mechanical wear or abrasion, erosion (from Latin erode-to gnaw away). In some instances, chemical attack accompanies physical deterioration as described by the terms: corrosion-erosion, corrosive wear, or fretting corrosion. Non- metals are not included in the present definition (1).

Corrosion is related to metals. This means that only a half reaction can be a true corrosion reaction. The second half -reaction though it describes a process essential for corrosion. Is not itself a corrosion reaction. By the word degradation in the definition, it is assumed that corrosion is an undesirable process. There are circumstances in which this is not true, in which case the process is not referred to as corrosion. The degradation involves not just a chemical but electrochemical reaction, electron transfer occurs between participants in the environment which is a convenient name to describe all species adjacent to the corroding metal at time of reaction. Environments that cause corrosion are called corrosive. A metal is corrodible (1).

2.2 Classification of Corrosion Process:

A logical and scientific classification of corrosion process, although desirable, is by no means simple. This is due to the enormous variety of the surrounding media, varied heterogeneities in metal and the diversity of corrosion reaction. However, corrosion may be classified on the basis of (1,24) :

1. Mechanisms of corrosion process.
2. The nature of environment.
3. The type of corrosion deterioration.
4. The type of corrosion reaction.

1- Mechanisms of Corrosion Process.

From the standpoint of mechanisms involved only two types of corrosion may be distinguished, viz, (i) chemical corrosion (ii) electrochemical corrosion.

i. Chemical Corrosion:

These types are subject purely to the basic law of chemical kinetics of heterogeneous reaction and refer to case of corrosion (uniform and non-uniform corrosion) which is not accompanied by generation of electric current.

According to this introduction, the chemical corrosion can be classified into (1, 34) :

A. Gaseous corrosion: is corrosion of metal in complete absence of moisture on the surface and this term refers to corrosion of metal at elevated temperature (1).

B. Corrosion in non-electrolytes refers to action on a metal by aggressive organic substance that does not possess significant electrical conductivity (1,34).

ii. Electrochemical Corrosion

This type is subject to basic laws of electrochemical kinetics and generally refers to cases of corrosion of metals in electrolytes with possible generation of galvanic current in the so-called corrosion cell(1).

The corrosion leading to localized attack which may include the following (1, 34) :

1) Galvanic corrosion (or bimetallic corrosion) is caused by contact of two or more metal of different electrochemical potentials (galvanic metal/metal macro cell).

2) Corrosion initiation owing to formation of local corrosion cells (galvanic micro cell within a metal) as follows (1,34) :

i. Structural selective corrosion (graphitization).
ii. Selective dissolution (dezincification, dealuminifcation).
iii. Pitting.
iv. Intercrystalline corrosion.
v. Stress corrosion cracking (SCC).
vi. Corrosion fatigue.
vii. Layer (subsurface) corrosion, or exfoliation.
viii. Thermo- galvanic corrosion.

3) The following are caused by creation of differential aeration cells (oxygen concentration in macro cells) and initiated in the environments (1):

i) Filiform corrosion.

ii) Crevice corrosion.

iii) Deposit corrosion.

iv) Water line corrosion.

4) The following are propagated as a result of conjoint action of active – passive cells and differtial aeration cells, and characteristics of passive metals (1):

i. Pitting.

ii. Crevice corrosion.

iii. Inter crystalline corrosion.

iv. Stress corrosion cracking.

5) Stray current corrosion or electro corrosion. This is caused by the formation of electrolytic cells (macro-cells) (e.g. the corrosion of underground pipe line by stray currents (1).

2- Nature of Environments: corrosion phenomena can be grouped after environment in following ways, viz (1, 34) :

i. Atmospheric corrosion.

ii. Marine corrosion.

iii. Biological corrosion.

iv. Hydrogen cracking.

v. Radiation cracking.

vi. Liquid metal corrosion.

vii. Molten salt corrosion.

viii. Acid corrosion.

ix. Corrosion in electrolytes.

3- Type of Corrosion Deterioration.

It is costmary to subdivide corrosive effect as general or surface corrosion where the attack is evenly distributed along the metal surface. Local corrosion or pitting where attack is concentrated on very small area. Inter crystalline corrosion where attack is centered on the grain boundaries. If all area on the metal surface corrodes at the same or similar rate, it is known as general corrosion, which may be uniform or non- uniform (1).

This may manifest itself in several ways, viz,

i. Stain corrosion.
ii. Pin point corrosion.
iii. Transcrystalline corrosion.
iv. Pitting corrosion.
v. Intercrystalline corrosion.
vi. Sub surface corrosion.

4-Type of Corrosion Reaction (1).

Shreir (1) classified the main types of corrosion reaction as follows:

i. Film free chemical interaction in which there is direct chemical reaction between a metal and its environment.

ii. Electrochemical reaction which involves transfer of charge across an interface. These electrochemical reactions have been further subdivided into three types (1,34) :

A. Inseparable anode/cathode type, for example, the uniform dissolution of metal in acids.

B. Separable anode/cathode type. In this case certain area of metal can be distinguished experimentally predominantly anodic or cathodic.

C. Interfacial anode/cathode type. Here the metal surface remains filmed, one interface will be anode and other will be cathode in metal /gas and metal/vapor reaction.

2.3 Liquid Petroleum Transportation:

Crude oil must undergo refining before it can be used as product. Once oil is pumped from the ground, it travels through pipelines to tank batteries. A typical tank battery contains a separator to separate oil, gas, and water (17).

After the crude oil is separated, the crude oil is kept in storage tanks, where the oil is then moved through large-diameter and long-distance trunk lines to refineries, other storage tanks, tanker ships, or railcar. The pressure in the trunk lines is initiated and maintained by pumps to overcome friction, changes in elevation, or other pressure-decreasing factors. Drag reducing agents (DRAS) are also used to improve throughput by decreasing the effects of friction. Pump stations are located at the beginning of the line and are spaced along the pipeline at regular intervals to adequately propel the oil along. In 1998, there were 80 companies operating crude oil pipelines in the United States. Once oil is refined, product pipelines transport the product to a storage and distribution terminal. The products include gasoline, jet fuel, diesel fuel, ammonia, and other liquids. Other product pipelines transport liquefied petroleum gases (LPG) and liquefied natural gas (LNG) and highly volatile liquids (HVL) such as butane and propane (17).

Once oil is refined, product pipelines transport the product to a storage and distribution terminal. The products Breakout tanks are aboveground tanks used to relieve surges in a liquid pipeline system, or to receive and store liquid transported by a pipeline prior to continued transportation by the pipeline (16, 17, and 18).

2.4 Corrosion in Petroleum Industries:

The petroleum industry contain a wide variety of corrosive environments, for example oilfields are situated in tropical area where high humidity salt bearing winds and air borne sand take the toll of structure and equipment, costly pipe line convey the crude oil often itself activity corrosive toward iron and steel –to long distance either to refineries or to coastal installations where ocean-going tankers may be loaded via submarine pipeline (19, 20).

In the refineries, the vast quantities of cooling water required for their operation, often necessitate the use of sea water, so that intake lines ,condenser and coolers all required special protection against corrosive attack. Finally, the refinery products must be distributed giving rise to special corrosion problems in oceangoing tankers and underground pipeline. It is convenient to group all these environments in relation to corrosion problems, mainly into three broad areas, viz. (1) production, (2) transportation and storage, and (3) refinery units. The corrosion experienced in these areas may be divided into two classes, viz (19, 20).

(1) That due to fluid being produced and hence usually internal, and

(2) That due to environments in which the equipment is placed and hence usually external.

2.4.1 Production:

The internal corrosion experienced in typical oil and gas wells is normally associated with hydrogen sulphide, carbon dioxide and organic acids present in the oil, brine or gas. Internal corrosion is normally referred to as being sour (from" sour oil wells") or sweet ("sweet oil wells") according to the higher or lower sulphur content (mainly H_2S) of the oil(18,19).

Sulphate corrosion result in large deep pits and heavy iron sulphate scale this attack is not restricted to the well equipment only, but continues on into pipelines and tankers also (20).

Corrosion in the absence of hydrogen sulphide is most frequently associated with carbon dioxide as chief corrosive agent; with organic acids contributing to the attack, three methods are used to mitigate this corrosion, viz coated tubing, inhibitors, and special alloy steel. Coated tubing has found the most favor, and air –dried and backed epoxy resins are now being in increasing amount for almost coating installation (21).

The external corrosion of well casing is now recognized as major problems, due the huge repair costs involved. The most common cause of casing corrosion is due to (a) sulphate reducing bacteria, and (b) local concentration cells. A variety of corrosion prevention methods are used to mitigate casing corrosion. These are (21):

1) Adding inhibitors so these are uniformly dispersed over the entire casing.

2) Cathodic protection.
3) Using protective barriers like cementing the casing.

2.4.2 Transportation and Storage:

Petroleum products are transported by tankers, pipeline, railway tank-cars, and tank trucks. The most sever internal corrosion problems occur in tank age. If the crude is sour, early perforation of fixed roof sheets is likely. The use floating or aluminum roofs and coating are the most common preventive method used. The coatings in most common use are coal tar based. The tank may also be subjected to external corrosion attack. This can be prevented with coating or by using cathodic protection. Whether the attack is external or internal or both, providing the tank with a concrete bottoms prevents further corrosion (21).

Ordinary carbon steel which is used for the construction of tankers is exposed to aggressive natural environments of salt water and marine atmosphere. Most serious exposure of steel to sea water occurs during the return (ballast) voyage when the tanks are void of cargo. Although corrosion during cargo voyage is probably relatively small, the nature of different types of cargo has a profound effect on the overall corrosion. Gasoline – carrying tankers present a more severe internal corrosion problems than oil tanks because the gasoline keeps the metal too clean. Oil leaves a film which serves an effective barrier against general corrosion. Internal corrosion of storage tanks is due chiefly to saline water which settles and remains on the bottoms. Coating based on vinyl or epoxy resins and cathodic protection are mainly used. For domestic fuel oil tanks alkaline sodium chromate (sodium nitrate) is an effective inhibitor (1).

Rust formation on the internal walls 0f pipelines caused by water precipitated from products may reduce the line throughout and may give rise to contamination of the products. Formation of the rust may be prevented by lining the pipe or rust formation may be inhibited by the injection of inhibitor (a few part per million) such as amine and nitrite into product stream. Corrosion of external walls of the pipeline varies enormously according to the nature of soil or water, access of oxygen and other factors (21, 22)

2.4.3 Refinery Units:

Crude oil always contains impurities which frequently lead to severe corrosion problems in processing. Condensed products from the distillation process are frequently contaminated with such substance as sulphuric acid, naphthenic acid and hydrogen chloride. Considerable corrosion is, therefore, liable to accrue on the product side of the condenser and cooler tube. Corrosion generally takes the form of uneven general wastage and insoluble corrosion products such as copper sulphate are frequently formed. The most widely used tube martial are brasses with high zinc content. When sea water or brackish water is used for cooling, there is a possibility of corrosion on the water side in the heat exchanger equipment. Carbon steel, stainless steel or monel tube cannot be used, owing to their susceptibility to pitting in sea water. Brass and red brass are used satisfactorily (19).

2.5 Agitation and Mixing of Liquids:

Many processing operations depend for their success on the effective agitation and mixing of fluids. Though often confused, agitation and mixing are not synonymous. Agitation refers to the induced motion of material in a specified way usually in circulatory pattern inside some sort of container (25).

Mixing is the random distribution, into and through one another, of two or more initially separate phases. A single homogenous material, such as tankful of cold water, can be agitated, but it can not be mixed until some other material is added to it.

The term of mixing is applied to variety of operation, differing widely in the degree of homogeneity of the "mixed" material (25).

2.5.1 Purpose of Agitation:

Liquids are agitated for a number of purposes, depending on the objective of the processing step. These purposes include:

1. Suspension solid particles.
2. Blending miscible liquids, for example, methyl alcohol and water.
3. Dispersing a gas through the liquid in small bubbles.
4. Dispersing a second liquid, immiscible with the first, to form an emulsion or suspension of line drops.
5. Promoting heat transfer between liquid and a coil or jacket (25).

2.5.2 Agitated Vessels:

Liquids are most often agitated in some kind of tank or vessel, usually cylindrical in form and with a vertical axis. The top of the vessel may be open to the air, more usually it is closed. The proportions of the tank vary widely, depending on the nature of the agitation problem. A standardized design such as that shown Fig. (2.1), however, is applicable in many situation. The tank bottom is rounded, not flat, to eliminate sharp corner or regions into which fluid currents would not penetrate. The liquid depth is approximately equal to the diameter of the tank. An impeller is mounted on an overhung shaft, that is, a shaft supported form above (26). The motor drives shaft. Sometimes directly connected to the shaft but more often connected to it through a speed-reducing gearbox. Accessories such as inlet and outlet lines, coils, jackets, and wells thermometer or other temperature measuring devices are usually included.

The impellers cause the liquid to circulate through the vessel eventually return to the impeller. Baffles are often included to reduce tangential motion.

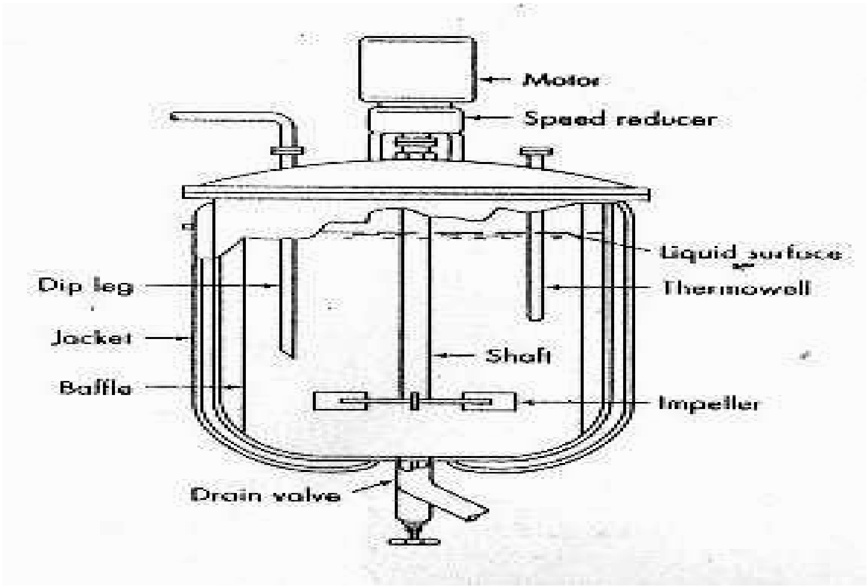


Fig. (2.1) Typical Agitation Process Vessel (26).

2.5.3 Impellers:

Impeller agitators are divided into two classes. Those that generate currents parallel with the axis of the impeller shaft are called axial flow impeller and those that generate currents in radial or tangential directions are called radial flow impellers.

The three main types of impeller for low-to moderate viscosity liquids are propellers, turbine, and high efficiency impellers. Each type includes many variations and subtype, which are not considered here. For very viscous liquids, the most widely used impellers are helical impellers and anchor agitators (25).

2.5.4 Turbine:

Five types of turbine impeller are shown in Fig. (2.2), the simple straight blades turbine shown Fig. (2.2.b) pushes the liquid radially and tangentially with almost no vertical motion at the impeller. The currents that generated travel outward to the vessel wall and then flow either upward or downward. Such impellers are sometimes called puddles. In process vessel they typically turn at 20-150 rpm. The disk turbine, with multiple straight blades mounted on a horizontal disk as shown in Fig. (2.2.a, b, d.), like the straight blade impeller, creates zones of high shear rate; it is especially useful for dispersing a gas in liquid. Also widely use for gas dispersion is the concave blade CD-6 disk turbine as shown in Fig. (2.2.c). A pitch blade turbine as shown in Fig. (2.2.e) is used when good overall circulation is important (25).

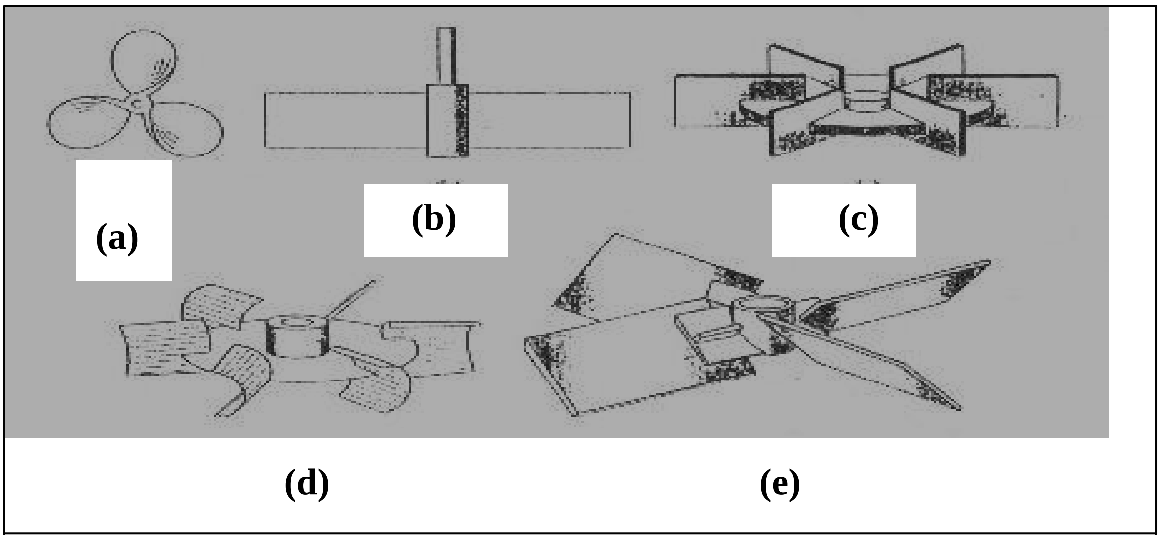


Fig.(2.2) Impellers for Liquids of Moderate Viscosity:(a) Three Blade Marine Propeller(b) Simple Straight Blade Turbine(c) Circle Disk Turbine (d) Concave Blade CD-6 Impeller(e) Pitched Blade Turbine (25).

2.5.5 Standard Turbine Design:

The designer of an agitated vessel has unusually large number of choices to make as to type and location of the impeller. The proportions of the vessel, the number and properties of the baffles, and so forth each of these decisions affect the circulation rate of the liquid, the velocity patterns, and the power consumed. As starting point for design in ordinary agitation problems, a turbine agitator of the type as shown in Fig. (2.3) is commonly used. Typical proportions are in Table (2.1):

Table (2.1) Design Equations of Agitator (Vessel) (25) .

$$\frac{D_a}{D_t} = \frac{1}{3} \quad , \quad \frac{H}{D_t} = 1 \quad , \quad \frac{J}{D_t} = \frac{1}{12}$$

$$\frac{E}{D_t} = \frac{1}{3} \quad , \quad \frac{W}{D_a} = \frac{1}{5} \quad , \quad \frac{L}{D_a} = \frac{1}{4}$$

Where:

D_a: diameter of impeller.

D_t: diameter of tank (cylinder).

E: distance from center of impeller to bottom of tank (cylinder).

H: height of tank (cylinder).

J: width of baffles.

L: length of impeller.

W: width of impeller.

The number of baffles is usually four, the number of the impeller blades ranges from (4-16) but it is generally (6-8). Special situation may, of course, dictate different proportions from these listed above: it may be advantageous, for example, to place the agitator higher or lower of the tank, or a much deeper tank may be needed to achieve the desired process result. The listed standard proportions, nonetheless, are widely accepted and are the basis of many published correlation of agitator performance (25).

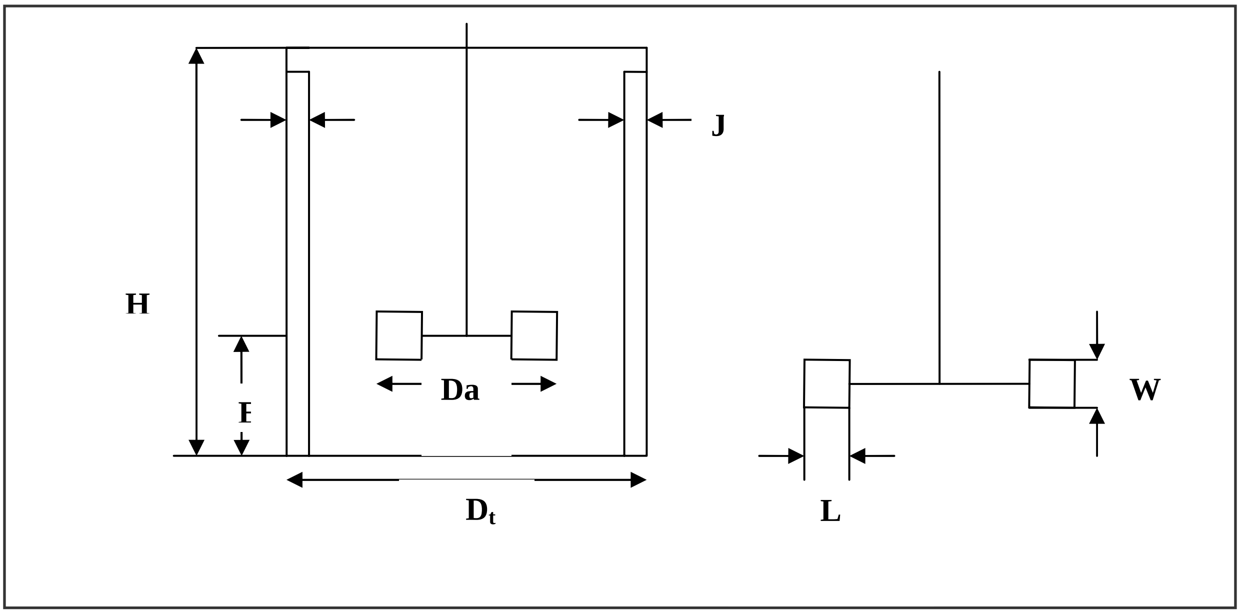


Fig. (2.3) Measurements of Turbine (25).

2.5.6 Mixing of Liquids:

The key to effective mixing for liquids is to create multiple flow patterns in the fluid being mixed. This motion is imparted to a fluid "pocket" as it contacts the blade on the rotating agitator. The momentum of this pocket will keep it in motion until it either contacts the wall of the vessel, or runs into another moving pocket. The nature of the liquids and suspensions themselves affect fluid flow and mixing properties as well. Specific properties of concern are the fluid densities, viscosity, temperatures, pressures, and volatility. These properties have been related in a dimensionless formula called the Reynolds Impeller Number defined here:

$$Re = \frac{\rho \times D_a^{\,2} \times N_I}{\mu} \tag{2.1}$$

where:

D_a = impeller diameter (m)

N_I = rotational speed of the impeller (rps)

ρ = fluid density (kg/m^3)

μ = fluid viscosity (kg/m.s.)

Some observations regarding the Reynolds impeller number:

A. If Re <= 10, flow is laminar. If Re > 10000, flow is turbulent, and between 10 and 10000 there is a transition range where both laminar and turbulent flow elements exist.

B. Doubling the impeller diameter will quadruple Re. This follows, as the impeller will sweep an area four times larger when the diameter is doubled.

C. Temperatures and pressures are accounted for in Re as they affect both density and viscosity. These factors are useful for sizing and selections of tanks, impellers, and the associated driving equipment (29).

2.5.7 Liquid- Liquid Dispersions:

Despite these variation, a basic relation exists between hold up **(**ψ**)** (the volume fraction of dispersed phase in the system), the interfacial area (**a**) per unite volume, and the bubble or drop diameter **(**D_P). If the total volume of dispersion is taken as unity, the volume of dispersed phase, by definition, is (ψ). Let the number of drops or bubbles in this volume are **(**n**).** Then if all the drops or bubbles were spheres of diameter **(**D_P**)**, the total volume would be given by (29):

$$\Psi = \frac{\Pi \times n \times D_P^{\,3}}{6} \tag{2.2}$$

where:

Ψ: the volume fraction of dispersed phase in the system

n: the number of drops or bubbles in this volume

D_P: the drops or bubbles diameter (m)

The total area of drops or bubbles in this volume would be

$$a = \Pi \times n \times D_P^{\,2} \tag{2.3}$$

Dividing equation (2. 3) by equation (2. 2) and rearranging give

$$a = \frac{6 \times \Psi}{D_P} \tag{2.4}$$

The interfacial area per unit volume of dispersion is proportional to the hold up and inversely proportional to the drop size. Usually large area is desired to give high rate of mass transfer or reaction.

To account for a distribution of drops size, an equivalent average diameter **(**D_S**)** is used based on the total volume and total area of dispersed phase. The diameter **(**D_S**)** is the volume surface mean diameter (the Sauter mean diameter), and it can be calculated from equation (2.5) if the drop size distribution is known. If the interfacial area and holdup can be measured independently, the average drop size can be determined by using equation (2.6):

$$D_S = \frac{\sum_{i=1}^{n} n_i \times D^3{}_P}{\sum_{i=1}^{n} n_i \times D^2{}_P} \qquad (2.5)$$

$$D_s = \frac{6 \times \Psi}{a} \qquad (2.6)$$

where

Ψ: volumetric fraction gas or liquid holdup in dispersion (dimensionless)

n_i : the number of particle in each size range

D_{S}: the volume surface mean diameter (the sauter mean diameter) (m)

D_P: the drops or bubbles diameter (m)

Various types of equipment can be used to disperse liquid, say kerosene in water (an immiscible liquid). Astride tank: liquid-liquid dispersions have a high interfacial area, but they are not stable, since the drops will settle or rise and coalesce in the absence of agitation. Stable emulsions of very small droplets can be formed in colloid mills or other high shear device (28).

In a stirred tank the average drop size depends on a balance between breakup of large drops in regions of high shears and drop coalescence in regions of lower shear. Shear stress at the drop surface tends to deform the drop, and deformation is resisted by the interfacial tension and the viscosity of the dispersed phase. An important dimensionless group is the Weber number, denoted by (We) see equation (2.7), which for stirred tank is the ratio of the flowed kinetic energy at the impeller tip speed to surface tension stress based on impeller diameter (D_a) (28).

$$We = \frac{\rho_C \times (N_I)^2 \times D_a}{\sigma} \tag{2.7}$$

where

We**:** Weber number **(**dimensionless)

$\rho_{c:}$ density of continuous phase (Kg/m^3)

σ**:** interfacial tension **(**N/m)

D$_{\mathbf{a:}}$ impeller diameter (m)

N$_I$: rotational speed of the impeller (rps)

One of the several proposed correlation for the dispersion of the liquid with stander six blade turbines is $^{(25)}$:

$$\frac{D_S}{D_a} = 0.058 \times (1 + 5.4 \times \psi) \times We^{-06} \tag{2.8}$$

where:

D$_S$: volume surface mean diameter of drops or bubbles (m).

D$_a$: impeller diameter (m)

Ψ: volumetric fraction gas or liquid holdup in dispersion (dimensionless)

We: Weber number (dimensionless)

The term (1+5.4 Ψ) reflects the increase in frequency of coalescence with increasing droplet concentration. Equation (2.8) is based on the data for dispersion of low viscosity liquid in small tank. When the dispersed phase is quite viscous, large drops are produced, because the viscous drops resists deformation. A correlation factor $(\mu_d/\mu_{c)}{}^{0.1}$ (where μ_c: is the viscosity of continuous phase in liquid – liquid dispersion, $\mu_{d:}$ the viscosity of dispersed phase) could be added to equation (2.8) for a rough estimate of the viscosity effect. There is no data for large tank, but some what greater average drop size might be expected since the increased circulation times would give greater chance for coalescence $^{(28)}$.

Static mixer can also used to make liquid- liquid dispersions. By considering the surface energy of a drop and the disruptive energy due turbulent velocity fluctuations, (D_S) is predicted to vary with fractional power of the Weber number and friction factor (pipe flow) (25):

$$\frac{D_S}{d} = c \times We^{-0.6} \times f^{-0.4} \tag{2.9}$$

where

We: Weber number and it is equal $We = \frac{\rho \times V^2 \times d}{\sigma}$ (dimensionless)

ρ: density of continuous phase (Kg/m^3)

c: constant

d: pipe diameter (m)

V: average velocity (m/s.)

f: friction factor is equal $\frac{\Delta P \times D}{2 \times \rho \times V^2 \times L}$ (dimensionless)

Data for law viscosity drops dispersed in water in small Kenics mixer (D=0.5 to 1 in.) can be fitted to equation (2.9) with(C= 0.35).

The friction factor was (0.42) for (Re =10,000 to 20,000). Much larger drops were formed when the viscosity was (20 to 200 gm/m.s), but data are scattered and the effects of (Re) and (Ψ) are also uncertain (28).

2.5.8 Flow Pattern in Agitation:

The flow pattern in agitation tank depends upon the fluid properties, the geometry of the of the tank, type of baffles in the tank, the characterization of the liquid, especially its viscosity, the agitator itself, the liquid velocity at any point has three components, and the overall flow pattern in the tank depends on the variation in these three velocity components from point to point. If an agitator is mounted vertically in the center of tank with no baffles, a swirling flow patterns usually develops. Generally this is undesirable, because excessive air entrainment, development of a large vortex and surging, especially at high speed. The turbine impeller drives the liquid radially against the wall, where it divides, with one portion flowing upward, near the surface and back to the impeller, the other flowing downward.

2.5.9 Phase Formation and Phase Inversion:

In case of batch agitation, the gravity forces will cause two immiscible liquids to lie in layer above the other as long as the agitator is at rest. The problem of what types of dispersion will result when the equipment is started up, and hence the problem of which of two fluids will form the continuous phase and which disperse phase, still cannot be answered in general. The choice between these two types of dispersions sometime has an important effect on the interfacial area which results. Available data in the literature permit the prediction to be (28):

1. In general the fluid which surround the agitator when the latter is at rest become the continuous phase.
2. If the two liquids are present with very different volume fractions, the one with the smaller volume fraction is dispersed.
3. If the volume fraction of the two liquid are similar (0.5±0.2) the rate of rotation and the" previous history" of the dispersion are important in deciding which phase become dispersed.

2.6 Break Up and Coalescence of Droplets in Agitated Dispersion:

In dispersion of two liquids by turbulent agitation, break up and coalescence of droplet occur continuously. Break up may be caused either by viscous shear force or by turbulent pressure fluctuation. For a known flow field both break up and coalescence have been evaluated theoretically.

Coalescence occurs when two droplet collide. If the droplet pair is exposed to turbulent pressure fluctuation, and kinetic energy of adhesion between them, the contact will be broken before coalescence is completed.

2.7 Petrochemical Corrosion under Single and Multiphase Flow:

Corrosion –erosion normally occurs under turbulent flow conditions. The flowing fluid may be single phase see Fig. (2.4), as in corrosion of copper tubing by potable water (5, 6, 7) see Fig. (2.5). Multiphase flows see Fig.(2.6) with various combinations of gas, water, oil, and sand can cause sever corrosion of oil and gas production system(8,9,10), Figs. (2.7, 2.8, and 2.9).

These may be classified into two general categories, viz. (1) those present crude oil, and (2) those associated with process. The most severe corrosion problems occur under conditions of disturbed turbulent flow (11, 12) at sudden changes in flow system geometry, such as bends, heat exchanger, tube inlet, orifice plate, valve fitting, and in turbo machinery including pumps, compressor, turbine, and propellers. Surface defects in the form of small protrusion or depression such as corrosion pits, deposit, and weld beads can give rise to distributed flow on smaller scale but sufficient to initiate corrosion (13,14).

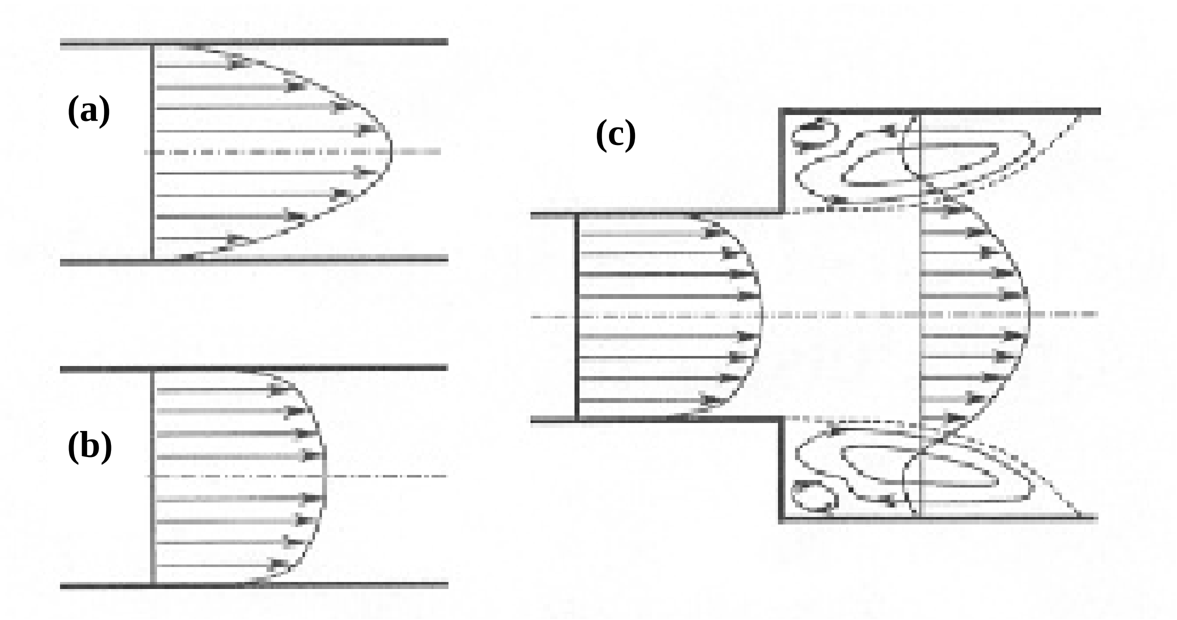


Fig. (2.4) Single Phase Pipe flow (a) Developed Laminar Flow, Showing Parabolic Velocity Profile.(b) Developed Turbulent Flow, Showing Logarithmic Profile With Large Gradients Near the Wall.(c) Developed Turbulent Flow with Separation and Recirculation, Showing Complex Velocity Field (5).

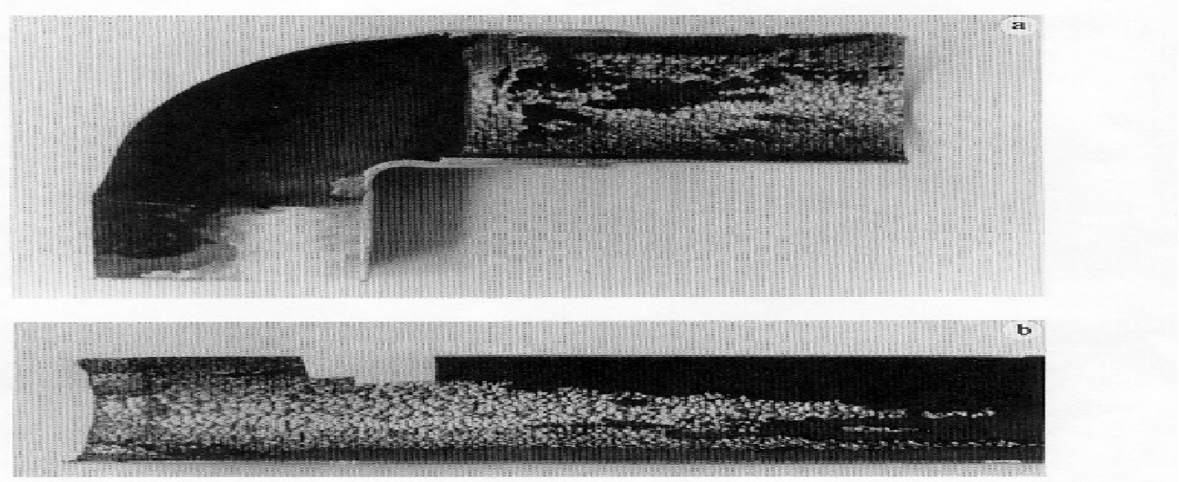


Fig. (2.5) Erosion-Corrosion of (53 mm Diameter) Copper Tubing by Water (a) The Attack at the Step Where the Tubing Fitted into Elbow. (b) Once Started, the Attack Progressed Along the Tube as Result of Additional Disturbed Flow Created by the Corrosion Surface (6).

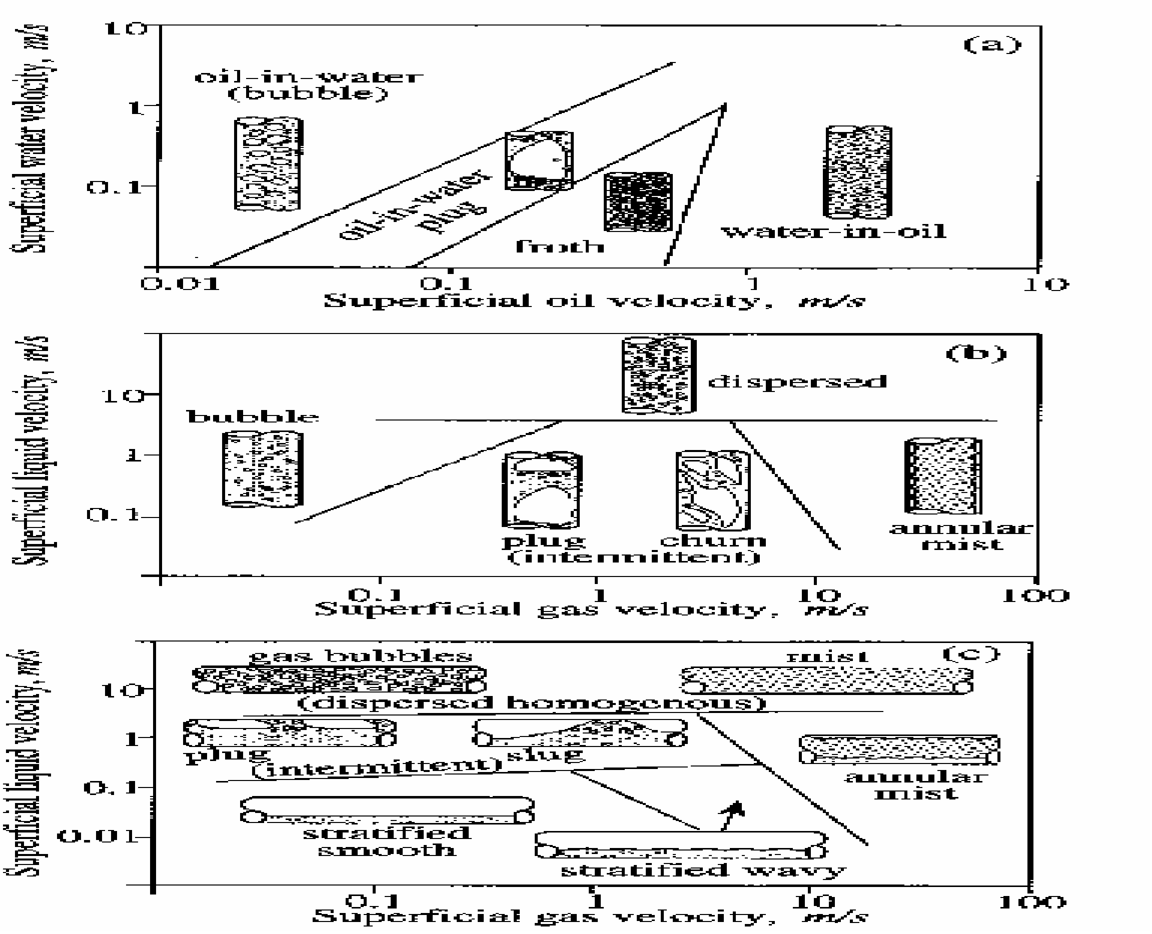


Fig.(2.6) Qualitative Two Phase Flow Structure in Pipe (a) Oil –Water in Vertical Pipe (b) Liquid -Gas Vertical Pipe (c) Liquid -Gas in Horizontal Pipe (6, 7).

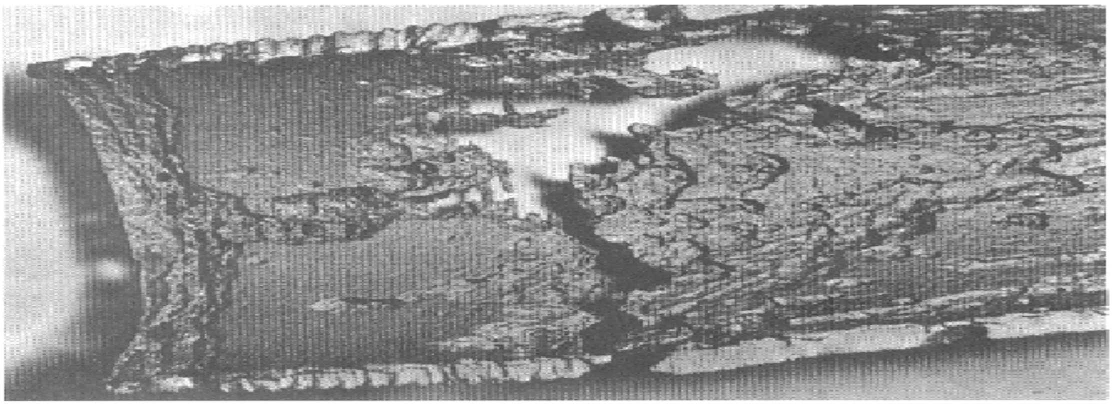


Fig.(2.7) Corrosion of (14 mm Diameter) API L-80 Oil Well Tubing. Environment: Crude Oil/CH_4/$CO_2$and (1%wt.) H_2O: Temperature (200 ^oC), Velocity (6.4-7.9)m/sec, Corrosion Rate >10 mm/y (9).

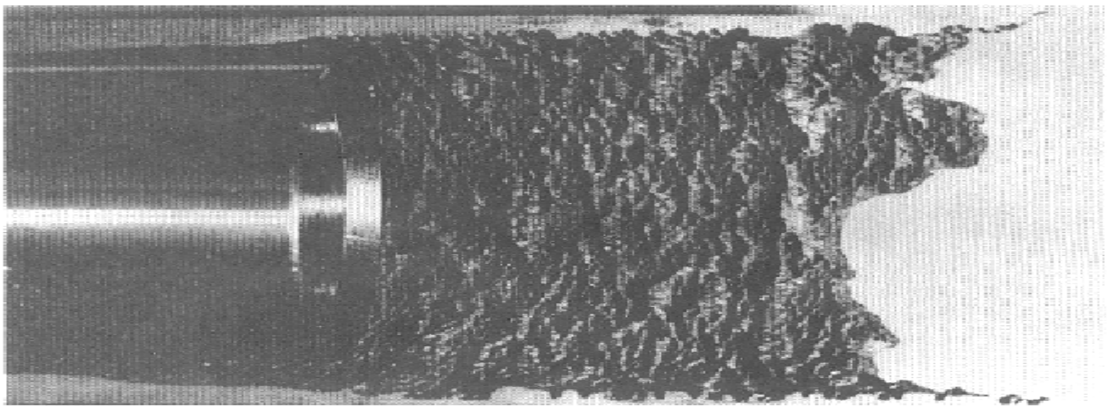


Fig.(2.8) Impingement-Type Corrosion of AISI(4140(15 mm Flow Coupling and Subsurface Safety Valve in Natural Gas Condensate Production, Minor Species CO_2,H_2O, Temperature(79 ^oC),Velocity Value(9 m/s.) (9).

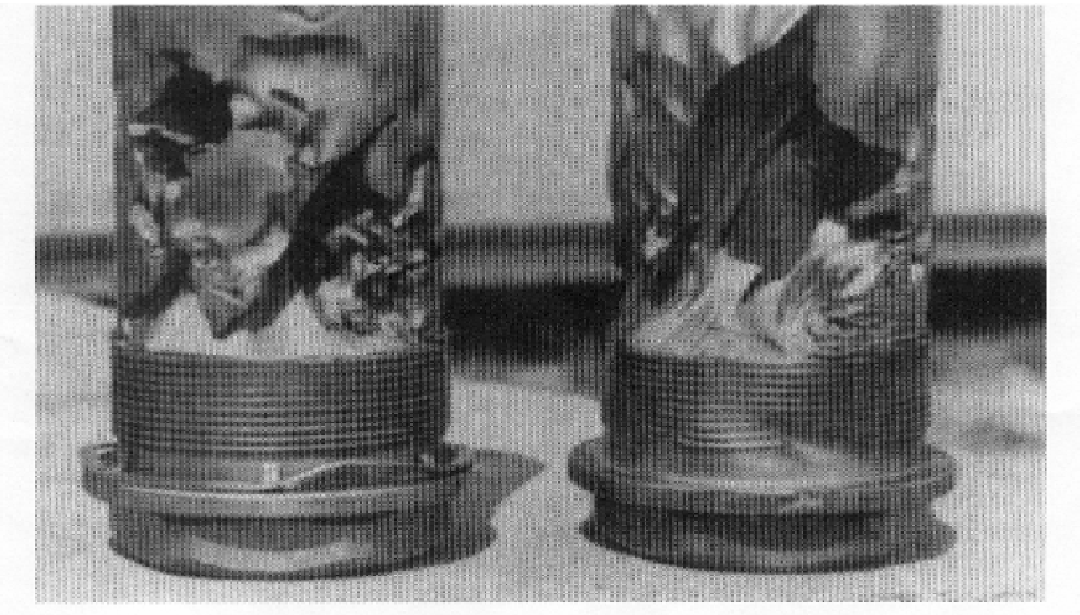


Fig. (2.9) Erosion of Tungsten Carbide Choke Beans Inside Steel Holder from an Oil Well with Sand Production. Note the Highly Polished, Streamline Appearance of the Corrosion Pattern Sub-Critical Flow Occurred in This Well and These Assemblies (10).

Chapter Three

Corrosion and Effect of Environmental Conditions

3.1 Introduction:

Corrosion is the degradation of a metal by an electrochemical reaction with its environment (30, 31), or it is an interaction of a metal with its surroundings (32). Corrosion in aqueous and atmospheric environment is an electrochemical process because corrosion involves the transfer of electrons between a metal surface and an aqueous electrolyte solution. It results from the overwhelming tendency of metals to react electrochemically with oxygen, water, and other substances in the aqueous environment (33).

The importance of corrosion studies is threefold. The first area of significance is economic including the objective of reducing material losses resulting from the corrosion of piping, tanks, metal components of machines, ships, marine structures and so on. The second area is improved safety of operating equipment, which through corrosion may fail with catastrophic consequences. The third is conservation applied primarily to metal resources (34).

The majority of corrosion reactions in aqueous environments occur by an electrochemical mechanism. So, many factors affect the distribution, rate, and mode of corrosion that selection of an appropriate material for particular application requires a sound understanding for the fundamental processes which occur during chemical attack (35).

3.2 Partial Anodic and Cathodic Reactions:

In the corrosion process, metal atoms in crystalline lattice are transformed to metal ions in the corrosion environment with the reaction:

$$M \rightarrow M^{+} + e^{-} \tag{3.1}$$

This is chemical oxidation. By Definition, this process occurs on an area of metal surface called an anode. An oxidation of the type written in Eq.(3.1) cannot occur without a corresponding reaction somewhere in the system. The reduction reaction consumes electrons and by definition occurs at cathode area. Both the oxidation and reduction reactions proceed at the same rate during corrosion. Any change in the system, which affects the rate of one, must of necessity affect the other. Thus attempts at reducing corrosion rates may be directed toward changing either local oxidation or local reduction rates.

The anodic reaction is dissolution of the metal to form either soluble or insoluble ionic products or an insoluble compound of metal usually an oxide. Several cathodic reactions are possible depending on what reducible species are present in the solution. Typical reactions are the reduction of dissolved oxygen gas or the reduction of hydrogen ions

$$O_2 + 2H_2O + 4e = 4OH^{-} \qquad \text{neutral environment} \tag{3.2}$$

$$O_2 + 4H^{+} + 4e = 2H_2O \qquad \text{acidic environment} \tag{3.3}$$

$$2H^{+} + 2e = H_2 \qquad \text{acidic environment} \tag{3.4}$$

The flow of electrons between the corroding anodes and non-corroding cathodes forms the corrosion current, the value of which is determined by the rate of production of electrons by the anodic reaction and their consumption by the cathodic reaction. A driving force that causes the electrons to flow between anode and cathode is the difference in potential between the anodic and cathodic sites. This difference exists because each oxidation or reduction reaction has associated with it a potential determined by the tendency for the reaction to take place spontaneously. The potential is a measure of this tendency (32). The cathodic process is most important to the man in the field because physical and chemical factors in the environment markedly affect the rate of electrochemical reaction. A thorough knowledge of the manner in which the corrosion rate is affected by the cathodic process is most important to successful design and material selection (35).

3.3 Polarization:

When the metal is not in equilibrium with a solution of its ions, the electrode potential differs from the equilibrium potential by an amount known as the polarization. Other terms having equivalent meaning are overvoltage and overpotential. The symbol commonly used is (η). Polarization is an extremely important parameter because it allows useful statements to be made about the rates of corrosion process. In practical situations, polarization sometimes defined as the potential change away from some other arbitrary potential and in mixed potential experiments, this is the free corrosion potential (31).

The change in the electrode potential from equilibrium potential depends on the magnitude of the external current and its direction. The direction of potential change always opposes the shift from equilibrium and hence opposes the flow of current or is of galvanic origin. For flows in a galvanic cell, for example, the anode always becomes more cathodic in potential and the cathode becomes more anodic, the difference of potential becoming smaller (34).

3.3.1 Activation Polarization:

For any given electrode process under specified conditions, charge transfer at a finite rate will involve an activation overpotential (η^A), which provides the activation energy required for the reactant to surmount the energy barrier that exists between the energy states of the reactant and product. The activation energy is given by (35, 36):

$$E^A = Z \times F \times \eta^A \tag{3.5}$$

where (E^A)is in joules per mole and (Z)is the number of electrons involved in one act of the rate-determining step. The activation overpotential, and hence the activation energy varies exponentially with the rate of charge transfer per unit area of electrode surface, as defined by the well-known Tafel equation (23, 35):

$$\eta^A = a + b \log i \tag{3.6}$$

where (i) is the current density, and (a) and (b) are the Tafel constants which vary with the nature of the electrode process and electrolyte solution. Thus (η^A) will be linearly related to (log i) at overpotentials greater than 0.01 V and the position and slope of the curve will be dependent on the magnitudes of (a) and (b), which are in turn dependent on the equilibrium exchange current density (i_o), the transfer coefficient α and the number of electrons (Z) involved in one act of the rate-determining step. The total equation for cathodic process can be expressed in the form:

$$\eta_c^A = \frac{R \times T}{\alpha_c \times Z \times F} \ln i_O - \frac{R \times T}{\alpha_c \times Z \times F} \ln i_C \tag{3.7}$$

And since 2.303 R×T/F ln x=0.059 log x at 25 °C.

$$\eta_c^A = \frac{0.059}{\alpha_c \times Z} \log i_O - \frac{0.059}{\alpha_c \times Z} \log i_C \qquad \text{at } 25\ ^{o}\text{C.} \tag{3.8}$$

where (η_c^A) is the activation overpotential of the cathodic process. Similarly the activation overpotential of the anodic process is given by $^{(37)}$:

$$\eta_a^A = \frac{0.059}{\alpha_a \times Z} \log i_a - \frac{0.059}{\alpha_a \times Z} \log i_O \qquad \text{at } 25\,^{o}\text{C.} \qquad (3.9)$$

The overpotential is displacement of the potential from its reversible value, i.e.

$$\eta = E_P - E_r \qquad (3.10)$$

Since $E_{p,c} < E_{r,c}$ (more negative)

$$\eta_C = E_{P,C} - E_{r,C} < 0 \qquad (3.11)$$

Hence, the cathode overpotential is always negative. Since $E_{p,a} > E_{r,a}$ (more positive), then

$$\eta_a = E_{P,a} - E_{r,a} > 0 \qquad (3.12)$$

The anode overpotential is always positive $^{(37)}$. Eq. (3.6) can be written in the following form $^{(23)}$:

$$\eta = \pm \beta \log \frac{i}{i_O} \qquad (3.13)$$

where (β) is constant and is frequently termed β-slope or Tafel constant.

It is generally accepted that the activation polarization is the controlling factor during metal reactions $^{(23, 37)}$ Activation polarization is a function of the nature and concentration of the species being reduced, surface roughness and composition, and temperature. In addition it is sensitive to traces of reducible impurities in the system $^{(35)}$.

3.3.2 Concentration (Transport or Diffusion) Polarization:

The rate of an electrode reduction also depends on mass transfer, i.e., the rate at which the reactant is transported to the electrode and the rate at which the product is transported away from the electrode. Transport through the solution to and from the metal surface occurs by the diffusion, ionic migration (transport of electrical charge through the solution), and convection. Of this diffusion through the thin layer of the solution adjacent to the metal surface, the diffusion layer (δ_d) is usually of greatest significance. However, this is not always the case in practical systems, particularly where dissolved oxygen is the cathodic reactant and in certain circumstances the rate of diffusion through the bulk solution to the metal - solution interface may be rate determining. The limiting current density (the maximum possible rate/unit area under the conditions prevailing) for cathodic process is given by:

$$i_L = \frac{D \times Z \times F \times C_b}{\delta_d \times (1 - t+)} \tag{3.14}$$

the term (1- t_+) can be neglected if ions other than the species involved in the electrode process are responsible for ionic migration. The equation for concentration polarization is given by (23, 36):

$$\eta^C = \frac{R \times T}{Z \times F} ln(1 - \frac{i}{i_L}) = \frac{R \times T}{Z \times F} ln \frac{C_S}{C_b} \tag{3.15}$$

$$\eta^C = \frac{0.059}{Z} log(1 - \frac{i}{i_L}) \qquad \text{at } 25\ ^\circ\text{C} \tag{3.16}$$

and it is evident that the smaller the (i_L) the greater the magnitude of the overpotential due to concentration (transport). Unlike activation polarization, concentration polarization is not controlled by the kinetics of charge transfer and the magnitude of (η^c) will be the same for any cation (providing Z, D, Cb, are the same) and metal surface. Thus the rate - controlling parameter in the concentration polarization is (i_L), and it will be seen that any factor in Eq.(3.14) that causes (i_L)to increase will result an increase in corrosion rate, providing the latter is solely determined by the kinetics of the cathodic process(23). A graphical representation of Eq. (3.15) is shown in Fig.(3.1). Concentration polarization does not become apparent until the net reduction current density asymptotically approaches the limiting current density. Examination of Eq.(3.15) indicates that when the net reduction current is equal to the limiting current, concentration polarization is equal to infinity, and when the net reduction current is very small the concentration polarization is negligible(23,36).

3.3.3 Combined Polarization:

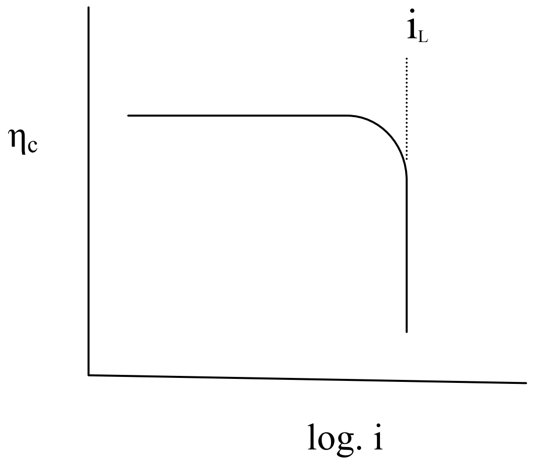
Both activation and concentration polarization usually occur at an electrode. At low reaction rates, activation polarization usually controls, while at higher reaction rates concentration polarization becomes controlling. The total polarization of an electrode is the sum of the contribution of activation polarization and concentration polarization

$$\eta_T = \eta^A + \eta^C \tag{3.17}$$

where (η_T) is total overvoltage. During anodic dissolution, concentration polarization is not a factor and the equation of kinetics of anodic dissolution is given by: $\eta_{diss} = \beta \log \frac{i}{i_o}$ (3.18)

During reduction process such as hydrogen evolution or oxygen reduction, concentration polarization becomes important as the reduction rate approaches the limiting diffusion current density. The overpotential for reduction process is given by combining Eqs.(3.13) and (3.15) with appropriate signs:

$$\eta_{red} = -\beta \log \frac{i}{i_O} + \frac{R \times T}{Z \times F} \log(1 - \frac{i}{i_O}) \tag{3.19}$$



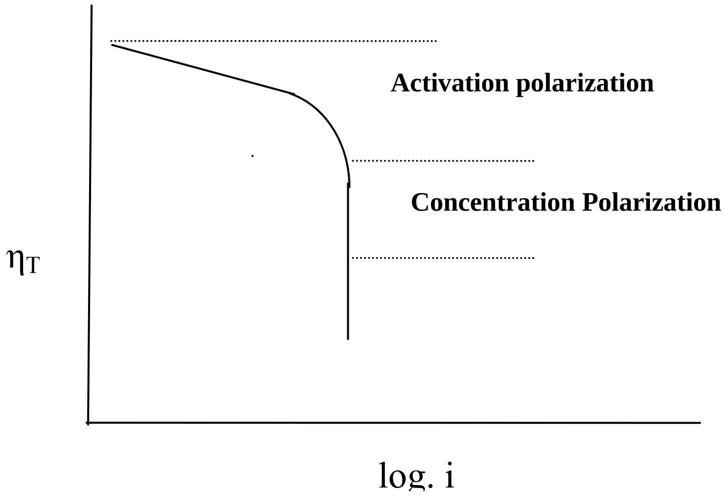


Fig. (3.1) Concentration Polarization (23). **Fig.(3.2) Combined Polarization** (23)

Eq. (3.19) is graphically illustrated in Fig. (3.2) which applies to Reduction reaction, and Eq.(3.18) applies to almost all anodic dissolution reactions. Exceptions to Eq.(3.18) are metals which demonstrate active-pasive behavior. Using only three basic parameters namely, β, i_o, and i_L the kinetics of virtually every corrosion process can be precisely described (23).

3.3.4 Resistance Polarization:

Since in corrosion the resistance in metallic path for charge transfer is negligible, the resistance overpotential η^R is determined by factors associated with the solution or with the metal surface. Thus resistance overpotential may be defined as

$$\eta^R = I \times (R_{soln} + R_F) \qquad (3.20)$$

where (R_{soln}) is the electrical resistance of the solution which is dependent on the electrical resistivity (Ω.cm) of the solution and (R_f) is the resistance produced by surface of the site. Thus in addition to the resistivity of the solution, any insulating film deposited either at the cathodic or anodic sites, that restricts or completely blocks the contact between the metal and the solution, will increase the resistance overpotential, although the resistivity of the solution is unaffected.

3.4 Limiting Current Density:

The limiting current is defined as the maximum current that can be generated by a given electrochemical reaction, at a given reactant concentration, under well-established hydrodynamic conditions, in the steady state. This definition implies that the limiting rate is determined by the composition and transport properties of electrolytic solution and by the hydrodynamic conditions at the electrode surface .

In the mass transfer boundary layer (or diffusion layer), whose thickness is indicated by (δ_d), the reactant concentration varies from the bulk value to practically zero at the electrode, this is the limiting-current condition. Determination of mass transfer coefficient involves the measuring of limiting currents in the cathodic reaction process. Measurement of limiting currents is an experimental technique that has been quite widely employed in mass transfer experiments. It is relative simplicity and flexibility make limiting current method a powerful tool in experimental studies of forced and free convection. At the limiting current the rate of transport of reactant to the interface is smaller than the rate at which it can be potentially consumed by the charge transfer reaction; as a result, at the interface the concentration of this species approaches zero (38). The flux of reacting species is given by:

$$N_A = \frac{i_L}{Z \times F \times (1 - t_+)} \qquad (3.21)$$

When concentration of the reacting species relative to the total ionic concentration of the electrolyte is small, $t_+ << 1$, Eq.(3.21) becomes;

$$N_A = \frac{i_L}{Z \times F} \qquad (3.22)$$

from the measured current, a mass transfer coefficient, K , defined by;

$$N_A = K \times (C_b - C_S) \tag{3.23}$$

may be calculated. Since at the limiting current we set $C_s = 0$, hence

$$K = \frac{i_L}{Z \times F \times \Delta C} \tag{3.24}$$

3.5 Differential oxygen concentration:

Corrosion can often take place in pipelines or under equipment in which aqueous liquids are being transported (flow differential oxidation corrosion). This usually occurs at positions where there is difference in velocity between different potions of the liquid, i.e. at bends, nozzles, constriction, and etc. when liquid containing oxygen flows rapidly past a given section of pipe the oxygen can be supplied far more quickly to the surface than it can in parts where the liquid is comparatively stagnate .in consequence the stagnant part of the pipe become the anode and corrodes (1).

The section of the pipe in which water moves rapidly becomes the cathode. This form of corrosion can be avoided only by insuring that the water is properly deoxygenated. Differential oxidation corrosion, of particular importance to the oil industry or other industries where organic liquids are being stored in steel vessel where corrosion takes place at the bottom of tanks if traces of moisture have settled .The bottom of the tank then becomes the anode and the reaction-taking place,

$$H_2O \rightarrow H^+ + OH^- \tag{3.25}$$

$$Fe \rightarrow Fe^{++} + 2e^- \tag{3.26}$$

$$Fe^{++} + 2OH^- \rightarrow Fe(OH)_2 \tag{3.27}$$

the area of the vessel in contact with the oil or other organic liquids becomes the cathode. Since this area is very large and is kept from corroding by the oil film on top, it acts as a most effective cathode. The oil has oxygen dissolved in it and, in general the amount is sufficiently large to cause a rapid cathode reaction (1):

$$4H^{+} + 4\ e + O_2 \rightarrow 2H_2O \qquad (3.28)$$

as oil often contain NaCl and other salts, reaction can very rapid, the same kind of corrosion is often found in oil pipelines and other equipment containing organic liquids if the design includes an elbow where water can collect. The rate of corrosion that takes place at the bottom of oil filled vessel is usually rapid because anodic area is small and cathodic area is large (1).

Corrosion of this kind may be prevented by the following methods:

1) By constructing the bottom of oil by a metal that is cathodic to steel
2) By using glass drainage vessel at the bottom of vessel to enable any water to be drawn off.
3) By using an electric warning device embodying a circuit gap, which becomes conducting when immersed in water or another aqueous solution.

3.6 Nernst Diffusion Layer:

One of the first approaches to mass transfer in electrode processes was given by Nernst in 1904(38). He assumed a stationary thin layer of solution in contact with electrode. Within this layer it was postulated that diffusion alone controlled the transfer of substances to the electrode. Outside the layer, diffusion was negligible and concentration of electro-active material was maintained at the value of bulk concentration by convection. This hypothetical layer has become known as “Nernst diffusion layer (δ_d)”. Fig. (3.3) gives a schematic diagram of this layer. Nernst assumed that the concentration varied linearly with distance through the layer. The thickness of this layer is given by:

$$\delta_d = \frac{D}{K} \qquad (3.29)$$

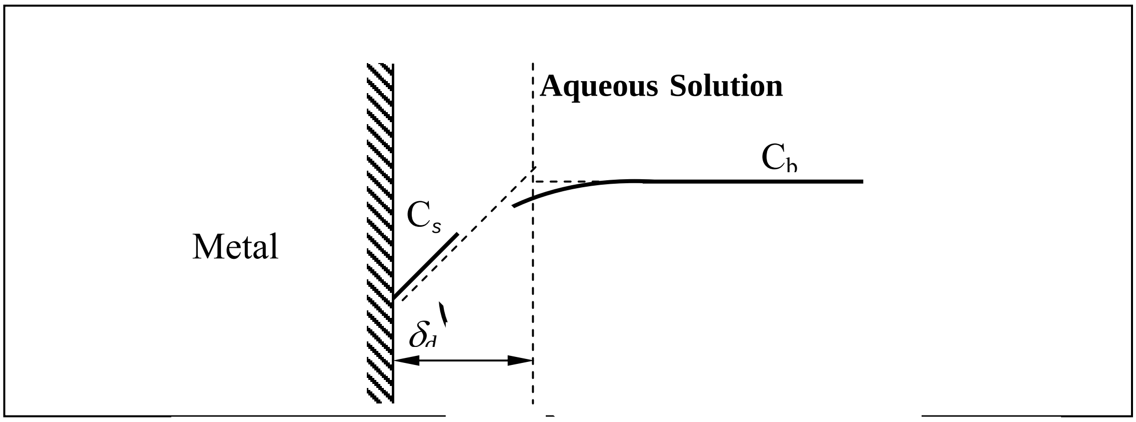


Fig.(3.3) Nernst Diffusion Layer (38).

The diffusion layer thickness is dependent on the velocity of the solution past the electrode surface. As the velocity increases, δ_d decreases and the limiting current density increases (32). The time interval required to set up the diffusion layer varies with the current density and limiting diffusion rate, but it is usually of the order of 1 second while it is 10^{-4} second needed to establish the electrical double layer, which makes it is possible to distinguish between η^A and η^c experimentally. The diffusion layer may reach a thickness of 100-500 µm, depending upon concentration, agitation (or velocity), and temperature (40, 41).

3.7 Factors Affecting Corrosion Rate:

If a metal is corroding under cathodic control it is apparent that the velocity of the solution will be more significant when diffusion of the cathodic reactant is rate controlling, though temperature may still have an effect. On the other hand if the cathodic process requires high activation energy, temperature will have the most significant effect. The effect of concentration, velocity, and temperature are complex and it will become evident that these factors can frequently outweigh the thermodynamic and kinetic considerations.

3.7.1 Effect of Concentration:

The effect of oxidizer additions or the presence of oxygen on corrosion rate depends on both the medium and the metals involved. The corrosion rate may be increased by the addition of oxidizers, oxidizers may have no effect on the corrosion rate, or a very complex behavior may be observed. By knowing the basic characteristics of a metal or alloy and the environment to which it is exposed, it is possible to predict in many instances the effect of oxidizer additions (23).

For diffusion-controlled process, an increase in concentration of the diffusing species in the bulk of the environment increases the concentration gradient at the metal interface. The concentration gradient provides the driving force for the diffusion process. Thus the maximum rate at which oxygen can be diffused to the surface (the limiting diffusion current) would be essentially directly proportional to the concentration in solution. Fig. 3.4 is example of the cathodic polarization diagram which is operative for this system (35).

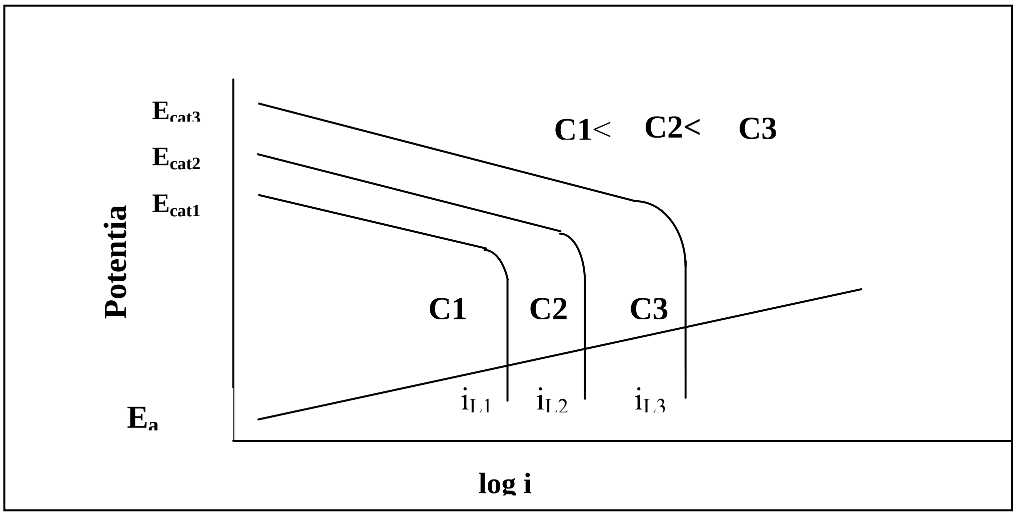


Fig. (3.4) Effect of Concentration on i_L (35)

3.7.2 Effect of Velocity:

Velocity primarily affects corrosion rate through its influence on diffusion phenomena. It has little effect on activation-controlled processes. The manner in which velocity affects the limiting diffusion current is a marked function of the physical geometry of the system. In addition the diffusion process is affected differently by velocity when the flow conditions are laminar as compared to a situation where turbulence exists. For most conditions the limiting diffusion current can be expressed by the equation:

$$i_L = K \times U^n \qquad (3.30)$$

where (K) is a constant, (U) is the velocity of the environment relative to the surface and (n) is a constant for a particular system. Values of n vary from 0.2 to 1 (35, 45). Fig. 3.5 shows the effect of velocity on the limiting current density.

The corrosion rate would be directly proportional to the limiting diffusion current until the intersection of anodic and cathodic polarization curves occur at a current less than the limiting diffusion current. At higher velocities the corrosion rate will be relatively independent of velocity until cavitations or erosion changes the physical conditions of the system (32). This is illustrated in Fig. (3.6).

The effect of velocity on corrosion rate, like the effect of oxidizer addition, complex and depends on the characteristics of the metal and the environment to which it is exposed. Figure (3.7) shows the typical observations when agitation or solution velocity is increased.

For corrosion processes which are controlled by activation polarization, agitation and velocity have no effect on the corrosion rate as illustrated in curve B. If corrosion process is under cathodic control, then agitation or velocity increases the corrosion rate as shown in curve A, section 1. This effect generally occurs when an oxidizer present in very small amounts as in the case of dissolved oxygen in acids or water. If the process is under diffusion control and the metal is readily passivated, then the behavior corresponding to curve A, section 1 and 2, will be observed.

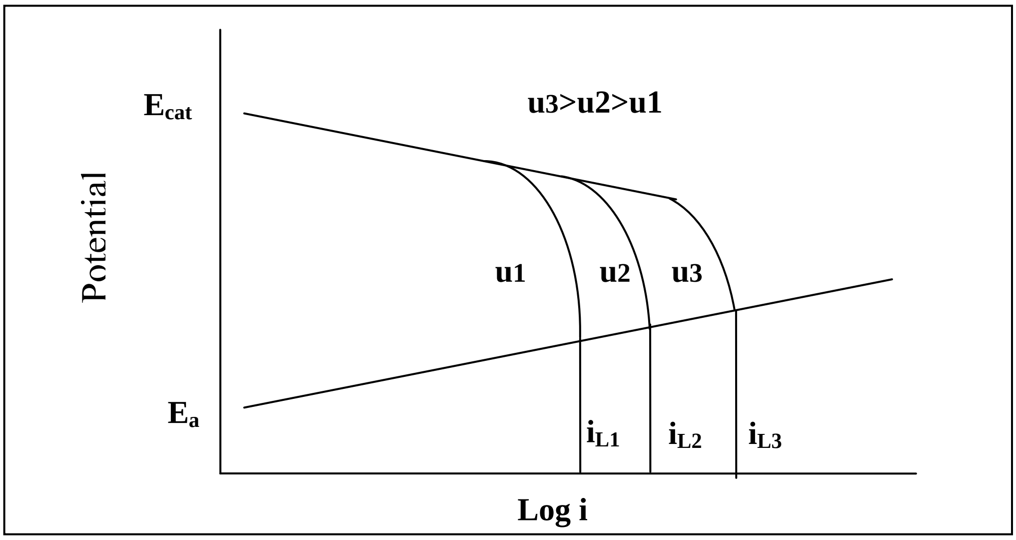


Fig.3.5: Effect of Velocity on i_L (35)

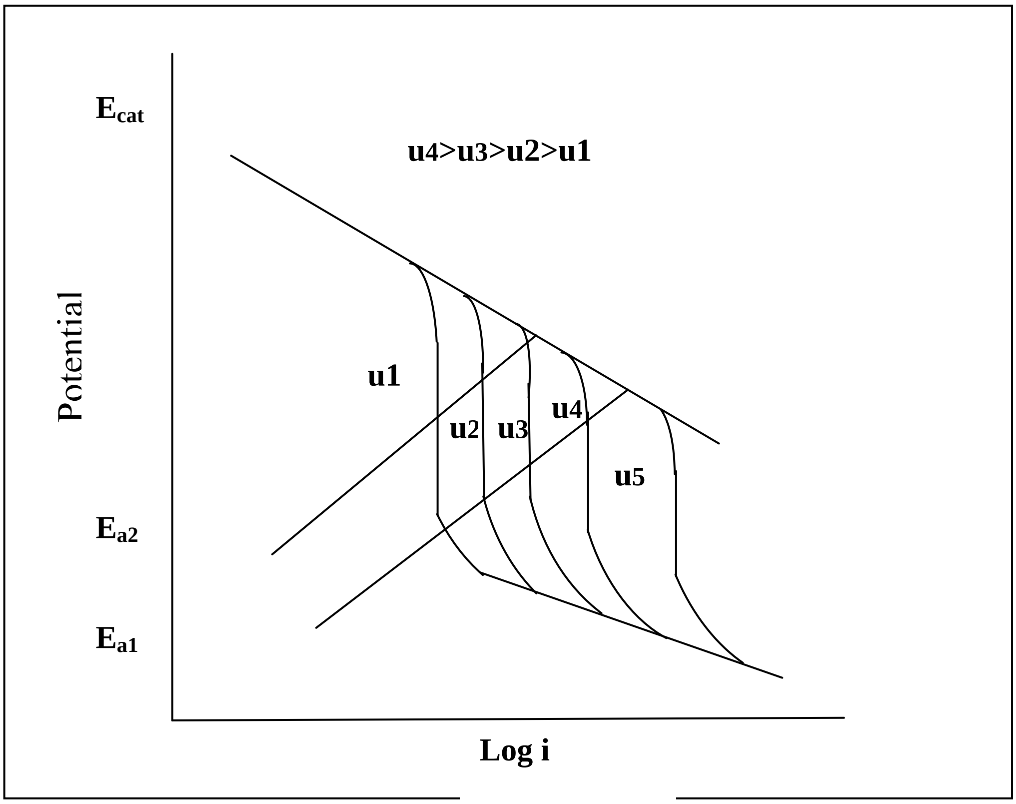


Fig. 3.6: Effect of Position and Slope of Anodic Curve.

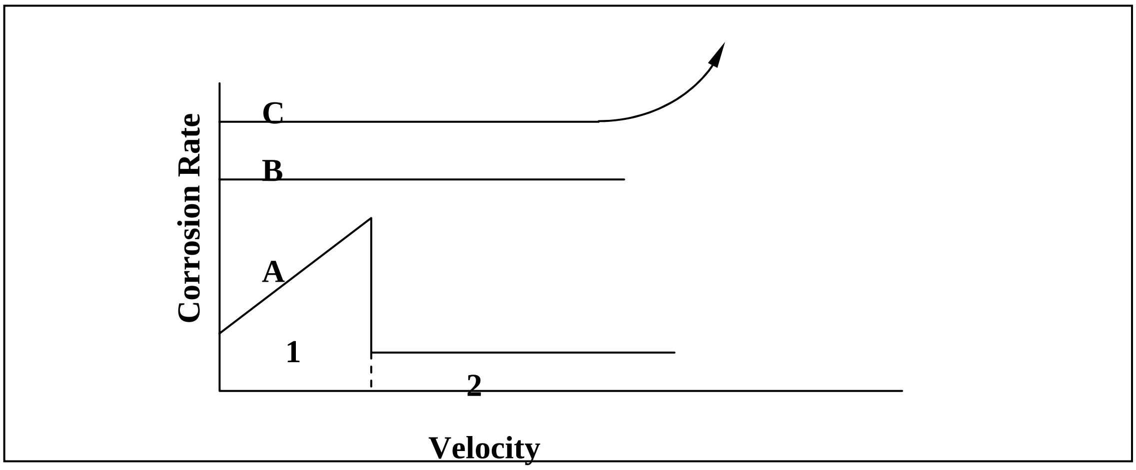


Fig. (3.7) Effect of Velocity on the Corrosion Rate [(23)].

Some metals owe their corrosion resistance in certain medium to the formation of massive bulk protective films on their surface. When materials such as these are exposed to extremely high corrosive velocities, mechanical damage or removal of these films can occur, resulting in accelerated attack as shown in curve C. This is called erosion corrosion [(23)].

3.7.3 Turbulent Flow:

Turbulent flow conditions in pipelines bring about marked increase in the rate of corrosion due to a greater agitation of the liquid at the metal surface, and amore intimate contact between environments and the metal than in the case of laminar flow. It increases the supply of the corrosive agent and transport, through the solution, of corrosion products from metal surface. In addition, there is pure mechanical factor like the tearing away of corrosion products from metal surface by the shearing stress between the metal and liquid, which is particularly high under turbulent conditions. The type of flow, laminar or turbulent, obtained depends on the velocity and amount of fluid handled and also on the geometry (design) of the equipment. Besides high velocity, bends, deposit, sharp changes in corrosion section, and other irregularities that hinder the linear flow condition, may result in corrosion [(1)].

3.7.4 Effect of Temperature:

Temperature increases the rate of almost all the chemical reactions. When the rate-determining step is the activation process, the temperature changes have the greatest effect. In general, if diffusion rates are doubled for a certain increase in temperature activation process may be increased by 10-100 times, depending on the magnitude of the activation energy (45) .

3.7.5 Effect of Salt Content and Chloride Ion:

Chlorides have probability received most consideration in relation to their effect on corrosion. The effect of sodium chloride concentration on the corrosion of iron in air-saturated water at room temperature was found to increase the corrosion rate. The corrosion rate in air saturated water at room temperature was found to increase with increase of sodium chloride solution reaching maximum at about 3% NaCl (seawater concentration), and then decreases, the value falling below that of distilled water when saturation is reached (26 % NaCl). To understand this behavior, oxygen solubility in water decreases continuously with sodium chloride concentration, explaining the falling off of corrosion rate at higher sodium chloride concentration. The initial rise appears to be related to a change in the protective nature of the barrier rust film that forms on the corroding metal. On the other hand chlorides increase the electrical conductivity of the water so that the flow of corrosion currents will be facilitated (33, 36).

3.8 Oxygen Reductions and Transport:

Most aqueous solutions (ranging from bulk natural water and chemical solutions to thin condensed films of moisture) will be in contact with the atmosphere and will contain dissolved oxygen, which can act as a cathode reactant. The solubility of oxygen in water decreases significantly with the increase in temperature and slightly with concentration of dissolved salts. On the other hand, the concentration of H_3O^+ in acid solution, which is given by the PH, is high, and since this ion has a high rate of diffusion; its rate of reduction is normally controlled by the activation energy for electron transfer. Furthermore, the vigorous evolution of hydrogen that occurs during corrosion facilitates transport, so that the diffusion is not a significant factor in controlling the rate of the reaction except at very high current densities. As PH in acid solution increases the hydrogen evolution reaction becomes kinetically more difficult and requires a high overpotential. Oxygen reduction is more significant than hydrogen evolution in near-neutral solutions, and that in the case of former, transport of oxygen to the metal surface will be more significant than activation-controlled electron transfer. A further important factor is that in near-neutral solutions solid corrosion product will be thermodynamically stable and will affect the corrosion rate either by passivating the metal or by forming barrier that hinders transport of oxygen to the metal surface (36).

The rate of corrosion processes with oxygen depolarization is determined mostly by the rate of oxygen diffusion to the metal surface. This kind of corrosion is extremely important, since it includes practically important process such as corrosion of iron and steel in neutral salts solutions, corrosion of zinc in several neutral solutions, various cases of copper corrosion. In the majority of practical cases, the concentration of oxygen in the solution corresponds to the oxygen solubility in particular electrolyte. If the solution has a certain amount of oxygen, but the system is closed so that no additional oxygen can enter the system, then the corrosion process with oxygen depolarization can proceed only until the oxygen supply is exhausted. When the metal is placed in open container, oxygen can reach the cathodic sections by means of diffusion from the air through the solution, and the corrosion process might cause complete destruction of the metal (41) . The transport of oxygen from the atmosphere to the metal solution interface involves the following steps (43):

1. Transport of oxygen across the atmosphere /solution interface.
2. Transport through the solution (by diffusion and by natural and forced convection) to the diffusion layer.
3. Transport across the static solution at the metal /solution interface (the diffusion layer δ_d) by diffusion.

The process involves the following reactions (42):

1) For the cathode polarization, diffusion of oxygen from the solution toward the cathode $O_2 = O_2$ (3.31a)

2) Adsorption of oxygen and dissociation of molecules into atoms:

$$O_2 = 2O \qquad (3.31b)$$

3) Ionization: $O+2e = O^{--}$ (3.31c)

4) Formation of hydroxyl ion:

$$O^{-} + H_2O + 2m\, H_2O = 2OH^{-}.m\, H_2O \qquad (3.31d)$$

5) Transfer of hydroxyl ions from the cathode into the bulk of the solution:

$$OH^{-} = OH^{-} \qquad (3.31e)$$

3.9 Corrosion and Mass Transfer Correlations:

Many attempts were made to express the corrosion process as a mass transfer operation when the process is under diffusion control using modified form of Reynolds analogy (such as Chilton and Colburn analogy).

Fluids flowing past a corroding surface often affect the way an alloy corrodes in an environment. An acceleration of the corrosion rate caused by fluid moving past the alloy surface would make corrosion rate predictions based on stagnant tests inaccurate (47). For reaction rate that is diffusion controlled, the limiting current density is obtained from Eq.(3.24)

$$i_L = Z \times F \times K \times \Delta C \qquad (3.32)$$

Thus the basis of the LCD technique in determining K is to measure LCD at fixed ΔC. Also if k is known then measuring i_L allows the determination of ΔC, which will be the bulk concentration. If this approach can be applied to a corrosion process in which both an anodic and cathodic reaction occur, and if either reaction is diffusion controlled then the rate of corrosion will be given by:

$$Corrosion\ Current = Z \times F \times K \times \Delta C \qquad (3.33)$$

The value of ΔC will be the bulk concentration of cathodic reactant for systems, which are cathodically controlled and will equal the solubility limit of the relevant product when the anodic reaction is diffusion controlled. It is found from dimensional analysis that (48):

$$Sh = cont. \times Re^X \times Sc^Y \qquad (3.34)$$

x is usually between (0.3 - 1) for single phase flow (44) (there is limited studies on mass transfer correlation valid for multiphase flow in the open literature (48), y is typically 0.33. Substituting for k yields:

$$Corrosion\ Current = Z \times F \times \Delta C \times conts. \times (\frac{D}{d}) \times (\frac{u \times d}{\nu})^X \times (\frac{\nu}{D})^Y \qquad (3.35)$$

i.e., corrosion current can be predicted without any tests if the relevant parameters are known. However this would predict no corrosion at zero velocity and natural convection would have to be added at low to zero flow velocities (44).

Marangozis (49) used the theory of mass transfer to predict the corrosion rate of magnesium in hydrochloric acid. The corrosion rate was measured by weight loss method using rotating cylinder electrode. It was concluded that mass transfer theory is a powerful tool for analysis, interpretation, prediction, and correlation of rates of corrosion of magnesium in hydrochloric acid.

Ellison and Schmeal (50) presented a model for corrosion of carbon steel in 60-96% weight sulfuric acid. Two devices were used, rotating cylinder and pipeline. Corrosion rate under turbulent flow conditions was measured using weight loss method. The temperature of acid was 60^{o}C and controlled to within $\pm 2^{o}$C. The results for rotating cylinder indicated that the dissolution current proportional to power n with velocity where 0.6< n <0.8.

Poulson (52) studied the influence of fluid flow on the corrosion rate for different geometries (rotating disk, rotating cylinder, impinging jet, nozzle, and tube) using electrochemical technique. For pipe flow he obtained the following correlation for fully developed turbulent flow (52)

$$Sh = 0.0165 \times Re^{0.86} \times Sc^{0.33} \qquad (3.36)$$

For local Sh:

$$\frac{Sh_L}{Sh} = 11.15 \times Re^{-0.277} \times \left(\frac{d}{L}\right)^{0.33} \qquad (3.37)$$

This predicts entrance effects to decrease with increasing Re and even at Re of 10^4 they will have disappeared before 1 diameter. The author stated that the corrosion rates, even when controlled by diffusion, are not always simply related to mass transfer.

Using rotating cylinder electrode, Silverman (43) studied the effect of fluid flow on the corrosion rate. Experiments were carried out at room temperature on mild steel sample at rotation rate of 500 and 5000 rpm, weight loss was measured for 30 min, 60 min, 1hr, and 24hr. The purpose was to estimate the degree of mass transfer control. The authors concluded that, (i) mass transfer has a relation to shear stress and Sc affects the relation, (ii) fluid velocity can affect corrosion rate through erosion. (iii) when the corrosion creates a rough surface, the corroding cylinder would most likely be rough. The friction factor and subsequent velocity sensitivity would be function of this roughness.

Vilambi and Chin (51) carried out an experimental and theoretical investigation for turbulent mass transfer to a rotating cylinder. They analyzed the reduction of ferricynide ion on the rotating cylinder as a mass transfer operation to express the corrosion rate in terms of mass transfer parameters and obtained the following equation for 800 < Re < 80000 and Sc=1900,

$$Sh = 2.79 \times Re^{0.61} \tag{3.38}$$

They found that Eq.(3.38) agrees with Eisnberg et. al. (56) to within $\pm 12.5\%$. The following expression for the Nernest diffusion layer was obtained:

$$\delta_d = 0.36 \times (\frac{d}{Re^{0.61}}) \tag{3.39}$$

Smith et. al. (57) studied the effect of flow parameter on the cathodic protection of steel plate in seawater. A formula that describes the transport of oxygen to the surface of a metal under cathodic polarization in seawater was presented for turbulent flow conditions. The formula was given for the limiting current density of oxygen reduction

$$i_L = \frac{D \times Z \times F \times C_b}{78.3 \times Sc^{\frac{-1}{3}} \times \mathrm{Re}^{\frac{-9}{10}} \times X \times (\frac{t}{P})} \qquad (3.40)$$

where (X) is the distance from the leading edge, (t) is the thickness of the calcareous deposit, and (p) is the porosity of the deposits. Eq.(3.40) fits the experimental results with some scater.

3.10 Corrosion Inhibition:

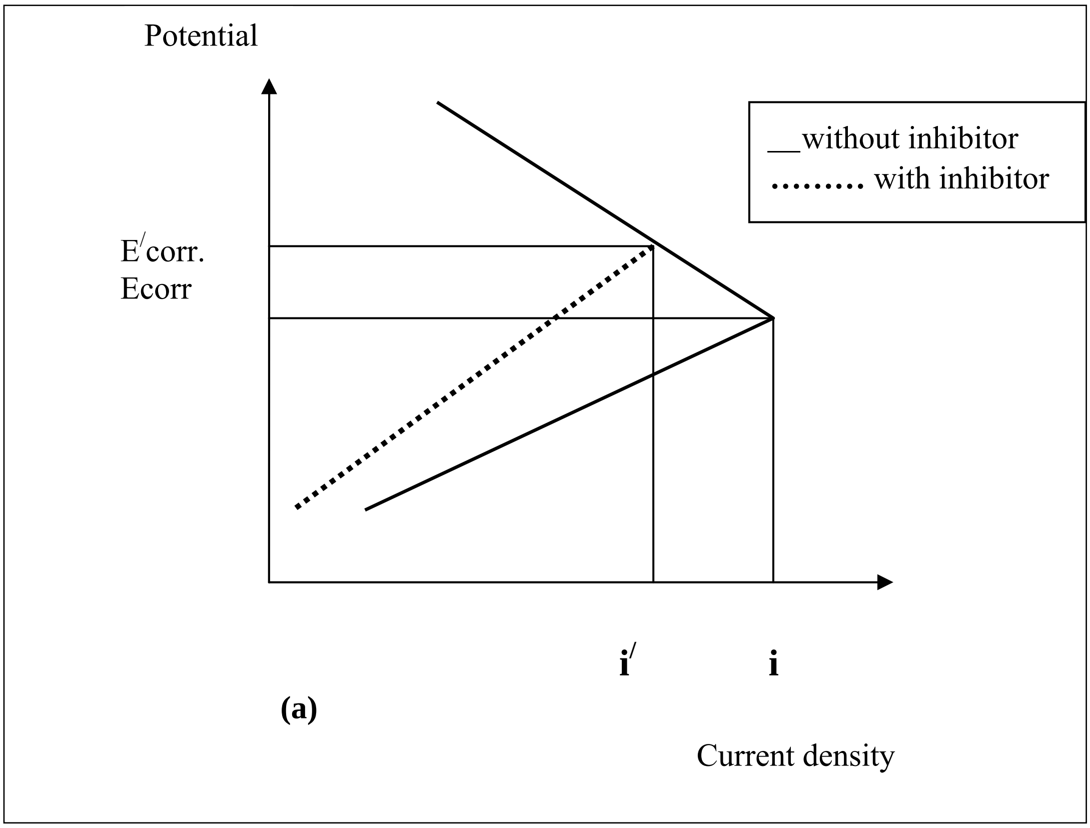
In corrosion inhibition addition of a certain chemicals in small quantity are made to the corrosive environment which causes a substantial reduction in the rate of corrosion of a metal either by reducing the probability of its occurrence or by reducing the rate of attack or by doing both. It should, however, be noted that the environment can in some cases, be made less aggressive by other methods, removal of dissolved oxygen, or adjustment of PH, while using a corrosion inhibitor for a specific problem, it is essential to make proper selection of corrosion inhibitor, as no universal corrosion inhibitor exists. Moreover, inhibitors that are valuable for some corrosion problems can be harmful to other under certain situations. In low concentration, inhibitors are often found to function as corrosion stimulators. However when various methods of protecting metals are inapplicable, corrosion inhibitors can sometimes be employed to advantage (1) .

There are certain limitations to this type of corrosion prevention as well, viz, contamination of environment and toxicity .Besides, they generally loss their effectiveness as the concentration and temperature of environment increase.

3.10.1 Inhibitor Classification

It is well known that corrosion is an electrochemical phenomenon; hence inhibition may be defined as a decrease of the velocity of electrochemical electrode reaction. From kinetic point of view, inhibitor may be defined more accurately, by corresponding decrease of the velocity of partial steps of electrode reactions. For convenience all kinds of substance which cause inhibition could be called inhibitor.

Depending on the mechanism of their inhibiting action on the electrochemical corrosion, inhibitors can be classified as (i) anodic type (ii) cathodic type and (iii) mixed type as shown in Fig.(3.8). According to their nature inhibitors can be differential as soluble and insoluble, acidic, basic and natural, volatile and nonvolatile, organic and inorganic etc.



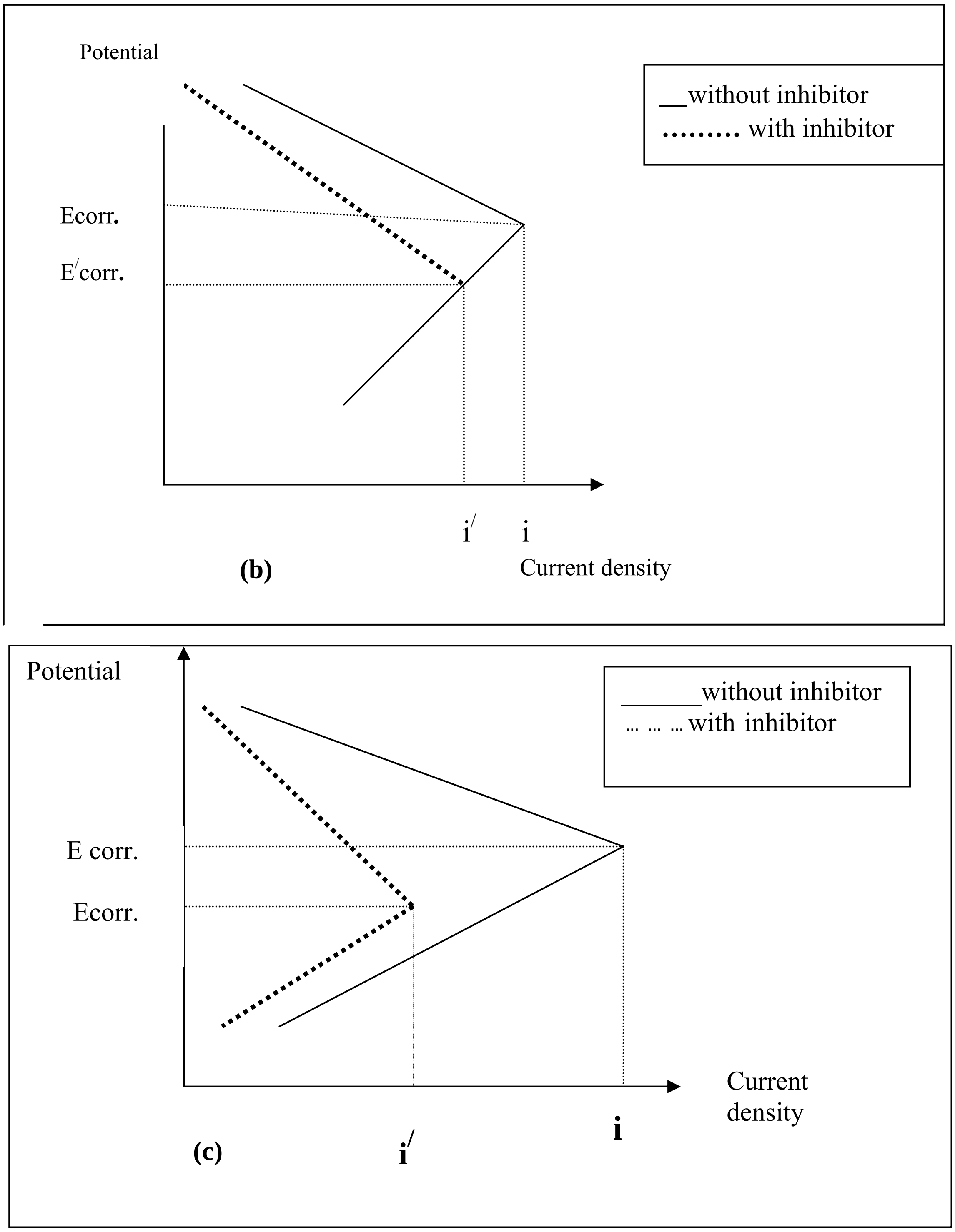


Fig (3.8) Mechanism of Action of Corrosion Inhibitors Based on Polarization Effects (a) Anodic Inhibitors. (b) Cathodic Inhibitors. (c) Mixed Inhibitors (1).

3.10.2 Mechanism of Inhibition:

1. Adsorption theory: the adsorption theory of protective activity has been proposed by most of workers, which says that inhibitors are adsorbed on the metal surface forming protective layer. The adsorption was considered either as physical adsorption or chemisorptions.

The physical adsorption may be due to adsorbed species and the electric charge on the metal at the metal/solution interface, that is, on the so called "null –charge potential"($E_{corr.} - E_{eq} =0$) on the surface the anodic or the cathodic section of the corroding metal. Physical adsorption does not involve the bonding on the electrode but requires electrical variables viz., potential or charge on the electrode. Thus, if under corrosion conditions the metal surface has (-ve.) charge, the adsorption of cations is favoured, and if the surface carries (+ve.) charge, the adsorption of anion takes place. At a surface charge about zero relative to solution, adsorption of both molecules and ions is possible. The deciding factor in choosing an adsorption inhibitor is, therefore the potential of the metal with respect to the solution, and this depends on (E_{corr}) and (E_{eq}) for the metal and electrolyte under consideration.

Besides electrostatic interaction, inhibitors can bond to metal surface by electron transfer to form a coordinate type of link. This process is favoured by the presence in the metal of vacant electron orbital of low energy, such as occurs in the transition metals; and by availability for relatively loosely bond electrons, such as may be found in anions, and natural organic molecules containing lone pair electrons or pi-electron systems with multiple, especially triple bond or aromatic rings. This theory cannot explain mechanism of inhibitor action fully as many of the surface active substance (1).

2. Film theory: this theory states that the effective protection of the metals by inhibitors is due to the formation on the metal surface of a layer of insoluble or slightly soluble corrosion products. However, in all cases, a preliminary stage of adsorption of the inhibitor can be envisaged and to the extent, the adsorption theory has fulfilled its purpose (1).

3. *Hydrogen overvoltage theory*: this theory postulates that inhibitors that are adsorbed on the metal either anodic or cathodic or in some cases both reactions. This leads to rapid polarization of anodic or cathodic sites and thus overall corrosion rate is retired (23).

Many known inhibitors are however, cathodic polarizer having no direct action on the anodic reaction. They block the cathodic regions on the metal surface and suppress the hydrogen evolution reaction; correspondingly the anodic reaction is reduced, and hence there is inhibition of corrosion (1) .

3.10.3 Anodic Inhibitor:

Those substances, which reduce the anode area by acting on the anodic sites and polarize the anodic reaction, are called anodic inhibitors. They displace the corrosion potential (E_{corr}.) in the positive direction and reduce corrosion current (i_{corr}.) thereby retard anodic reaction and suppress the corrosion rate. Anodic inhibitors are primarily inhibitors (inorganic) of oxidizing action. As oxidants they have a twofold nature, viz.(i)they acts as good depolarizers and therefore, accelerate the cathodic process (corrosion simulators), and(ii)they also lead to the formation of protective film on the anode (chemical passivators). In other word, they function either as cathodic simulators or anodic inhibitor. Their resulting action can therefore be different depending on conditions (23). .

3.10.4 Cathodic Inhibitor:

Those substances which reduce the cathodic area by acting on the cathodic sites and polarize the cathodic reaction are called cathodic inhibitors. They displace the corrosion potential ($E_{corr.}$) in the negative direction and reduce the corrosion current ($i_{corr.}$), there by retard cathodic reaction and suppress the corrosion rate (23)..

Cathodic inhibitors may be divided into three categories, viz, (i) those that absorb oxygen (de aerators or oxygen scavengers), examples of this type of inhibitors are sodium sulphite and hydrazine which remove dissolved oxygen from aqueous solution according to the reactions:

$$N_2H_4+O_2 \rightarrow N_2+2H_2O \qquad (3.41)$$

$$2Na_2SO_3+O_2 \rightarrow 2Na_2SO_4 \qquad (3.42)$$

(ii) Those that reduce the area of the cathode. Examples of this type of inhibitor include $Ca(HCO_3)_2$, $ZnSO_4$ and some other compounds with cations that migrate toward the cathode surface and react with cathodically formed alkali(mild) to produce insoluble protective film or layers thus reducing corrosion:

$$Ca^{+2}+2HCO^{-}_3+OH^{-} \rightarrow CaCO3\downarrow+HCO^{-}_3+H_2O \qquad (3.43)$$

$$Zn^{+2}+OH- \rightarrow Zn\,(OH)_2\downarrow \qquad (3.44)$$

(iii) Those that increase the hydrogen overpotential of the cathodic process (hydrogen-evolution reaction). Examples of this type include arsenic, bismuth and antimony ions which specially retard the hydrogen evolution reaction (23).

3.10.5 Mixed inhibitor:

Those substances, which affect both the cathodic and anodic reactions, are called mixed inhibitors. Such mixed inhibitors include the commercially available polyphosphates. Potential change in such a case is smaller and its direction is determined by the relative size of the anodic and cathodic effects (1, 23).

3.11 Inhibitors Substance Classification:

There are several classes of inhibitors conveniently designated as follows (i) Passivators (ii) Organic inhibitors (iii) Vapour phase inhibitor. The practice of corrosion inhibition is greatly influncd by new regulation that have been developed because of toxicity and enviromental effects resulting from industrial effluences.

Some substances indirectly facilitate inhibition of iron (and probably of some other matels, too) by making condtions more favorable for adsorbtion of oxygen .In this category are alkaline compounds (e.g. NaOH, Na_3PO_4 , etc).

It wsa found that passivation of iron by molybdates and tungstates both of which inhibit in the near natural water PH range, also require dissolved oxygen contray to the situation for chromate and nitrites. In this case dissolved oxygen may help create just enough additional cathodic area to ensure anodic passivation of the remaining restricted anode surface at the prevailing rate of reduction of ($MoO^{-2}{}_4$,$WO^{-2}{}_4$),where as the absence of O_2 (34) result in corrosion.

Sodium hexapolyphosphate $(NaPO_3)_6$, see Fig (3.9) are further examples of nonoxiding compounds that effectivly passivate iron in near natural range. Other factors enter as well; there is for example evidence of protective film formation of the diffusion –barrier type on the cathodic area. Such diffusion –barrier film probably account for the observed inhibition of steel exposed to as high as 2.5%NaCl solution. In low concentration of dissolved oxygen, corrosion of iron is accelerated by sodium hexa-polyphosphate because of its metal –ion-complexing properties see Fig. (3.9) calcium, iron and zinc polyphosphate are better inhibitors than the sodium but the reasons are not yet fully understood. This and the benzoate system require further studies to elucidate the mechanism of their action (34). The general properties of sodium hexapolyphosphate are as follows:

Chemical formula.......................................$(NaPO_3)_6$
Molecular weight...................................... 340
Bulk density, Kg/m^3 .... 1676.4 (flake)
Application……………………………….scale and corrosion inhibitors
Chemical description …………………….inorganic component
Form……………………………………..solids
Colour……………………………………colorless
Solubility..solubility in water complete.

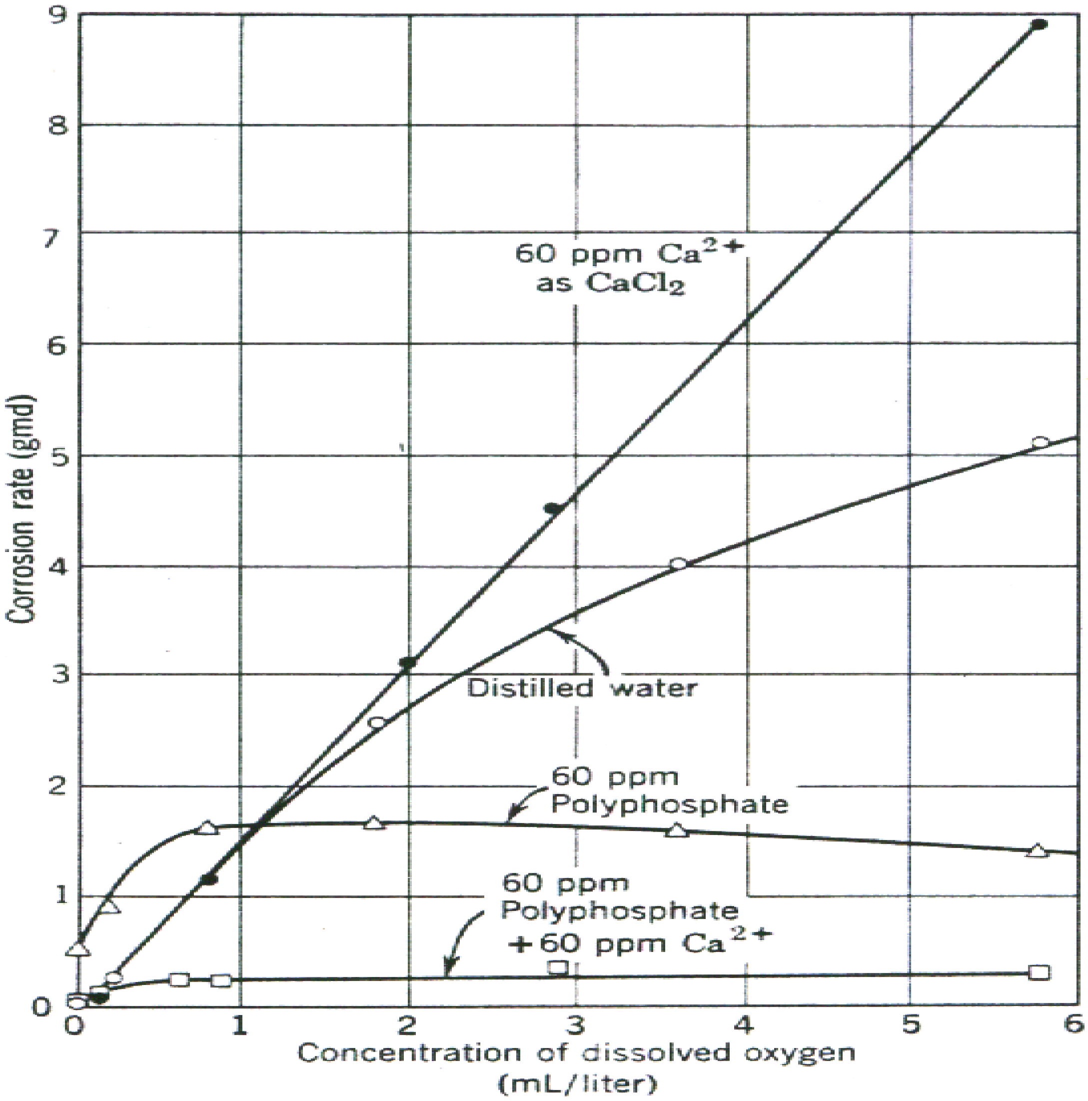


Fig.(3.9) Effect of Oxygen Concentration on Sodium Hexapolyphosphate as Corrosion Inhibitor of Iron as Showing Beneficial Effect of Dissolved O_2 and Ca^{2+},48 hr. Test (34).

Sodium nitrite is one of the oldest and cheapest corrosion inhibitors. It prevents rusting and has been widely used (as well as other nitrite salts) to line cans in which aqueous solutions are kept. Corrosion inhibitors are essential in metal-working fluids which are sprayed on the tips of cutting tools, so sodium nitrite or, in a few cases, an amine are components of most water-based cutting fluids, as much as 0.8% . The general properties of sodium nitrite are as follows:

Chemical formula...NaNO2
Molecular weight...69.00
Bulk density. Kg/m^3,..999.8-1144 (flake)

Sodium nitrite is an active oxidizing agent and is employed as such in corrosion inhibition, alkaline detinning of scrap tinplate, and in phosphating of metals. Sodium nitrite functions as a reducing agent toward such powerful oxidizing agents as dichromate, permanganate, chlorate, chlorine, etc(77).

In pipelines transporting gasoline and other petroleum products, where water is minor phase, sufficient nitrite or chromate solution may be continuously injected to give (2%) concentration in water phase, in this concentration gasoline is not corrosive to steel. At lower temperature underground, gasoline release dissolved water which in contact with large quantities of oxygen dissolved in gasoline (solubility of O_2 in gasoline is six times that in water),corrode steel ,forming voluminous rust products which clog the line; sodium nitrite enters water phase and effectively inhibits rusting., chromate is used for the same purpose but having the disadvantage that they tend to react with some constituents of the gasoline .

The corrosion rates of steel contact with water/ gasoline mixtures containing increasing amount of $NaNO_2$ are listed in table 3.1,

Table (3.1) Corrosion Rates of Mild Steel in Sodium Nitrite Solution Containing Gasoline (or other products), Rotating Bottle Tests Using Pipeline Water, PH=9, and Regular Gasoline; 14 Days Exposure, Room Temp (34).

%NaNO2	Corrosion rate (mm/y)
0	0.11
0.02	0.08
0.04	0.02
0.06	0
0.1	0

The minimum amount of $NaNO_2$ for effective inhibition is 0.06% (7×10^{-4} M) which because of impurities present in water is higher than the critical concentration in distilled water. Nitrites are inhibitors only above (PH=6), in more acid environments they decompose, forming volatile nitric oxide and nitrogen peroxide (34).

Chapter Four

Experimental work

4.1 Material Analysis:

The material used was low carbon steel .The metal specimen used was (12 mm in diameter) and (2.6m long). The chemical composition was as follow:

Table (4.1): Analysis of Specimen.

Comp	C	Si	Mn	P	Cr	Mo	Cu	V	Fe
Wt%	**0.0755**	**0.1507**	**0.416**	**0.0013**	**0.017**	**0.043**	**0.059**	**0.0478**	**Balance**

4.1.1 The Electrolyte:

1. Sodium chloride: NaCl, General Purpose Reagent (GPR) of purity 99.5% min., supplied by BDH Ltd, was employed.
2. Distilled Water.
3. Inhibitor: hexamine is used as a inhibiter for cleaning specimens only.
4. Inhibitor: sodium nitrite and sodium hexapolyphosphate as inhibitors to mitigate corrosion in two phase systems (1%wt. NaCl aqueous phase immiscible with Kerosene).
5. Kerosene as a second phase was obtained from Doura refinery.
6. Hydrochloric acid: HCl, technical hydrochloric acid of concentration 32%, supplied by rayon state establishment, Saddat Al-Hindiyah. As a cleaning electrolyte for the metal specimens (before each test), HCl of 3% concentration is used, which had been prepared according to dilution law:

$$C_1 V_1 = C_2 V_2 \qquad (4\text{-}1)$$

C_1: the first concentration.

V_1: the first volume.

C_2: the second concentration.

V_2: the second volume.

As example; in order to prepare 0.5liter of 3% concentration HCl from 32% HCl concentration, according to dilution law we need 0.46 liter of 32% HCl, added to 0.464 liter of distilled water. A 20% HCl is needed as a cleaning electrolyte for the metal specimens (after each test), which had been prepared using the same procedure given above. Besides, an amount of inhibiter (hexamine) was added to the 20%HCl to prevent corrosion. The best amount of inhibiter added was founded to be 60gm of hexamine per liter of 20% HCl, where the weight loss was zero, as shown in appendix (B).

4.1.2 Solvents Used:

The ethanol (C_2H_4O) of concentration $\cong$ 99% supplied by FLUKA, is used to clean the specimens.

4.1.3 Metal Specimens:

Carbon steel rod 2.6m long and 12mm diameter was cut and machined to 32.5 mm long and 5mm diameter specimens, as shown in Fig.(4.1) which was exposed to test solution. One end was machined and threaded to the length of 2.5 mm. Specimens were cleaned with dilute hydrochloric acid (see sction 4.1.4), washed with distilled water and dry cleaned with ethanol. They were annealed in vacuum furnace at 600 C^o for one hour and furnace cooled under vacuum to room temperature. This was carried out in order to remove residual mechanical stresses. Finally they were stored in a disccatorl until use.

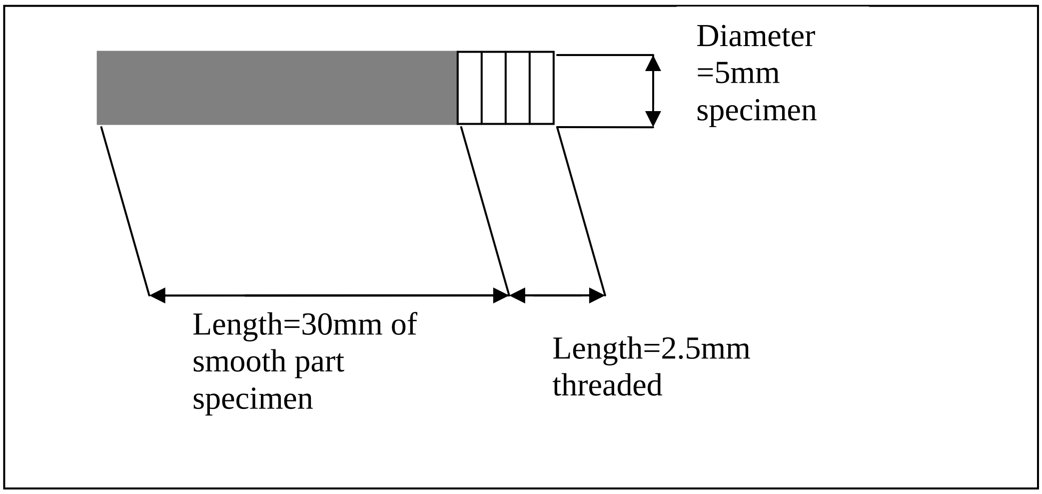


Fig (4.1) Side View of Metal Specimens

4.1.4 Specimen Preparation:

Specimens were abraded in sequence on papers of the following grades :220 and 400,washed with running tap water, dried with paper tissue, immersed in dilute hydrochloric acid solution for (1.5- 2)min see section (4.1.2), rinsed with tap water, immersed in ethanol(1.5- 2)min, and dried with paper tissue.

The dimensions of each specimen were measured with a vernier to the second decimal of milimeter, then left to dry for (14 hr.) in disiccator over silica gel, and accurately weighed to 4th decimal of gram.

4.1.5 Agitation System:

The agitation system consisted of cylindrical perspex the thickness T = 4 mm vessel diameter D_t=24 cm and H=30 cm height, filled with test solution to height equal to its diameter and coverd with flat perspex sheet. Four equally spaced vertical baffles made of perspex each of width equal to J=2 cm. A prespex 6-blade disc impeller of diameter equal to D_a=8 cm, blade length L=2 cm, blade width W=1.6 cm, as shown in Figs.(4.3 and 4.4) was used and located E=8 cm from the tank bottom as shown in Fig.(4.4). It was reported that the peformance of agitated vessel is independent of location of the impeller between (0.2 to 0.7) of the test solution height. It was rotated by motor (serial no. 061TMI 6, England), capable up to (1400 rpm).

Before each test the vessel was washed with tap water using liquid detergent, rinsed with tap water, and concentrated (HCl) to remove corrosion products and deposits, then washed witth tap water, followed by distilled water.

4.1.6 Heater and Controller:

A stainless steel heater, type Techne TE-8J, was used to obtain the required temperature in the bath. The heater was combined with thermostat to control the temperature within accuracy of $\pm 0.5^{o}$C as shown in Fig (4.2).

4.1.7 Water Bath:

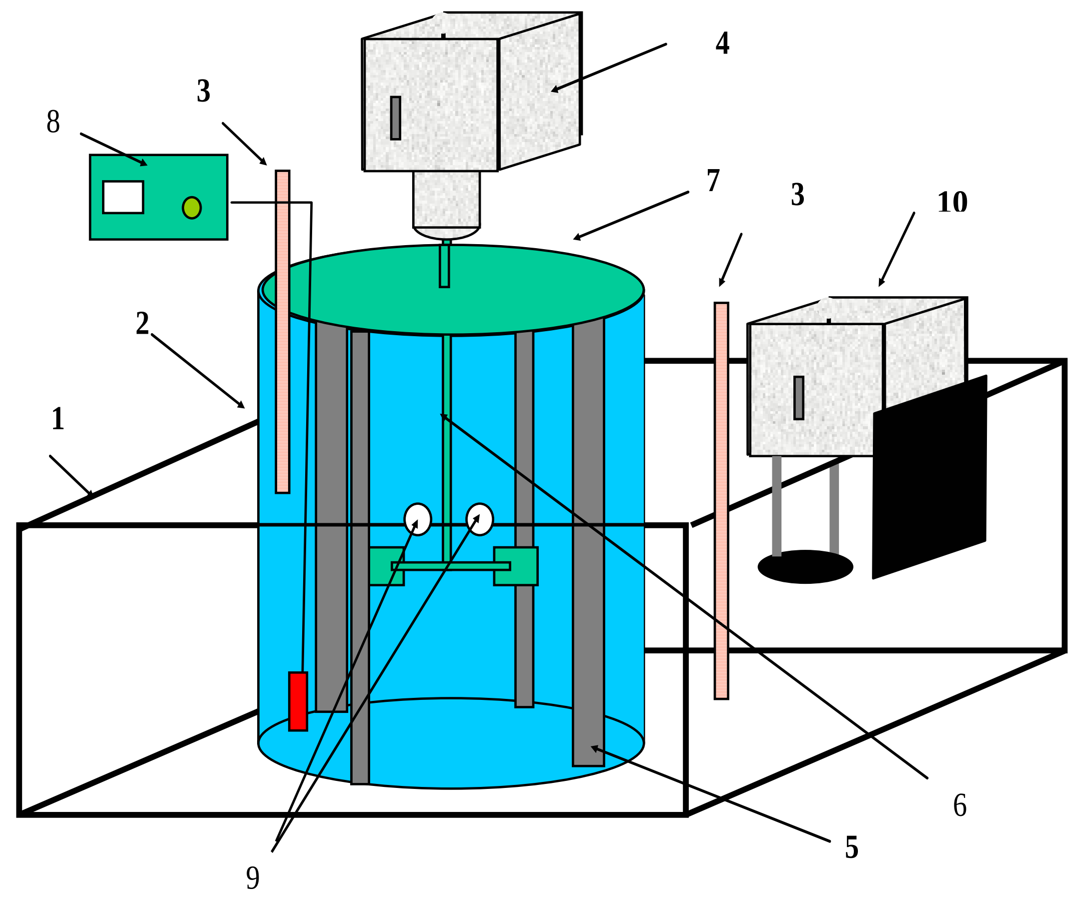
Water bath (length=80cm, width=60 cm, hight=30cm) made of perspex the water bath is filled with tap water, agitation system and heater was fixed insid the water bath as shown in Fig. (4.2).

4.1.8 Thermometers:

They were made of glass to measure temperature up to 100 ^{o}C.

4.1.9 PH Meter

They were measure the PH of aqueous solution ,PH=6.9 for distilled water used.



1	Water bath.	6	Shaft with CD-6 blade turbine.
2	Agitation cylinder.	7	Perspex cover.
3	Thermometer.	8	PH meter.
4	Agitation motor.	9	Location of fixed two specimens.
5	Baffles.	10	Heater and controller

Fig. (4.2) Diagrammatic Arrangement of Mixing System

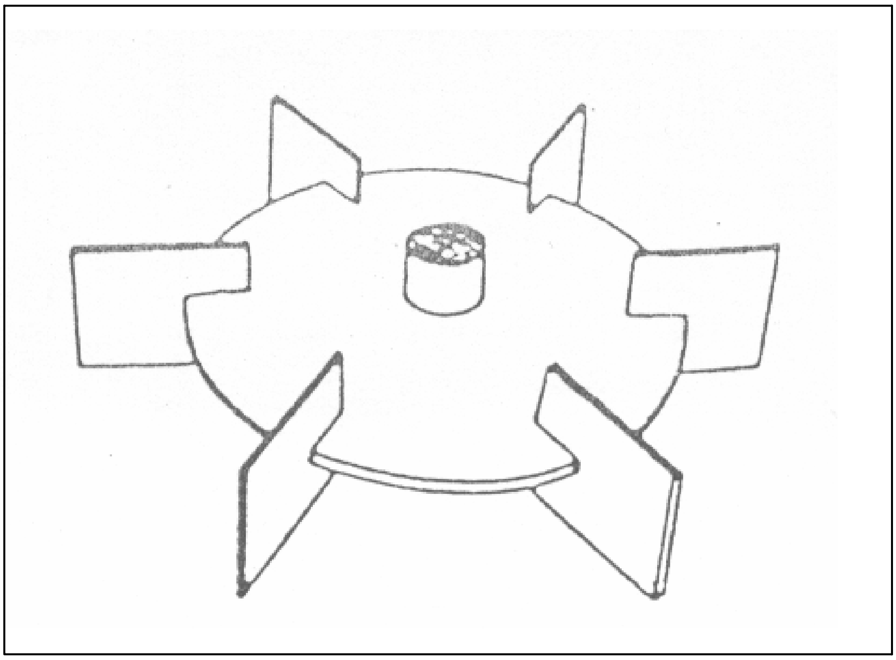
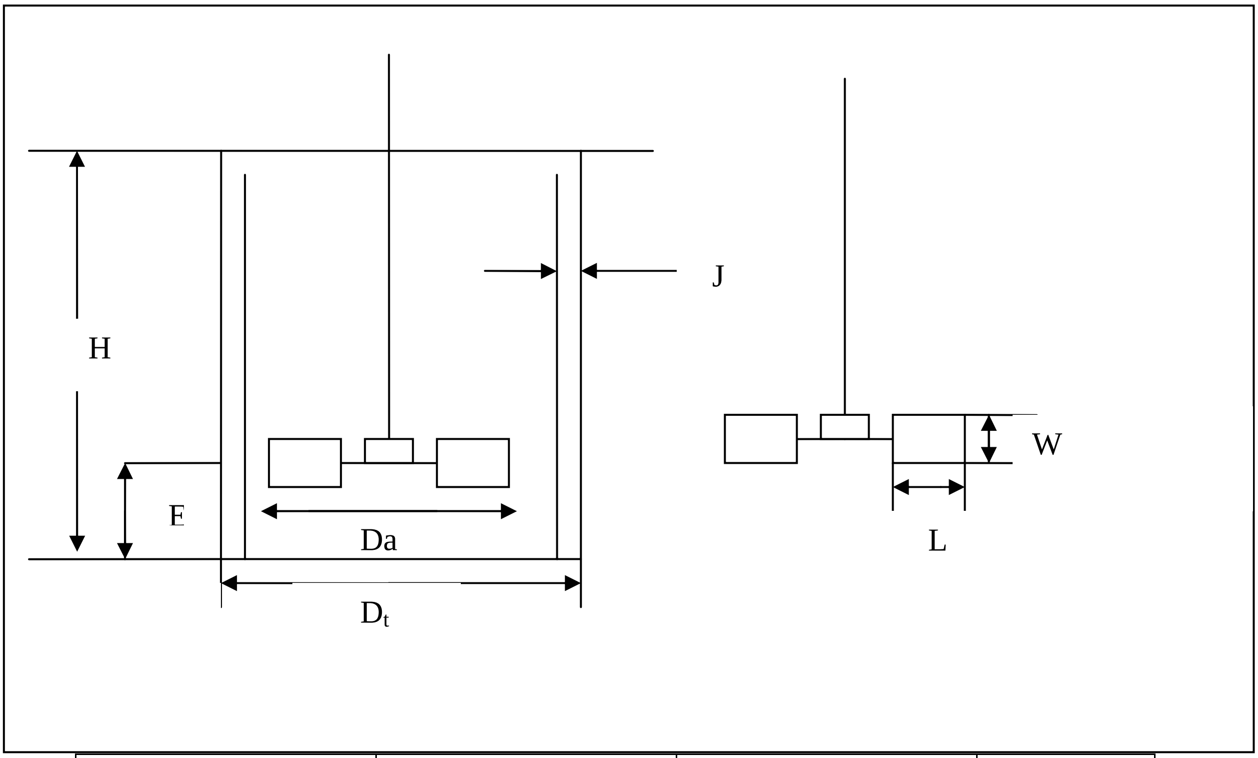


Fig. (4.3) Circular Disk Turbine (Six- blades).

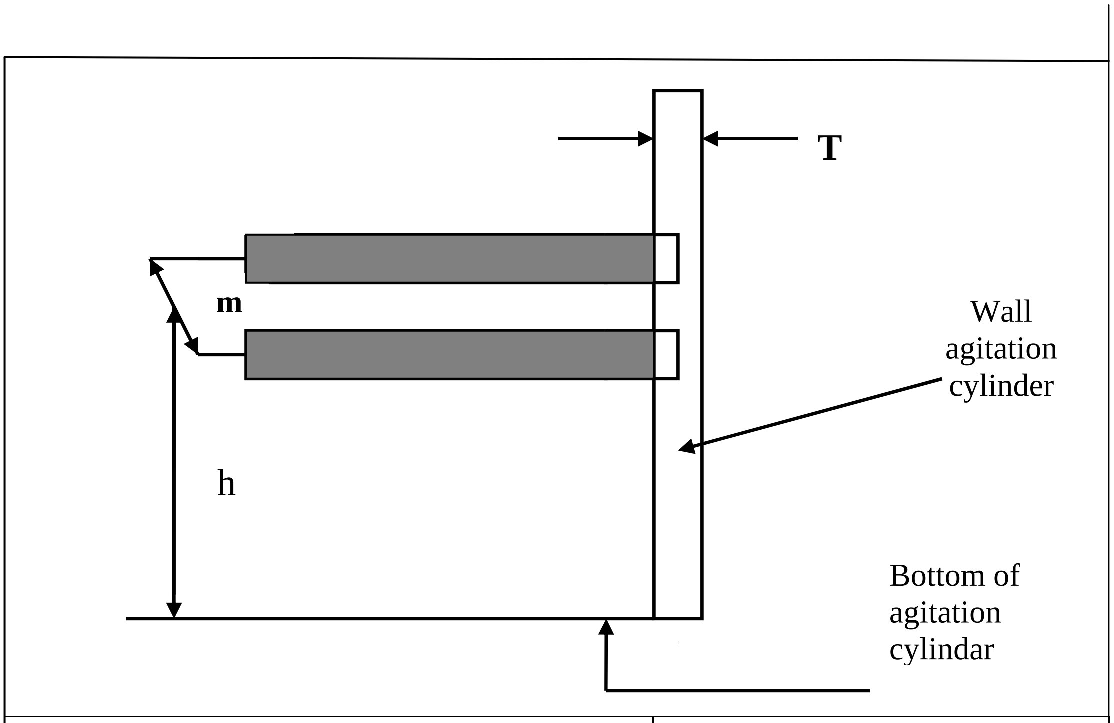


D_t =24 cm	**J=12 cm**	**W=1.6 cm**	**D_a=8cm**
H=30 cm	**E=8 cm**	**L=2 cm**	

Fig (4.4) Dimensions of Tank and Disk Turbine (Six- blades) Turbine

4.2 Procedure of Weight Loss Technique for Single and Two Phases:

The low carbon steel spcimens were prepared and screwed in postion tight enough to prevent any inward leakage of the test solution causing crevis corrosion. The low carbon steel specimen was screwed by Teflon before being fixed in the wall of agitation vessel. Two specimens were used in each test run. They were fixed at a distance (h=16 cm) from the bottom of agitation vessel and the distance between the two low carbon steel specimens was (m=1cm) as shown in Fig. (4.5)



Thickness of wall agitation cylindar(T)= 4mm	Distance between two specimens(m) =1cm
Height of two specimens from the bottom of agitation cylinder(h) =16 cm	

Fig (4.5) Arrangement of the Two Specimens in Agitation Vessel

After cleaning and drying the experimantal apparatus, brine solution (1%wt. NaCl dissolved in distilled water) was used for single phase in test runs. Kerosene and brine solution were used for two phase runs.

Sodium nitrite and sodium hexapolyphosphate were used as corrosion inhibitors. Two specimens were used in each test for repeatability check at constant temperature of $40^oC \mp 0.5$. The agitation vessel contained 12.2 liters of single or two phases mixture of prefixed weight or volume percentages. The test run lasted for exposure time of 5 h.

After each test specimens were visually observed, then washed with running tap water, cleaned with brush to remove the weakly adherent corrosion scale (reddish brown under which black layer), washed with distilled water, swabbed with a piece of paper tissue soaked with inhibited acid for(1.5-2)minutes to remove all adherent corrosion products, washed with running tap water, then distilled water, dried paper tissue, followed by rinsing with ethanol for (1.5-2) minutes, dried with paper tissue, then left for (14 hour) to dry in a desiccator over silica gel, and accurately weighed to 4th decimal of gram.

4.3 Polarization Studies Single Phase:

a) Working Electrode (Cathode):

Working electrode was rod specimen of carbon steel, the length of the cathode placed horizontally (30 mm, 5 mm outside diameter), see section (4.2.1), the working electrode is fixed at a distance (16cm from the bottom of agitation vessel), the distance between working electrode and auxiliary electrode was 1 cm.

b) Auxiliary Electrode (Anode):

Auxiliary electrode was a rod made of high conductivity graphite, 0.8cm outside diameter, and 5cm long.

c) Reference Electrode:

The cathodic potential was determined with respect to Saturated Calomel Electrode (SCE). A lugging capillary bridge leading to the reference electrode was mounted near the center along the cathode length to within (≅ 1mm) from the side of the cathode. The opening of the capillary tube near sample metal (cathode) was equal to (≅ 1mm) in diameter.

E) The Electrical Circuit:

The electrical circuit consisted of the following, see details in Fig. (4.6):

1) D.C Power Supply: A filtered *D.C* power supply which is often equipped with current and voltage limiters offers better stability and control and can be used for applying galvanostatic boundary condition. It is *(type 6291 A, Hewlett Packard with a range 0-50V and 5A).*

2) Multirange Ammeter: A digital multirange ammeter *(type 3466A, Hewlett Packard to monitor current (0-2A)* was used to measure the total current passing through the galvanostatic system.

3) Multirange Voltmeter: Two types of multirange voltmeter were used, one of these is to measure the working electrode/reference potential difference *(type 8000 A, Fluka, to measure voltage (0-1200V),* and the other to measure the overall voltage of the system, made by *MD 79/EV (Electronica Veneta), range max. 1000=V and 500 ~V.*

4) Multirange Resistor (Resistance Box): A variable resistance *(Dambridge type, variable resistance (0-0.1 MΩ)* with accuracy of 0.1 Ω was used.

g) Procedure: The working electrode was prepared as explained before (see section 4.1.5).

After electrolyte (NaCl solution) preparation, the electrolyte was stirred by using a glass rod in order to obtain a homogenous solution, and then the heater controller in bath was set to the required temperature 40±0.5 ^oC inside the agitation system for one hour to achieve thermal equilibrium before starting the experimental run. The metal specimen and auxiliary electrode were placed at a distance 16 cm above the bottom of agitation vessel. The electrical circuits, see Fig.(4.6) was connected after checking all the electrical connections. When the bath reached the required temperature, the agitator motor set to the velocity required (after five mints) the polarization electrical circuit was set to the (ON) position in order to draw the curve of any given condition (1%wt. NaCl concentration, according to galvanostatic technique by making the voltage of the D.C power supply constant at 10V and changing the current by altering the resistance of the circuit. At each setting of the resistance two parameters were recorded (potential and cathodic current) by the voltmeter and the ammeter respectively, i.e, to measure the cathodic portion of the polarization curve. Two minutes at least were allowed in order to record the steady state values of the polarization process.

After reaching ($E_{corr.}$) of the metal rod specimen, the run was ended by putting off the power supply . The system emptied and washed entirely by using distilled water to make sure that there was no electrolyte left in the system.

The above procedure was repeated exactly for other conditions and each run was repeated twice with a third run when repeatibility was in doubt.

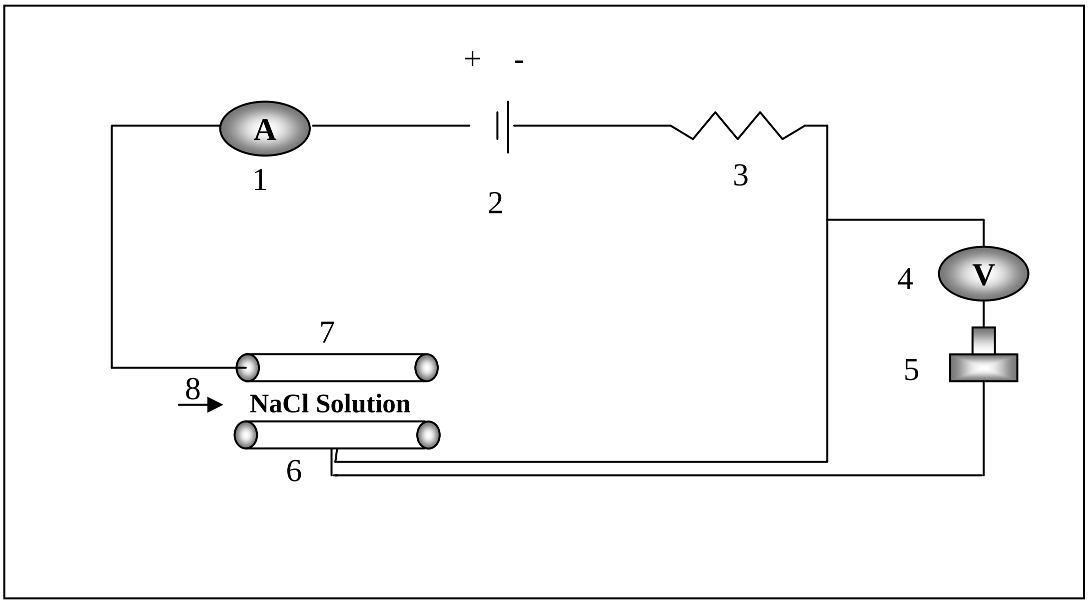


Fig.(4.6) The Electrical Circuit

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Table (4-2) Item Number with Details as Illustrated in Fig.4.6.

Item No.	Details
1	Multirange Ammeter
2	D.C Power Supply
3	*Resistance Box.*
4	*Multirange Voltmeter.*
5	*Saturated Calomel Electrode (SCE)*
6	*Cathode*
7	*Anode*
8	*NaCl Solution*

Chapter Five

Results

5.1 Introduction

Since corrosion of iron in natural waters is controlled by the rate of diffusion of oxygen to the surface, therefore factors affecting the rate of diffusion will affect the rate of corrosion or mass transport between the wall and the bulk of the solution.

In the present work the corrosion process, under isothermal conditions, is expressed in terms of many dimensionless groups to illustrate to what extent the corrosion process of carbon steel in 1%wt. NaCl aqueous solution, as single phase, and 1%wt. NaCl aqueous solution immiscible with kerosene as continuous phase can obey the mass transfer correlations.

The experimental results were introduced in the following manner:

Isothermal weight loss results which conver the results of weight loss determinations. In all cases the corrosion rate results were expressed in two ways. Firstly, in terms of the usual corrosion units. Secondly in terms of mass transfer groups.

5.2 Isothermal Weight Loss Results

Weight loss experiments were carried out to determine corrosion rates of carbon steel specimens in single phase 1%wt. NaCl solution and two phase 1%wt. NaCl solution/ kerosene over a range of Re and constant temperature of $40\,^{o}C \mp 0.5$

5.2.1 Corrosion Rate Results

Corrosion rates have been expressed in a variety of ways in the literature. Weight loss in grams or milligrams and per cent weight change are poor ways of expressing corrosion resistance because the sample shape and exposure time influence the results (24).

The results of weight loss experiments in the present work were expressed in different ways calculated readily from the weight loss of specimens. First expression is “gmd” which means gram lost per square meter per day and it is given by:

$$gmd = \frac{\Delta W}{A \times t} \qquad (5.1)$$

where

ΔW: is the average weight loss in (g), which was calculated by this equation

$$\left(\frac{W_{Specimen\ 1} + W_{specimen\ 2}}{2}\right).$$

A: is the area exposed to the corrosion environment in (m^2).

t: is the time of exposure to the corrosion environment in(days).

This expression takes into account the influence of area and time. Second expression used is the corrosion current calculated from weight loss by Faradays law:

$$i_C = Z \times F \times N \qquad (5.2)$$

where:

i_c :is the corrosion current density in (A/m^2).

F: is Faradays constant (96487 Columb / equivelant)

Z: is the number of electron freed by corrosion reaction (for iron Z=2).

N: is the mass of (Fe) reacted due to corrosion in ($gmol/m^2.s.$).

Corrosion rates of carbon steel specimens in aerated 1%wt. NaCl were expressed also in terms of i_L and Sh for the whole range of Re and constant temperature. The results of weight loss determinations are shown in appendix A., Tables A.1 to A.9 which show the results of corrosion rates for each test and Re at constant temperature in single phase and two-phase solutions.

5.2.2 Mass Transfer Results

Mass transfer coefficient can be estimated from data of weight loss measurements using E.q. (3.32) to obtain:

$$K = \frac{i_L}{Z \times F \times \Delta C} \tag{5.3}$$

where

K: is the mass transfer coefficient(m/s).

F: is Faradays constant (96487 Columb / equivalent).

Z: is the number of electron freed by corrosion reaction (for iron Z=2).

ΔC: is the bulk concentration of oxygen in solution, Z=4 for oxygen reduction.

i_L : is the limiting current density for oxygen reduction on Fe according to the combination of Eqs. (3.1) and (3.2) to produce:

$$O_2+2Fe+2H_2O = 2Fe^{2+}+4OH^- = 2Fe(OH)_2 \tag{5.4}$$

Hence, the reduction current of oxygen (i_L) will be equal the corrosion current of Fe, i.e. $i_L=i_c$, where i_c estimated via Eq.(5.2) from weight loss measurements. It is worthy to note that the molar flux of oxygen is half that of iron, i.e., $N_{O_2} = N_{Fe}/2$. Knowing i_L or i_c, the mass transfer coefficient can be estimated by Eq. (5.3). The mass transfer dimensionless groups, Sh , then can be calculated from K or i_L :

$$Sh = \frac{K \times d}{D} = \frac{i_L}{Z \times F \times \Delta C} \times \frac{d}{D} \tag{5.5}$$

where D is the diffusion coefficient for O_2 in the solution. The physical properties required for performing the above calculations, i.e., (C_b, D, μ, and ρ) are presented in appendix C for the aqueous single phase.

The corrosion rates were also expressed in terms of mass transfer dimensionless groups. The results of mass transfer calculations are given in appendix A which lists the values of mass transfer coefficient K and dimensionless group Sh for each condition at the specified Re. The results show that for all values of Re, increasing Re leads to increase K and Sh.

5.2.3 Reynolds Number

According to equation (2.1) Reynolds number can be calculated from equation below:

i)For single phase (aqueous solution of 1%wt. NaCl):

$$Re = \frac{\rho \times D_a^{2} \times N_I}{\mu} \tag{5.6}$$

where:

D_a = impeller diameter (m)

N_I = rotational speed of the impeller (rps)

ρ= fluid density (kg/m^3)

μ = fluid viscosity (kg/m.s)

(ii)For two-phases (aqueous solution of 1%wt. NaCl immiscible with kerosene):

$$Re = \frac{\rho_C \times D_a^{2} \times N_I}{\mu_C} \tag{5.7}$$

where:

ρ_C = density of continuous phase(Kg/m^3), see appendix C.

μ_C =viscosity of continuous phase (kg/m.s.), see appendix C**.**

5.2.4 Weber Number

According to equation (2.7) Weber number can be calculated from equation below:

$$We = \frac{\rho_C \times (N_I)^2 \times (D_a)^3}{\sigma} \qquad (5.8)$$

where

We: Weber number (dimensionless)

ρ_c : density of continuous phase(kg/m^3)

σ: interfacial tension(N/m).

D_a : impeller diameter (m)

N_I: rotational speed of the impeller (rps)

5.2.5 Sautar Diameter:

According to equation (2.8), Sauter diameter can be calculated from equation below:

$$\frac{D_S}{D_a} = 0.058 \times (1 + 5.4 \times \psi) \times We^{-06} \qquad (5.9)$$

where:

D_s: volume surface mean diameter of drops or bubbles (m).

D_a: impeller diameter (m)

Ψ: volumetric fraction gas or liquid holdup in dispersion (dimensionless)

We: Weber number (dimensionless)

5.3 Results by Weight Loss and Polarization Techniques:

5.3.1 Single Aqueous Phase (1%wt NaCl):

A) -Weight loss Technique:

The rotational velocities investigated were 262, 349, 438, 525, 600, 612, 800, 1000, 1200, and 1400 rpm leading to the following Reynolds numbers estimated by using Eq.(5.6) based on water physical properties : 41815, 55700, 69904, 83788, 95759, 97674, 127678, 159598, 191517, and 223437. As Re increased or rotational velocity increased, average corrosion rate increased. The experimental results are shown in Table 5.1.

B) - Polarization Technique:

As in weight loss results, the limiting diffusion current was determined by taking the average values between two points $i_L = \frac{i_{L1} + i_{L2}}{2}$, see Fig. (5.1). It was found that the limiting diffusion current increased with increasing rotational velocity (rpm), see Figs. (5.2&5.3), i.e. increasing Re.

Table -5.1-Expermintal Corrosion Results in Single Phase at Rotational Velocities of 262, 349, 438, 525, 600, 612, 800,1000,1200 and 1400 rpm (T=40 ^{o} C).

Revolution per min. (rpm)	Avearge weight loss. $(\Delta W)\times 10^4$ (g)	Avearge corrosion rate (C.R.) (gmd)	Reynolds number (Re)	Sherwood number (Sh)	Current density $(i_C=i_L)$ (A/m^2)	Mass transfer coffcient $(K)\times 10^5$ (m/s.)
262	36	35.2658	41815	470.2	1.4065	1.7690
349	43	42.1231	55700	561.6	1.6800	2.1130
438	49	48.0007	69904	639.9	1.9144	2.4078
525	57	55.8376	83788	744.4	2.2270	2.8010
600	64	62.6948	95759	834.9	2.5005	3.1412
612	64	62.6948	97674	834.9	2.5005	3.1412
800	69.5	68.0827	127678	906.6	2.7153	3.4111
1000	78	76.4093	159598	1017.4	3.0474	3.8280
1200	84	82.2870	191517	1095.8	3.2819	4.1228
1400	86	84.2462	223437	1121.9	3.3600	4.2210

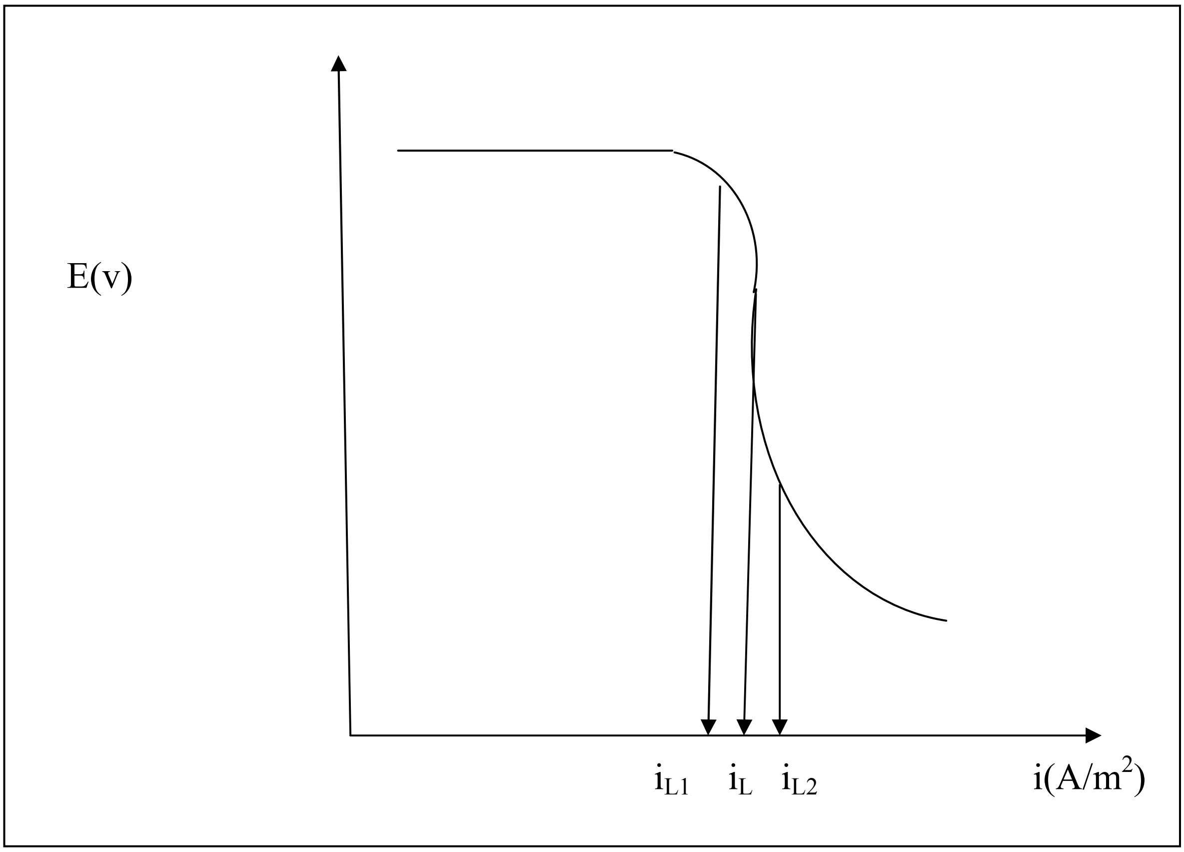

Fig.(5.1)Method of Determining the Limiting Currents

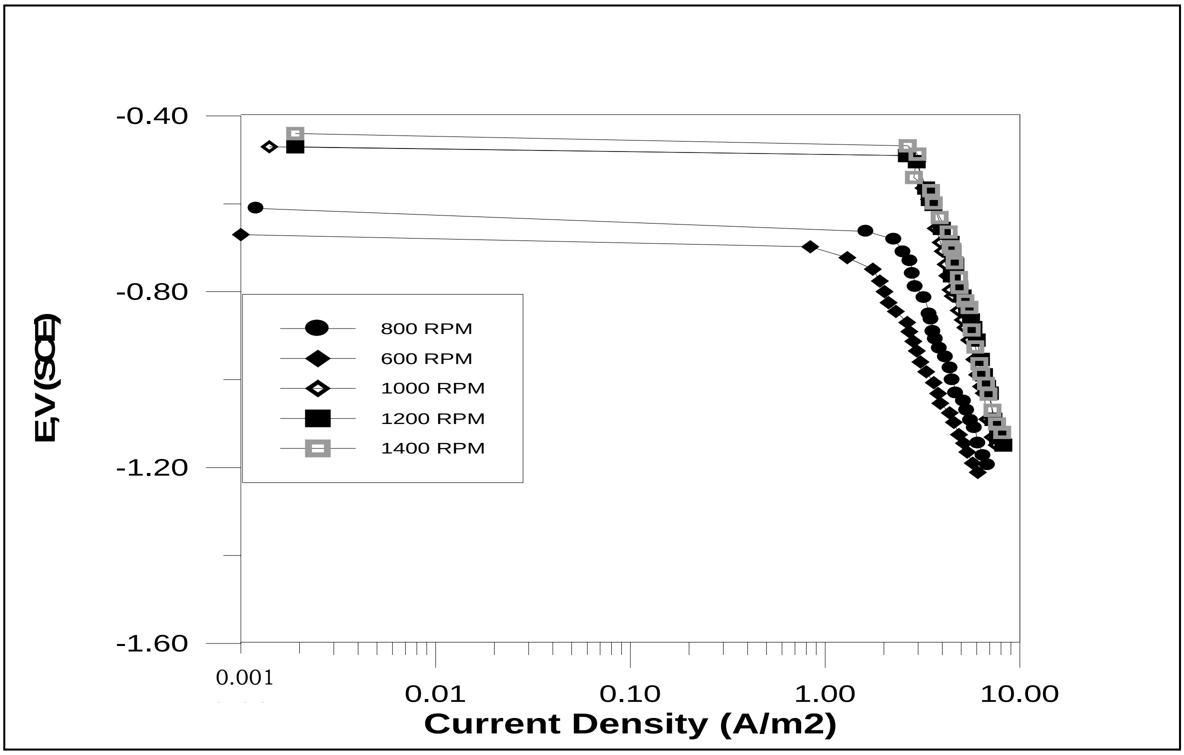

Fig.(5.2) Polarization Curves in 1%wt.NaCl Solution at (T=40^{o}C).

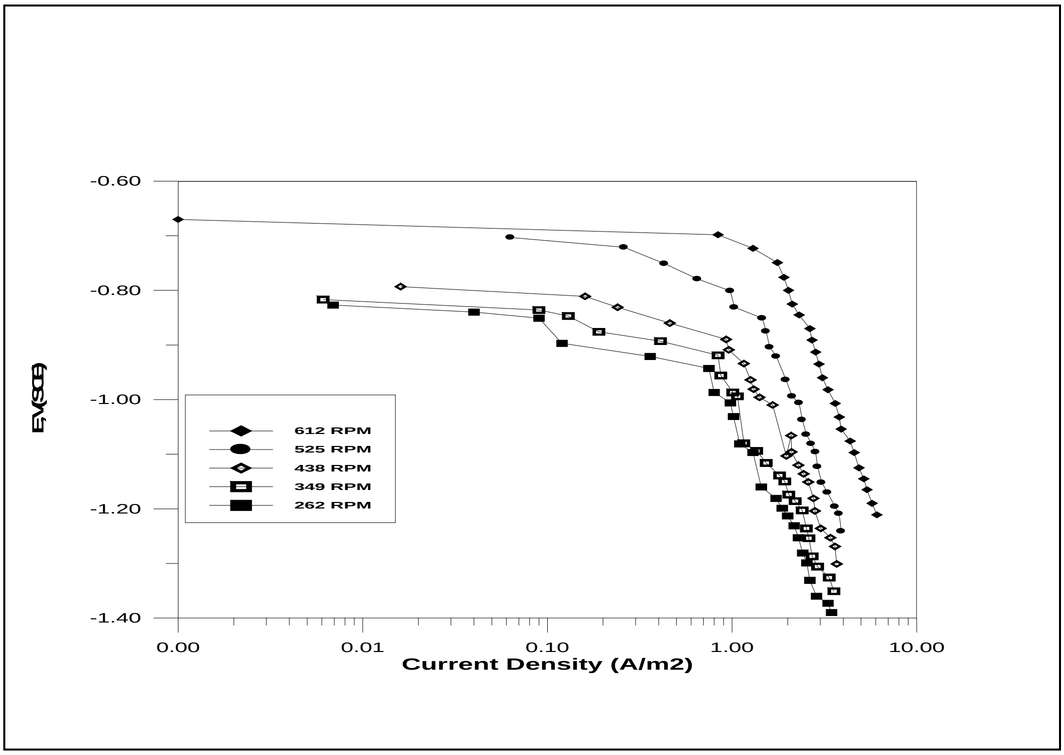

Fig. (5.3) Polarization Curves in 1%wt.NaCl Solution at (T=40°C).

5.4. Two-phase (Aqueous phase (1%wt. NaCl) / kerosene by Weight Loss Technique:

5.4.1 Two-phase (1%vol. &5%vol.) of Aqueous phase 1% wt. NaCl/ kerosene:

The following Reynolds numbers were investigated: (38428, 51238, 64047, 76856, and 89666) which were calculated by using Eq. (5.7) based on continuous phase (kerosene) physical properties (Appendix C). These were calculated for rpm of 600, 800, 1000, 1200&1400 rpm. As Re or rotational velocity (rpm) increased the average corrosion rate increased slightly Appendix A, tables 5.3&5.5.

The following Weber numbers were calculated in these solutions: (147344, 261946, 409290, 589378, and 802209), using Eq.(5.8) based on continuous phase (kerosene) physical properties. When Reynolds number increased Weber number increased too, the variation in average corrosion rates with Weber number were similar to these with Reynolds number. Furtherermore, the average drop diameter (Sauter mean diameter (D_S)) was also calculated using Eq.(5.9). The average corrosion rate increase as Sauter mean diameter (D_S) decreases with increased Reynolds number and Weber number, Tables 5.2,5.3,5.4&5.5.

The relation between average corrosion rate and the number of drops of aqueous phase per unit volume of two phase mixture is that corrosion rate increases as number of drops per unit volume of two phase mixture increases.

Table -5.2- Expermintal Results in Two –Phase 1%vol. Aqueous Phase/ Kerosene at Rotational Velocities of 600, 800, 1000, 1200,1400 rpm (T=40 ° C).

Revo. Per min. (rpm)	Ave. weig. loss. (ΔW) $\times 10^4$ (g)	Ave. Corr. rate (C.R.) (gmd)	Reynolds number (Re)	Sherwood number (Sh)	Current density ($i_C = i_L$) (A/m^2)	Mass tran. Coffc. (K) $\times 10^6$ (m/s.)
600	9.5	9.3062	38428	124	0.3711	4.6676
800	14.5	14.2043	51238	189.4	0.5665	7.1253
1000	19.5	19.1023	64047	254.7	0.7618	9.5817
1200	22.5	22.0411	76856	293.9	0.8790	11.0558
1400	30.5	29.8780	89666	398.4	1.1916	14.9876

Table -5.3- Expermintal Results in Two –Phase 1%vol. Aqueous Phase/ Kerosene at Rotational Velocities of 600, 800, 1000, 1200,1400 rpm ($T=40^{o}$ C).

Revo. Per min. (rpm)	Weber number (We)	Sauter mean diameter $(Ds)\times10^{6}$ (m)	Number of drops per cm^3 of two-phase mixture n/cm3
600	147344	3.8757	3.2824×10^{8}
800	261946	2.7443	9.2407×10^{8}
1000	409290	2.0996	2.0634×10^{9}
1200	589378	1.6870	3.9770×10^{9}
1400	802209	1.4021	6.9289×10^{9}

Table -5.4- Expermintal Results in Two –Phase 5%vol. Aqueous Phase/ Kerosene at Rotational Velocities of 600, 800, 1000, 1200,1400 rpm ($T=40^{o}$ C).

Revo. per min. (rpm)	Ave. weig. loss. $(\Delta W)\times10^{4}$ (g)	Ave. corr. rate (C.R.) (gmd)	Reynolds number (Re)	Sherwood number (Sh)	Current density $(i_C=i_L)$ (A/m^2)	Mass tran. Coffc. $(K)\times10^{6}$ (m/s.)
600	17	16.6533	38428	222	0.6641	8.3529
800	20.5	20.0819	51238	267.7	0.8009	10.073
1000	24.5	24.0003	64047	319.9	0.9572	12.039
1200	26.5	25.9595	76856	346	1.0353	13.021
1400	33.5	32.8168	89666	437.5	1.3088	16.461

Table -5.5- Expermintal Results in Two –Phase 5%vol. Aqueous Phase/ Kerosene at Rotational Velocities of 600, 800, 1000, 1200,1400 rpm ($T=40\,^{o}C$).

Revo. per min. (rpm)	Weber number (We)	Sauter mean diamter. $(Ds)\times10^{6}$ (m)	Number of drops per cm^3 of two-phase mixture n/cm3
600	147344	4.6700	1.8752×10^{8}
800	261946	3.3067	5.2822×10^{8}
1000	409290	2.5298	11.7962×108
1200	589378	2.0327	22.7395×10^{8}
1400	802209	1.6894	39.6099×10^{8}

5.4.2 Two-Phase (8%vol. &16.4%vol.) of Aqueous phase 1%wt.NaCl/ Kerosene:

The following Reynolds numbers were investigated: (38428, 51238, 64047, 76856, and 89666) which were calculated by using Eq. (5.7) based on continuous phase (kerosene) physical properties (Appendix C). These were calculated for rpm of 600, 800, 1000, 1200&1400 rpm. As Re or rotational velocity (rpm) increased the average corrosion rate increased slightly, see Appendix A, tables 5.6&5.8

The following Weber numbers were calculated in these solutions: (147344, 261946, 409290, 589378, and 802209), using Eq. (5.8) based on continuous phase (kerosene) physical properties. When Reynolds Number increased Weber number increased too. The variation in average corrosion rates with Weber number was similar to these with Reynolds number.

Furtherermore, the average drop diameter (Sauter mean diameter (D_S)) was also calculated using Eq. (5.9). The average corrosion rate increase as Sauter mean diameter(D_S) decreases with increased Reynolds number or Weber number, Appendix A, tables 5.6,5.7,5.8&5.9.

The relation between average drop diameter (Sauter mean diameter (D_S)) and corrosion is described by the fact that corrosion rate increases as the average drop Sauter mean diameter (D_S) decreases, see Tables5.6, 5.7, 5.8&5.9.

Furthermore the average corrosion rate increases as number of drops per unit volume of two phase mixture increases.

Table -5.6- Expermintal Results in Two –Phase 8%vol. Aqueous Phase/ Kerosene at Rotational Velocities of 600, 800, 1000, 1200,1400 rpm (T=40 ^{o} C).

Revo. Per min. (rpm)	Ave. weig. loss. (ΔW) $\times10^4$ (g)	Ave. corr. rate (C.R.) (gmd)	Reynolds number (Re)	Sherwood number (Sh)	Current density ($i_C=i_L$) (A/m^2)	Mass tran. Coffc. (K) $\times10^5$ (m/sec.)
600	68	66.6133	38428	888.1	2.6567	3.3415
800	75	73.4705	51238	979.5	2.9302	3.6855
1000	81	79.3482	64047	1057.9	3.1647	3.9804
1200	86	84.2462	76856	1123.2	3.3600	4.2261
1400	97	95.0219	89666	1266.9	3.7898	4.7667

Table -5.7- Expermintal Results in Two –Phase 8%vol. Aqueous Phase/ Kerosene at Rotational Velocities of 600, 800, 1000, 1200,1400 rpm ($T=40\,^{o}$ C).

Revo. Per min. (rpm)	Weber number (We)	Sauter mean diamter. (Ds) $\times 10^6$ (m)	Number of drops per cm^3 of two-phase mixture n/cm3
600	147344	5.2657	1.3080×10^8
800	261946	3.7285	3.6846×10^8
1000	409290	2.8526	8.2277×10^8
1200	589378	2.2920	15.862×10^8
1400	802209	1.9049	27.6302×10^8

Table -5.8- Expermintal Results in Two –Phase 16.4%vol. Aqueous Phase/ Kerosene at Rotational Velocities of 600, 800, 1000, 1200,1400 rpm ($T=40\,^{o}$ C).

Revo. per min. (rpm)	Ave. weig. loss. (ΔW) $\times 10^4$ (g)	Ave. corr. rate (C.R.) (gmd)	Reynolds number (Re)	Sherwood number (Sh)	Current density ($i_C = i_L$) (A/m^2)	Mass tran. Coffc. (K) $\times 10^5$ (m/sec.)
600	75	73.4705	38428	979.5	2.9302	3.6855
800	78	76.4093	51238	1018.7	3.0474	3.8329
1000	88	86.2054	64047	1149.3	3.4382	4.3244
1200	95	93.0627	76856	1240.7	3.7116	4.6683
1400	107	104818	89666	1397.5	4.1805	5.2581

Table -5.9- Expermintal Results in Two –Phase 16.4%vol. Aqueous Phase/ Kerosene at Rotational Velocities of 600, 800, 1000, 1200,1400 rpm (T=40 ^{o} C).

Revo. per min. (rpm)	Weber number (We)	Sauter mean diameter. (Ds) $\times 10^6$ (m)	Number of drops per cm^3 of two-phase mixture n/cm3
600	147344	6.9337	05729×10^8
800	261946	4.9095	1.6139×10^8
1000	409290	3.7562	3.6037×10^8
1200	589378	3.0180	7.0032×10^8
1400	802209	2.508	12.106×10^8

5.5 Two-Phase 8%vol. Aqueous phase (1%wt.NaCl) / kerosene with Inhibitor:

The inhibitors "sodium nitrite and sodium hexapolyphosphate" which were used to investigate their effect on corrosion rate. These inhibitors reduce the corrosion rate (i.e., the percent inhibition $= \frac{(C.R)_{uninhibited} - (C.R.)_{inhibited}}{(C.R.)_{uninhibited}} \times 100$).

When speed of rotational was increased the percent protection decreased and the average corrosion rate decreased when the concentration of inhibitors increased.

The effect of sodium hexapolyphosphate is better than sodium nitrite. These results are shown in Tables below (Tables 5.10, 5.11, 5.12, 5.13, 5.14, 5.15). The percent inhibition decreased with increasing Reynolds number. Sodium hexapolyphosphate is found more effective than sodium nitrite at different concentrations as shown in Tables below (Tables 5.10, 5.11, 5.12, 5.13, 5.14, 5.15).

Table (5.10) Corrosion Rate Results in Presence of the Inhibitor Sodium Nitrite at Concentration 485 ppm and without Inhibitor in Two-Phase of (8%vol.) Aqueous phase (1%wt. NaCl) with kerosene:

Rotational velocity (rpm)	Average corrosion rate without inhibitor (gmd)	Average corrosion rate with inhibitor (gmd)	Percent protection
600	66.6133	28.29	57.53%
800	73.4705	34.90	52.49%
1000	79.3482	42.43	46.61%
1200	84.2462	50.71	40.06%
1400	95.0219	60.42	36.41%

Table (5.11) Corrosion Rate Results in Presence of the Inhibitor Sodium Nitrite at Concentration 970 ppm and without Inhibitor in Two-Phase of (8%vol.) Aqueous phase (1%wt. NaCl) with kerosene:

Rotational velocity (rpm)	Average corrosion rate without inhibitor (gmd)	Average corrosion rate with inhibitor (gmd)	Percent protection
600	66.6133	20.436	69.32
800	73.4705	29.37	60.02
1000	79.3482	36.46	54.12
1200	84.2462	41.09	51.43
1400	95.0219	47.71	49.78

Table (5.12) Corrosion Rate Results in Presence of the Inhibitor Sodium Nitrite at Concentration 1940 ppm and without Inhibitor in Two-Phase of (8%vol.) Aqueous phase (1%wt. NaCl) with kerosene:

Rotational velocity (rpm)	Average corrosion rate without inhibitor (gmd)	Average corrosion rate with inhibitor (gmd)	Percent protection
600	66.6133	9.059	86.4
800	73.4705	14.64	80.06
1000	79.3482	20.91	73.69
1200	84.2462	26.8	68.32
1400	95.0219	33.65	64.58

Table (5.13) Corrosion Rate Results in Presence of the Inhibitor Sodium Hexapolyphosphate at Concentration 20 ppm and without Inhibitor in Two-Phase of (8%vol.) Aqueous phase (1%wt. NaCl) with kerosene:

Rotational velocity (rpm)	Average corrosion rate without inhibitor (gmd)	Average corrosion rate with inhibitor (gmd)	Percent protection
600	66.6133	21.69	67.43
800	73.4705	26.64	63.74
1000	79.3482	35.05	55.9
1200	84.2462	45.64	46.03
1400	95.0219	38.6	59.37

Table (5.14) Corrosion Rate Results in Presence of the Inhibitor Sodium Hexapolyphosphate at Concentration 40 ppm and without Inhibitor in Two-Phase of (8%vol.) Aqueous phase (1%wt. NaCl) with kerosene:

Rotational velocity (rpm)	Average corrosion rate without inhibitor (gmd)	Average corrosion rate with inhibitor (gmd)	Percent protection
600	66.6133	10.13	84.79
800	73.4705	14.72	79.96
1000	79.3482	23.33	70.64
1200	84.2462	33.14	60.81
1400	95.0219	48.96	48.8

Table (5.15) Corrosion Rate Results in Presence of the Inhibitor Sodium Hexapolyphosphate at Concentration 40 ppm and without Inhibitor in Two-Phase of (8%vol.) Aqueous phase (1%wt. NaCl) with kerosene:

Rotational velocity (rpm)	Average corrosion rate without inhibitor (gmd)	Average corrosion rate with inhibitor (gmd)	Percent protection
600	66.6133	4.35	93.46
800	73.4705	8.42	88.53
1000	79.3482	14.78	81.4
1200	84.2462	25.05	70.39
1400	95.0219	39.19	58.75

5.6 Result in General

The present investigation is carried out in (1, 5, 8, and 16.4) %vol. aqueous phase. As %vol. of aqueous phase increased average corrosion rate increased too for a given value of rpm or Re. This means that $(C.R.)_{1\%\text{vol aqueous phase}} < (C.R.)_{5\%\text{vol aqueous phase}} < (C.R.)_{8\%\text{vol aqueous phase}} < (C.R.)_{16.4\%\text{vol aqueous phase}}$. These findings agree with previous results obtained by Rozenfeld (62), Slaiman and Kaify(63). The results in single aqueous phase showed that the average corrosion rate increased with increased (Re. or We.). The average corrosion rate in these two concentrations (1%vol. & 5%vol.) of aqueous solution at Re 38428, 51238, 64047, 76856, and 89666 were lower than corrosion in single phase (i.e., 1%wt. NaCl solution) at nearly similar conditions. On the other hand the average corrosion rate in the concentration of (8%vol &16.4%vol.) aqueous solution in two phase systems at Re 38428, 51238, 64047, 76856, and 89666 were higher than in single phase of (1%wt. NaCl solution) at equivalent conditions. These results agree with other investigation, such as Speller and Kendall (64), Whitman (65), and Wilson (66).

For the above results $(C.R.)_{100\%\text{vol aqueous phase at a given Re}} > (C.R.)_{1\%\text{vol aqueous phase}}$ and $(C.R.)_{100\%\text{vol aqueous single phase}} > (C.R.)_{5\%\text{vol aqueous phase}}$ but $(C.R.)_{100\%\text{vol aqueous phase at a given Re}} < (C.R.)_{8\%\text{vol aqueous phase}}$ and $(C.R.)_{100\%\text{vol aqueous phase at a given Re}} < (C.R.)_{16.4\%\text{vol aqueous phase}}$.

Chapter six

Discussion

6.1 introductions:

When discussing corrosion process in the presence of two immiscible liquids (i.e., water/oil) important corrosion factors must the considered, e.g., in the case of gasoline line. These factors are the presence of a separate water phase and the presence of oxygen. Consideration of these and additional factors show that complexities exist which may considerably modify the observable corrosion effect.

The presence of water is required to cause any corrosion at all, moreover, on clean steel water must be present as separate liquid phase in contact with the steel to cause appreciable corrosion or rusting, for example, gasoline containing water in solution caused no visible corrosion on polished steel specimens after several weeks, when temperature maintained sufficiently high so that there could be no condensation of moisture on the steel surface (67). In the present chapter the results presented in chapter five are discussed and interpreted

6.2 Single Phase (1 %wt. NaCl Aqueous Phase):

Natural water is relatively non-corrosive in absence of oxygen, the corrosion rate of steel is approximately proportional to the concentration of oxygen in water up to about saturation by air at one atmosphere. Salts dissolved in water have a marked influence on the corrosivity of water. Generally, the corrosivity of water containing dissolved salts increased with increasing salt concentration until a maximum is reached, and then corrosivity decreased. This may be attributed to increased electroconductvity because of the increased salt content, until the salt concentration is great enough to cause an appreciable decrease in the oxygen solubility.

6.2.1 Effect of Re on Corrosion Rate

The rate of corrosion increases many times under influence of agitation which enhances the amount of oxygen transfer to the metal specimens. Increased agitation under turbulent flow conditions increases the corrosion rate due to greater agitation of the liquid at the metal surface, and more intimate contact between environments and the metal (1). It increases the supply of corrosive agent and transport, through the solution, of corrosion products from metal surface. That means when Re (rotational velocity) increases the rate of corrosion increases too, see Fig. (6.1).

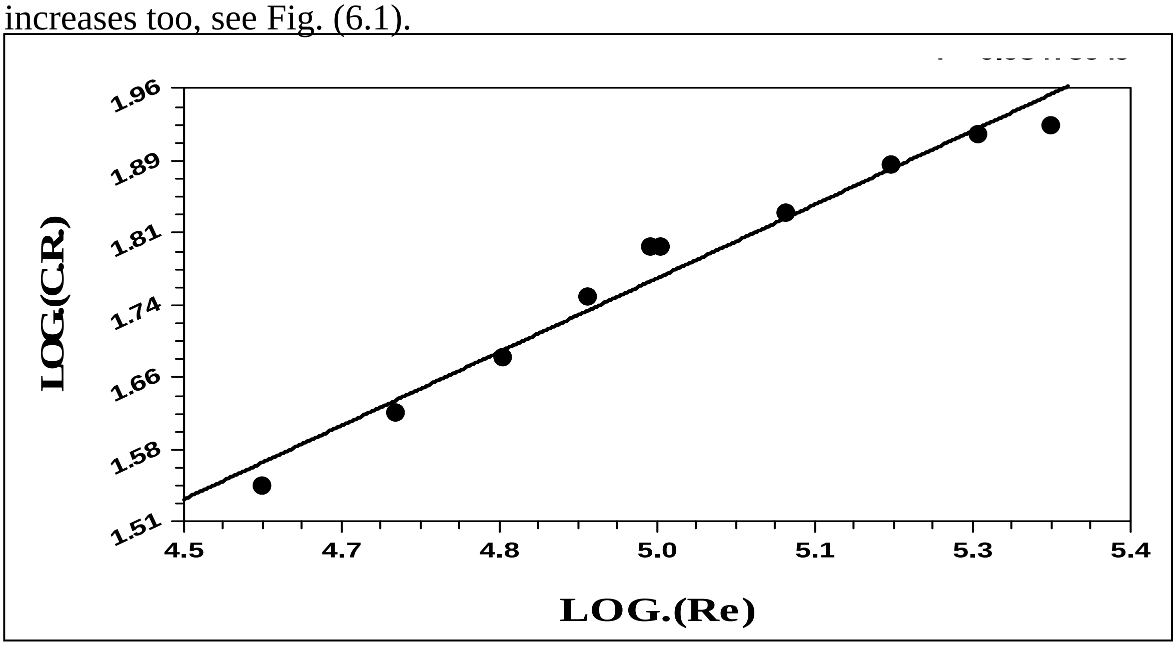

Fig.(6.1) Relation Between LOG.(C.R.) vs. LOG.(Re) for single phase 1%wt.NaCl (T=40°C, C.R. in gmd).

The experiments were carried out in single phase at the following Re: 41815, 55700, 69904, 83788, 95759, 97674, 127678, 159598, 191517, and 223437.

The results are shown graphically in Fig. (6.2) as Sh vs Re. It is shown that increasing Re leads to increase Sh (or mass transfer coefficient). This increase is due to the increased O_2 transported to the surface by eddy diffusion from the bulk of solution leading to increase mass transfer rate and consequently corrosion rate.

Using statistical method, assuming the dependence of Sh on Sc is 1/3, the following correlation is obtained:

$$Sh = 0.164 \times Re^{0.716} \times Sc^{0.33} \quad \text{at } 40\ ^{o}\text{C} \tag{6.1}$$

Such mass transfer correlation were also formulated by Poulson(52), &Ellison& Schmid(50). All these equations are similar in form to the equation of Chilton-Coulborn:

$$Sh = 0.023 \times Re^{0.8} \times Sc^{0.33} \quad \text{at } 25\ ^{o}\text{C} \tag{6.2}$$

Thus it can be stated that the present system is under mass transfer controlled, i.e., corrosion in 1% wt. NaCl aqueous solution is mass transfer controlled see Fig. (6.2).

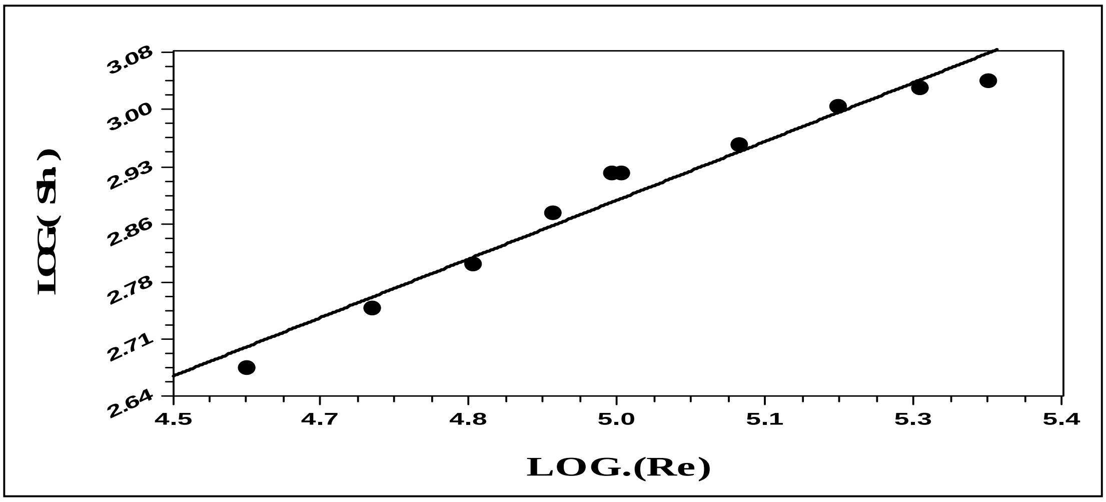

Fig.(6.2) Relation Between LOG.(Sh) vs. LOG.(Re) in 1%wt. NaCl, at rotational velocities from 262 to 1400 rpm (T=40 ^{o}C, C.R. in gmd).

6.3 Two- Phase of Aqueous Solution (1%wt. NaCl)/Kerosene:

The understanding of mixing operations in stirred tanks cannot be achieved without obtaining a better picture of the flow phenomena in them.

Weber (77) studied the flow hydrodynamics in turbulently stirred tank and found a very complicated picture of the flow pattern in the neighborhood of the six-blade turbine impeller.

In turbulent dispersion drops, show complicated motion, because they are acted on by turbulence components as well as mean flow currents of the surrounding liquid. Indeed a first step in the study of fluid and drops motion in turbulent dispersions may be fundamental and detailed knowledge of the turbulence characteristics of the liquid flow is important.

Some studies (67, 68) on turbulent flow characteristics indicated many inherent experimental difficulties, especially when applied to heterogeneous systems containing drops of the dispersed phase. Consequently, the experimental studies of turbulence in liquid system are still in the early stage of the development, or, at least, they are slowly developing.

In the light of above few lines it can be seen how much the hydrodynamics of agitation system is complex and become even more difficult to understanding in the case of dispersion system of immiscible liquids.

If a certain mass of liquid is placed in a turbulent stream of immiscible liquid, the liquid will break up under the influence of turbulence eddies. This phenomenon was first studied experimentally and theoretically by Tergubova (69).

The theory of this phenomenon was developed by Kolomogroff (70), based on the assumption of homogenous, isentropic turbulence. It is related to the fact that the velocity in a turbulent liquid stream varies from one point to another. Some attempts were made, theoretically and experimentally, to evaluate the effective relative velocity in turbulent dispersions (71). In these studies, however, some limitations were involved.

The droplet in turbulent dispersion responds to fluid motion depending on their diameter and density difference. For example, if droplets are large compared to the macro scale of turbulence, they will, at most, follow the bulk flow current as pointed out by Hinze (72).

Otake et al. (73) found that the magnitudes of turbulence component velocities of fluid are always larger than those of droplets.

Otack a et at.(74) pointed out that a difference exists between the predicated mass transfer coefficients based on the average dissipation rate ,as the energy distribution in stirred tanks is extremely non- uniform . However the turbulence fluctuations in stirred tank are far larger than that in pipe flow.

Corrosion rates even when controlled by diffusion are not always simply related to mass transfer, especially for specimen with non-uniform flow conditions (75). The influence of hydrodynamics on corrosion is a rather complicated process as corrosion is controlled by mass transport through a damped turbulent boundary layer followed by transport through a porous corrosion product layer as shown in Fig. (6.3). In two phase systems fluid hydrodynamics are even more complicated .In addition to this corrosion is enhanced as oxygen solubility in kerosene is many times higher than that of the aqueous phase.

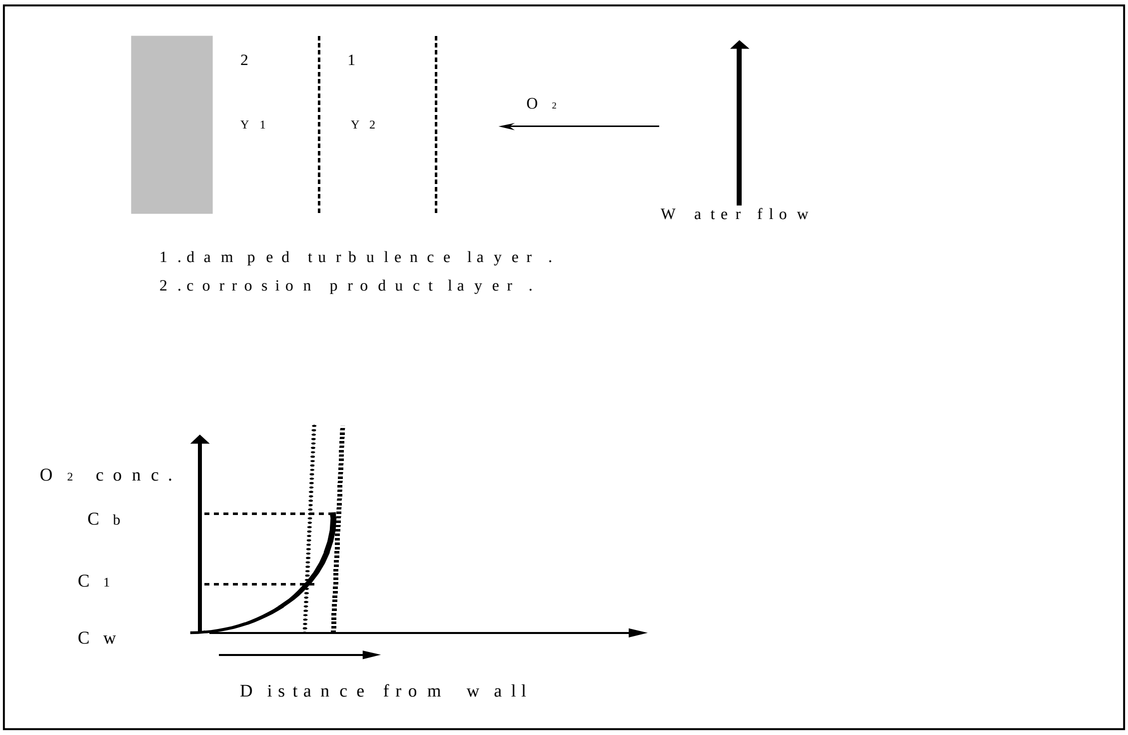

Fig (6.3) Oxygen Concentration Gradient near the Metal Surface

6.3.1 Low Concentration of Aqueous Phases (1&5%vol.):

A-Effect of Re on Corrosion Rate:

The influence of increased Re, i.e., increased turbulence , is to be increase the number of dispersed aqueous phase droplets which are found to be a function of We , therefore increasing Re or We would lead to more intimate contact between the dispersed phase droplets and metal specimens .

In two phases, increasing Re increases the corrosion rate by increasing the O_2 transport to the surface from dispersed and continuous phases leading to increase the corrosion rate. Also the increased Re causes an increase in turbulence within the bulk of fluid which lead to more transfer of O_2 from continuous phase (kerosene) to dispersed phase (water) of less dissolved O_2 concentration, hence shifting corrosion rate to higher values, see Figs.(6.4&6.5).

Furthermore, the corrosion rates in two phases (low concentration of aqueous phases (1&5%vol.)) remained lower than in single phase. This fact emphasized the important role of the second inert phase (i.e., kerosene) in reducing generally the absolute corrosion rates to be expected in single aqueous phase, see Figs.(6.4&6.5)

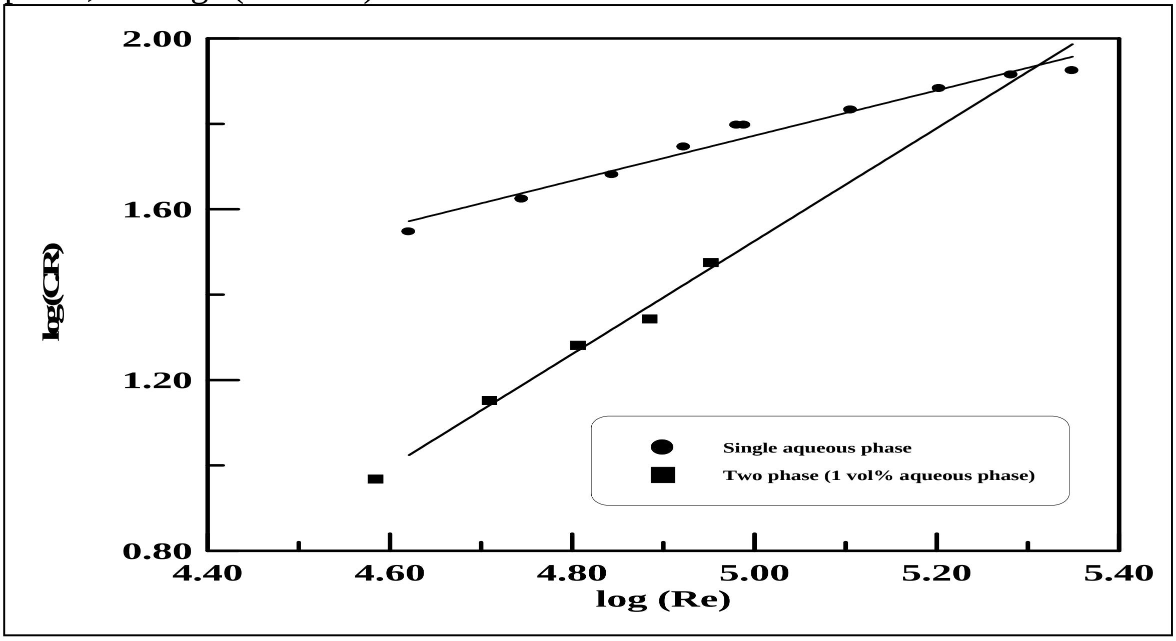

Fig.(6.4)Relation Between LOG.(C.R.) vs. LOG.(Re) in Two- Phase of 1%vol. Aqueous Solution 1%wt.NaCl / 99% vol. kerosene(T=40^{o}C, C.R. in gmd).

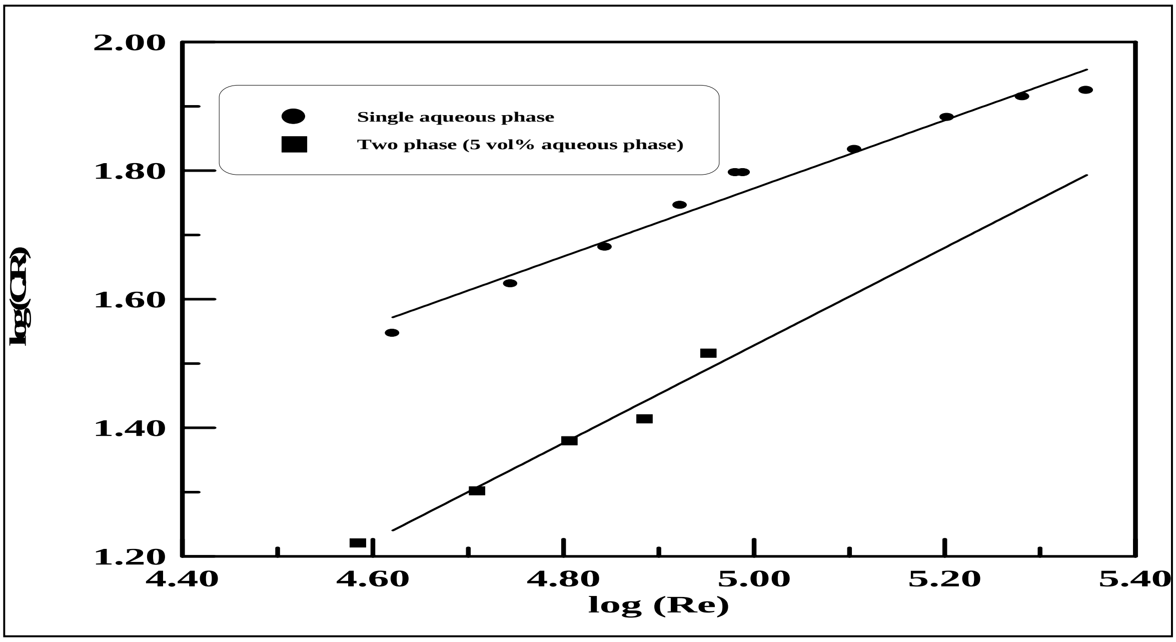

Fig.(6.5)Relation Between LOG.(C.R.)vs. LOG.(Re) in Two- Phase of 5%vol. Aqueous Solution 1%wt.NaCl/ 95% vol. kerosene(T=40^{o}C, C.R. in gmd).

B. Effect of Re on Sh :

Figures (6.6&6.7) show the variation of Sh with Re, using the best fit method to the data of two –phase , the following equations were obtained by plotting Sh vs Re, see Figs (6.6&6.7) :

(1%vol. aqueous phase): $Sh = 2.043 \times Re^{0.371} \times Sc^{0.33}$ at 40 ^{o}C (6.3)

(5%vol. aqueous phase): $Sh = 0.021 \times Re^{0.775} \times Sc^{0.33}$ at 40 ^{o}C (6.4)

comparing Eqs.(6.3&6.4) indicate that the higher the percent water is the higher the corrosion rate (or mass transfer coefficient). In other word the dependence of Sh on Re increases with increasing volume percent of water. Inspit of that the O_2 concentration in kerosene is higher than in water, the corrosion rate in single aqueous phase is higher than in two phases of 1&5%vol.of 1%wt. NaCl aqueous phase. This is attributed to the fact the aqueous phase (1%wt. NaCl) is more electrically conductive than two phase.

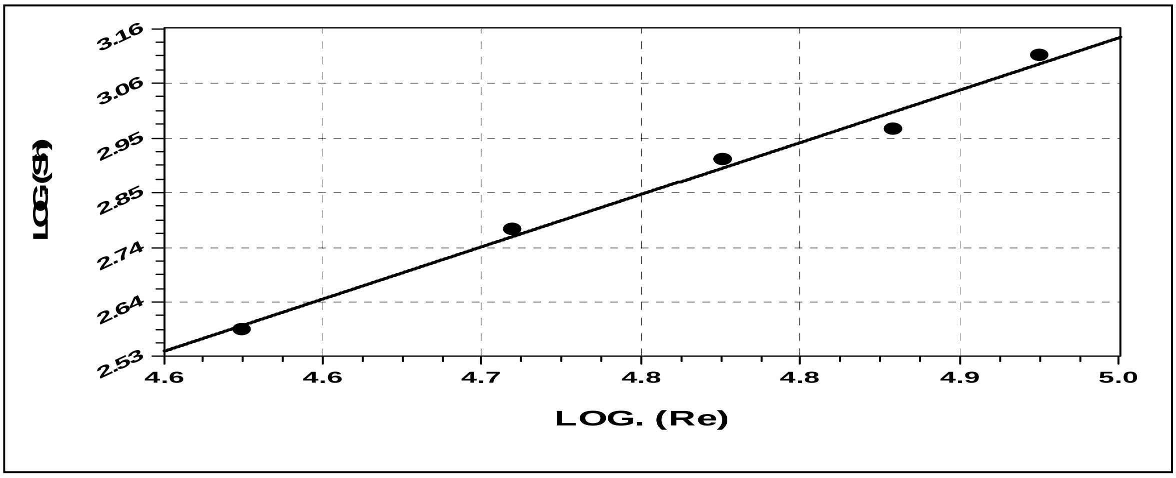

Fig. (6.6) Relation Between LOG.(sh) vs. LOG.(Re) in Two- Phase of 1%vol. Aqueous Solution 1%wt.NaCl /99% vol. kerosene(T=40°C).

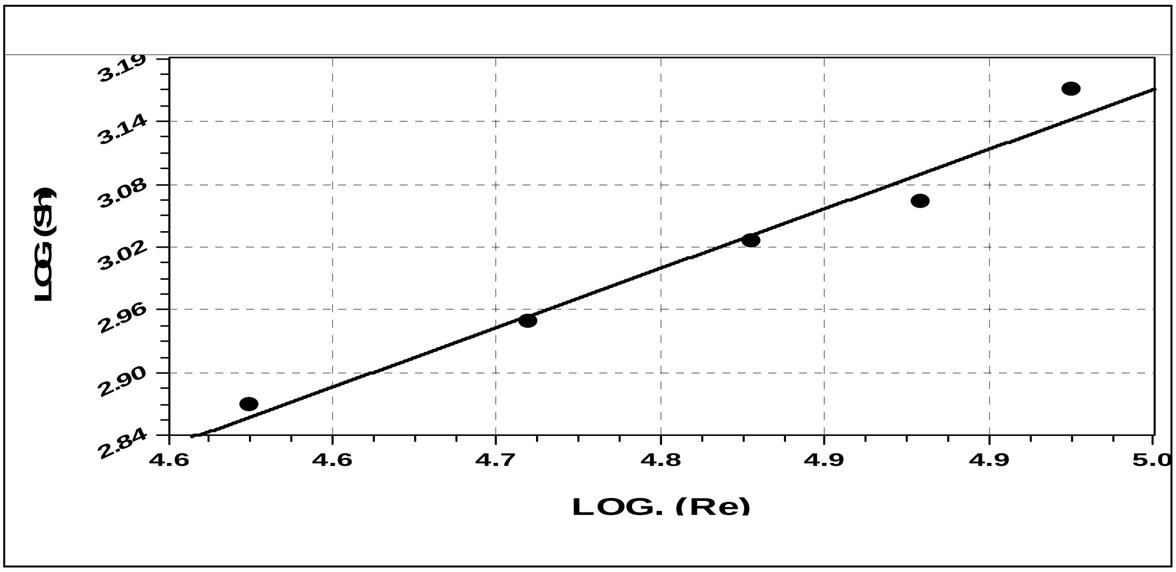

Fig. (6.7) Relation Between LOG. (sh) vs. LOG.(Re) in Two- Phase of 5%vol. Aqueous Solution 1%wt.NaCl/95% vol. kerosene(T=40°C).

C. Effect of We, Sauter Diameter and No. of Droplets on Corrosion Rate:

Increasing Re leads to increase We according to the data calculated in chapter five. At high values of We the dispersed phase is subdivided into more droplets leading to decrease the Sauter mean diameter. This would lead in turn to increase the mass transfer rate (O_2 transport) between phases due to two reasons, firstly is the increased turbulence (or micro- turbulence) , secondly the increased surface area of contact between two phases . These two factors lead to increase the corrosion rate. The higher values of We due to higher values of Re result in lower values of Sauter mean diameter, higher numbers of droplets (n) per cubic centimeter .and more mass transfer (or corrosion rate), see Figs(6.8 to 6.13)

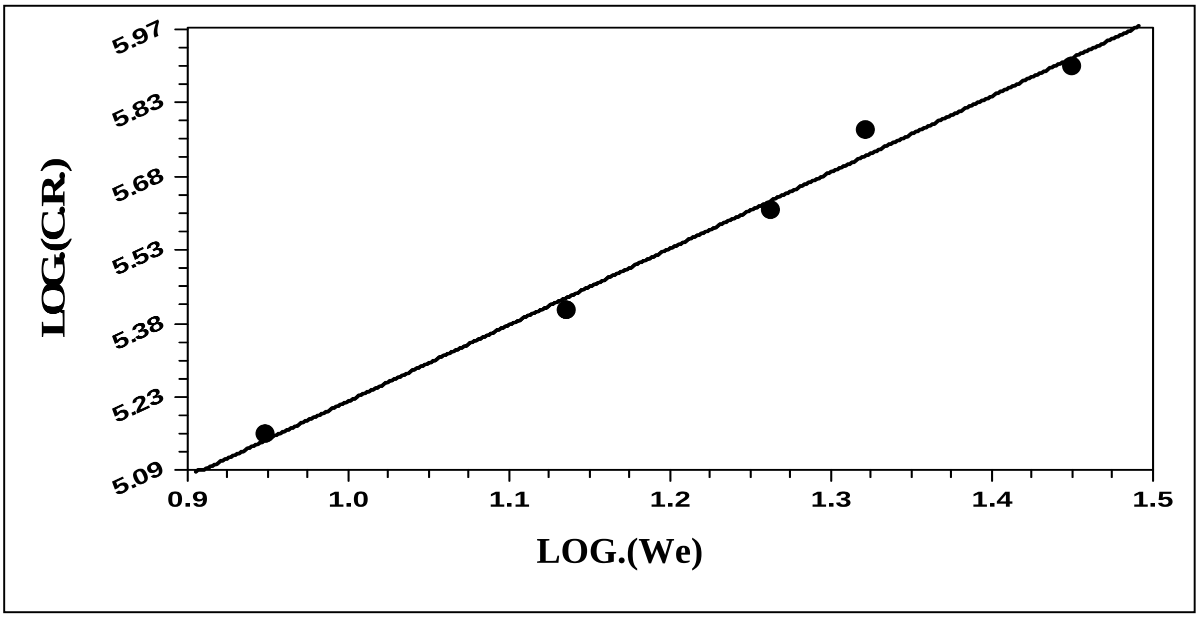

Fig.(6.8)Relation Between LOG.(C.R) vs. LOG.(We) in Two- Phase of 1%vol. Aqueous Solution 1%wt.NaCl /99% vol. kerosene(T=40^{o}C, C.R. in gmd).

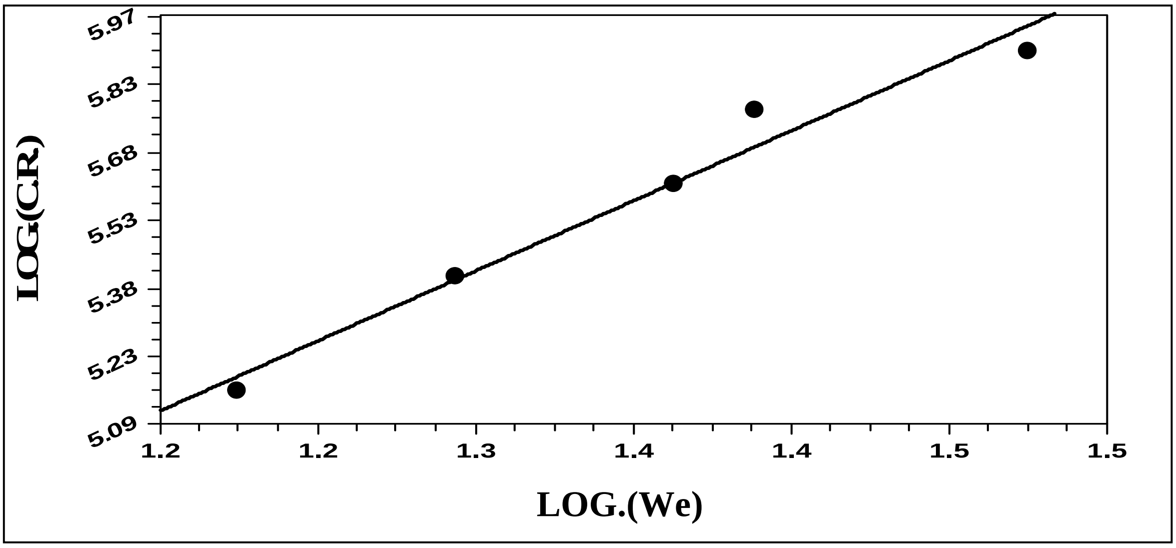

Fig.(6.9)Relation Between LOG.(C.R) vs. LOG.(We) in Two- Phase of 5%vol. Aqueous Solution 1%wt.NaCl /95% vol. kerosene(T=40^{o}C, C.R. in gmd).

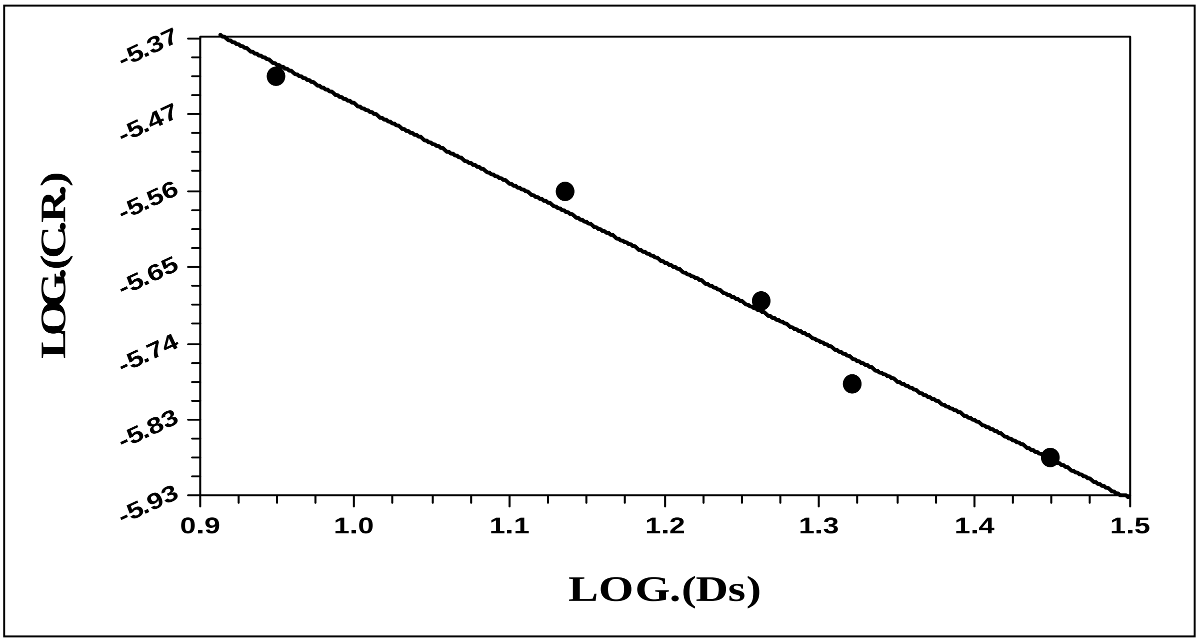

Fig.(6.10)Relation Between LOG.(C.R)vs. LOG.(Ds)(m) in Two- Phase of 1%vol. Aqueous Solution 1%wt.NaCl /99% vol. kerosene (T=40^{o}C, C.R. in gmd, and D_s in m.).

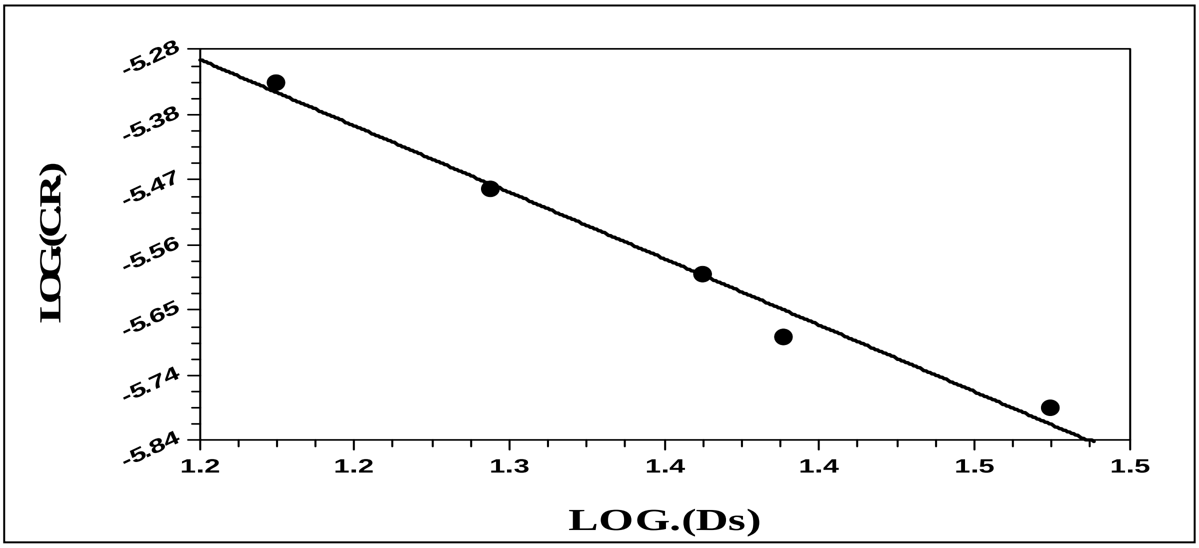

Fig.(6.11) Relation Between LOG.(C.R)vs. LOG.(Ds) in Two- Phase of 5%vol. Aqueous Solution 1%wt.NaCl 95% vol. kerosene(T=40^{o}C, C.R. in gmd and D_s in m).

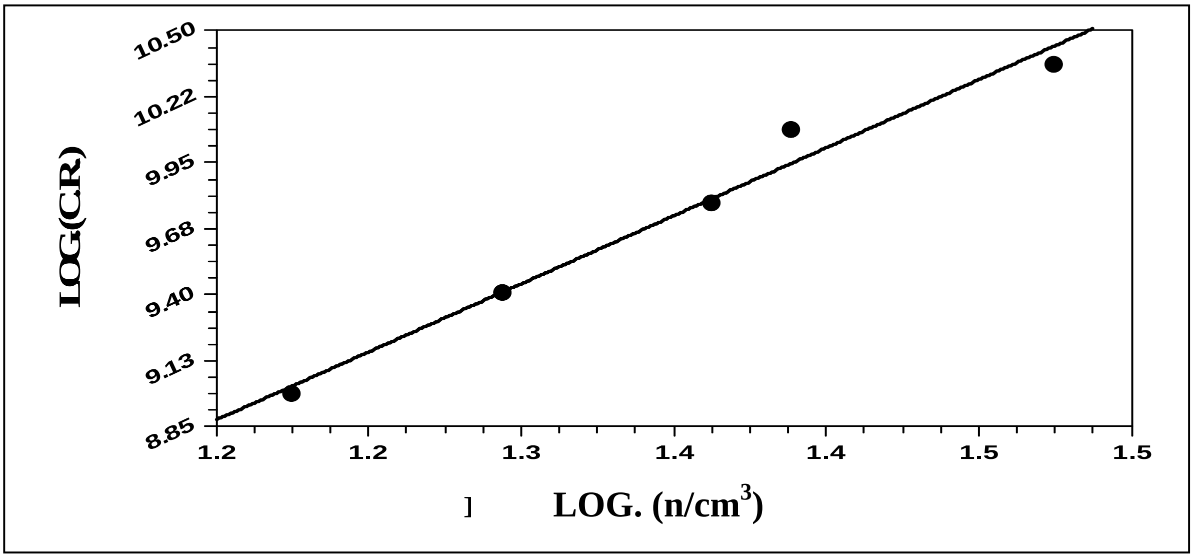

Fig.(6.12) Relation Between LOG.(C.R) vs. LOG.(n/cm^3) in Two- Phase of 1%vol. Aqueous Solution 1%wt.NaCl/99% vol. kerosene(T=40^{o}C, C.R. in gmd).

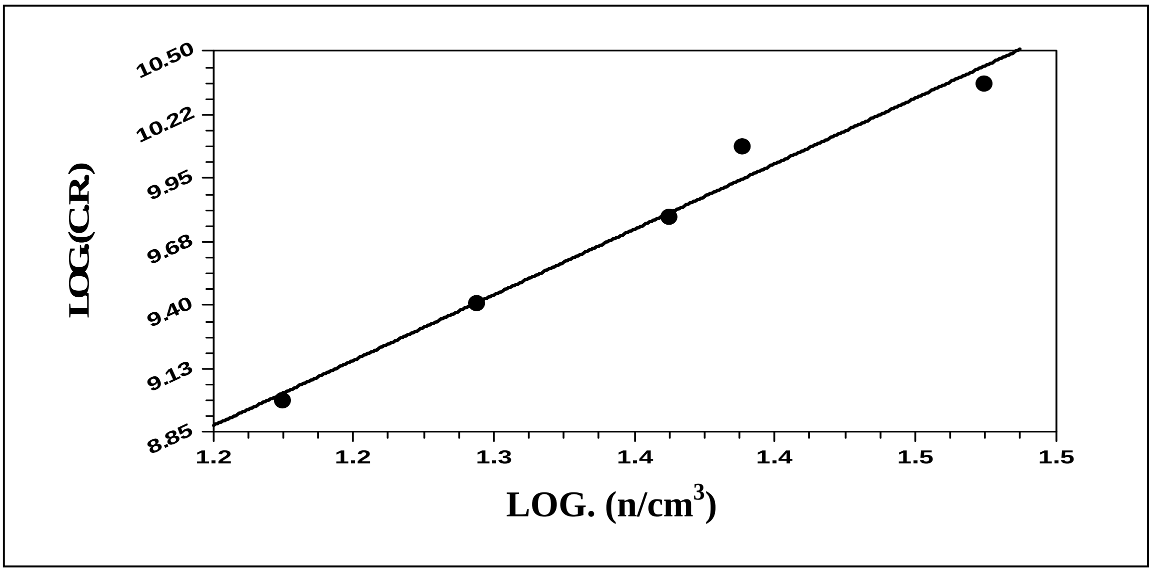

Fig.(6.13) Relation Between LOG.(C.R)vs. LOG.(n/cm^3) in Two- Phase of 5%vol. Aqueous Solution 1%wt.NaCl /95% vol. kerosene(T=40^{o}C, C.R. in gmd).

6.3.2 High Concentration of Aqueous Phase (8 &16.4%vol.):

A-Effect of Re on Corrosion Rate:

Re is function of rotational velocity in agitation system. Velocity primarily affects corrosion rate through its influence on diffusion phenomena. Turbulent flow conditions increase the rate of corrosion due to a greater agitation of the liquid at the metal surface. In two phases, increasing Re increases the corrosion rate by increasing the O_2 transport to the surface from the two phases. Also increased Re causes an increased turbulence within the bulk of the fluids which would lead to more transfer of O_2 from continuous phase to dispersed phase, see Figs (6.14&6.15).

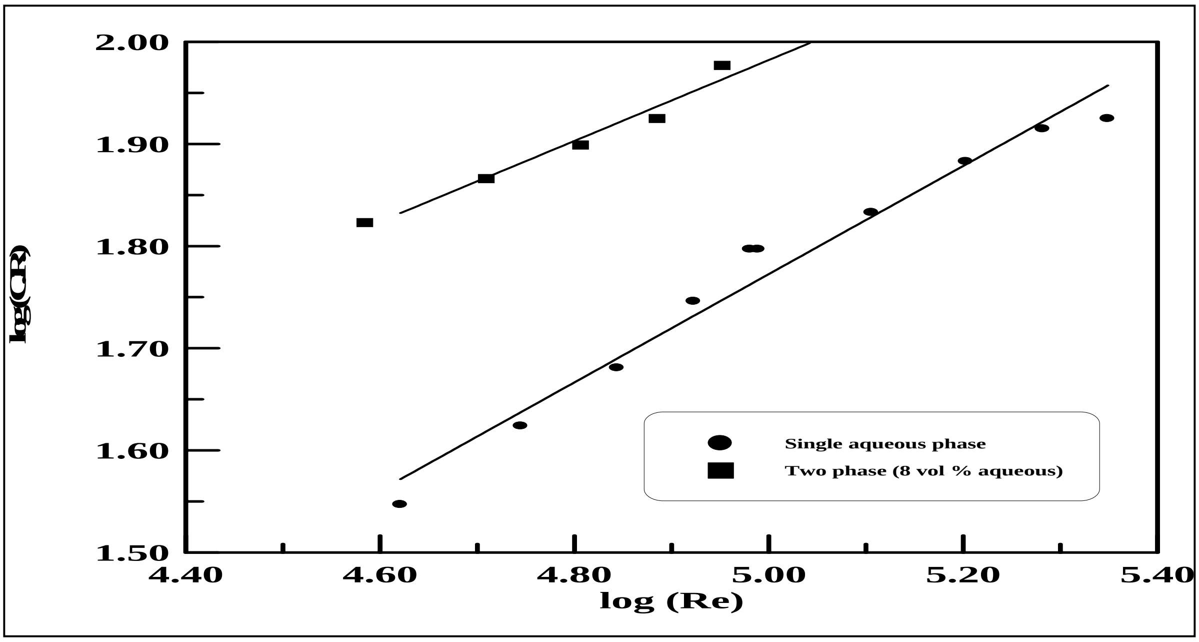

Fig.(6.14)Relation Between LOG.(C.R.)vs. LOG.(Re) in Two- Phase of 8%vol. Aqueous Solution 1%wt.NaCl /92% vol. kerosene(T=40°C, C.R. in gmd).

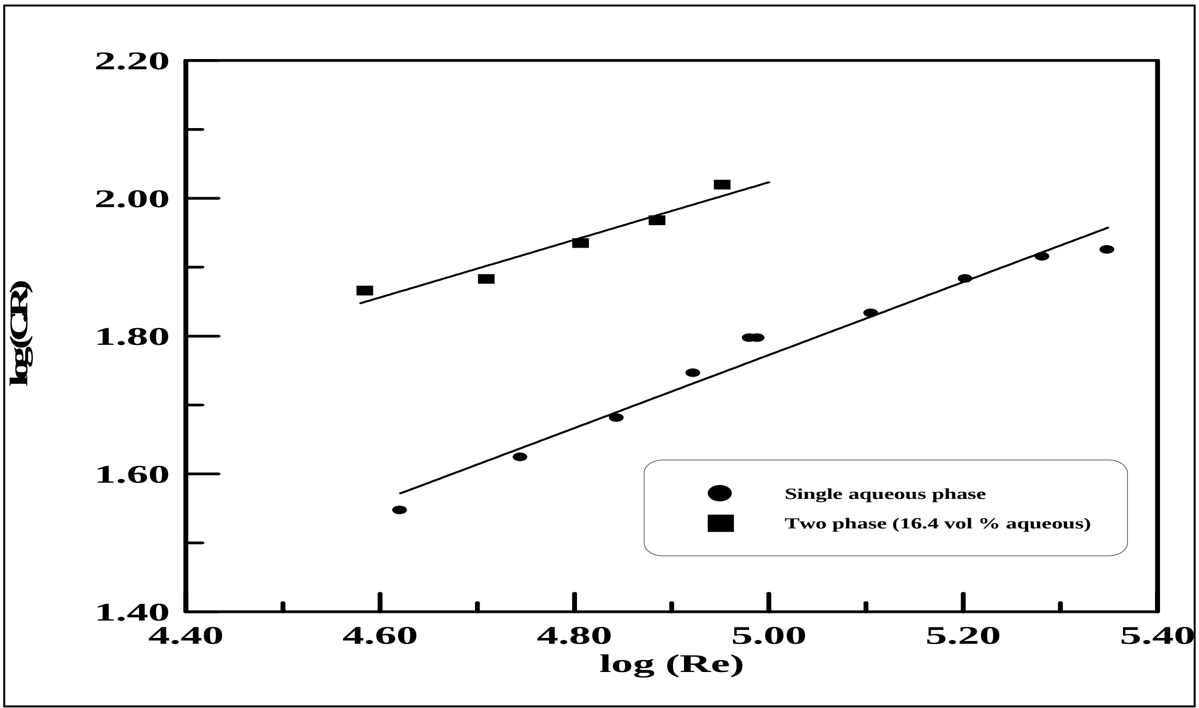

Fig.(6.15)Relation Between LOG.(C.R.)vs. LOG.(Re) in Two- Phase of 16.4%vol. Aqueous Solution 1%wt.NaCl /83.6% vol. kerosene(T=40°C,C.R. in gmd).

B. Effect of Re on Sh :

Using the best fit to data of two phase agitated systems, equations were obtained by plotting Sh vs Re, see Figs (6.16&6.17):

1. (8 %vol. Aqueous phase): $Sh = 2.199 \times Re^{0.447} \times Sc^{0.33}$ at 40 °C (6.5)
2. (16.4 %vol. Aqueous phase): $Sh = 4.166 \times Re^{0.405} \times Sc^{0.33}$ at 40 °C (6.6)

Higher percent aqueous phase gives higher corrosion rate (or mass transfer coefficient). In other word when agitation increased the protecting film on the metal specimen is destroyed totally or partially which would lead to increase corrosion rate with increasing Re. For this reason the rate increased with increased Re due to increased turbulence of continuous aqueous phase , see Figs(6.16&6.17).

The corrosion rate in 16.4%vol.solution is higher than in 8%vol. as shown in Figs.(6.14&6.15), and Eqs.(6.5&6.6).

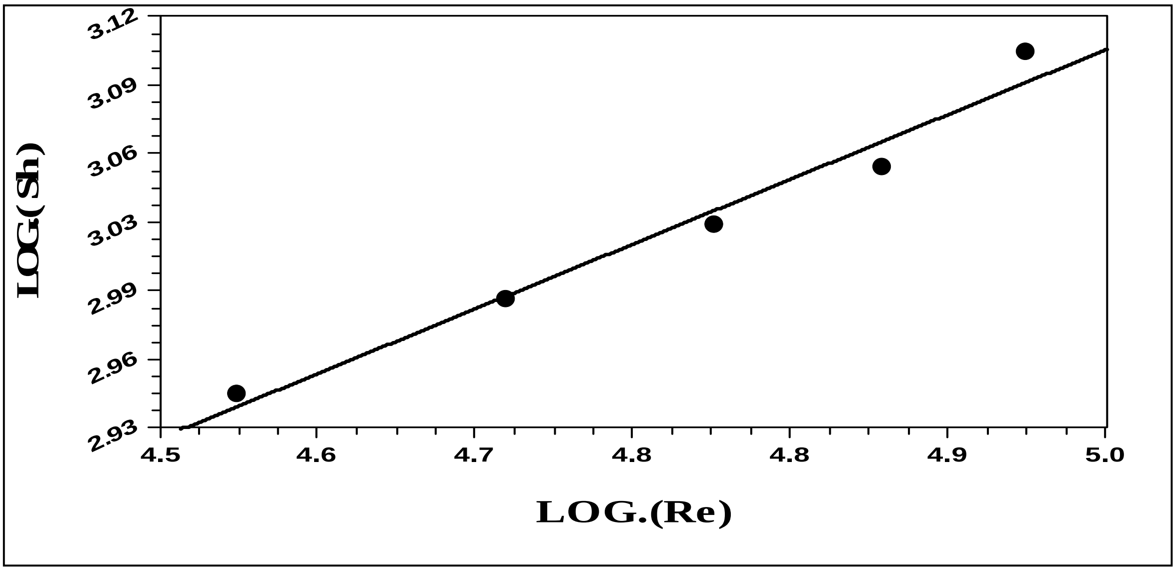

Fig.(6.16)Relation Between LOG.(Sh.)vs. LOG.(Re) in Two- Phase of 8%vol. Aqueous Solution 1%wt.NaCl /92% vol. kerosene(T=40°C).

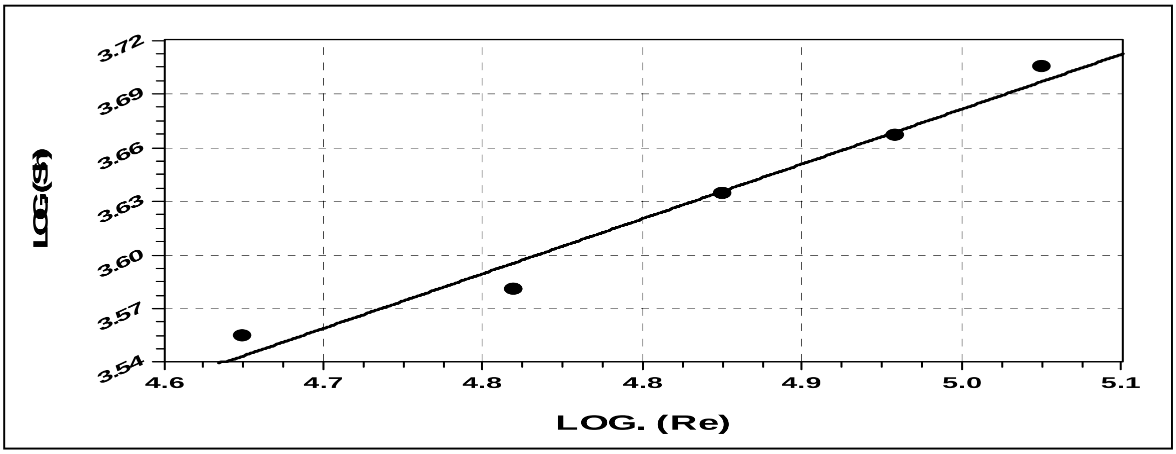

Fig.(6.17)Relation Between LOG.(Sh.)vs. LOG.(Re) in Two- Phase of 16.4%vol. Aqueous Solution 1%wt.NaCl/83.6% vol. kerosene(T=40°C).

C. Effect of We, Sauter Diameter and No. of Droplets on Corrosion Rate:

The size of droplets was found to be a function of We according to equation (5.9). Increasing We would lead to smaller diameter of droplets and greater number of them per cubic centimeter of solution (two phase). Thus agitation leads to more intimate contact between the dispersed phase and the metal specimens resulting in higher corrosion rate with increasing Re values as found in 8%vol., 16.4 %vol. aqueous phase (1 %wt. NaCl)/see Figs.(6.18 to 6.23)

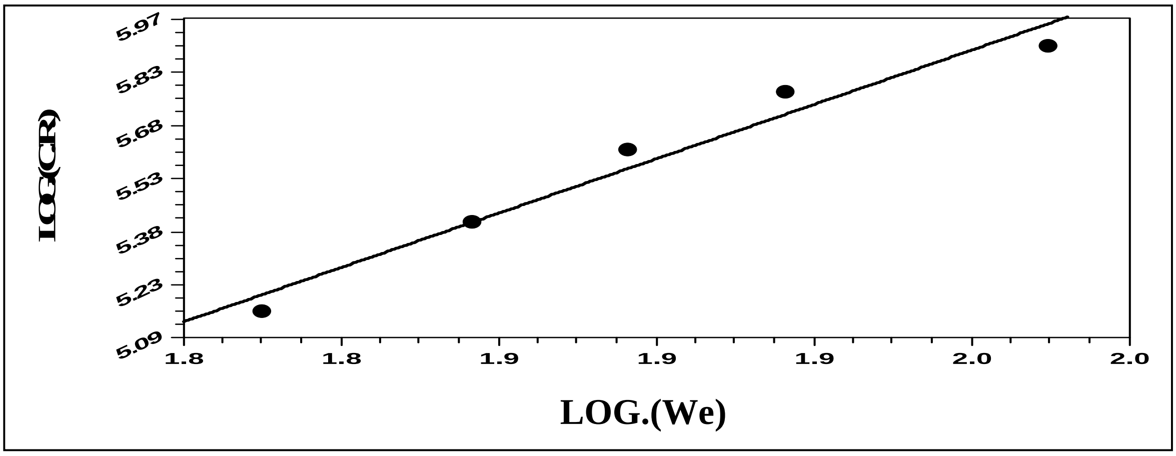

Fig.(6.18)Relation Between LOG.(C.R)vs. LOG.(We) in Two- Phase of 8%vol. Aqueous Solution 1%wt.NaCl /92% vol. kerosene(T=40°C,C.R. in gmd).

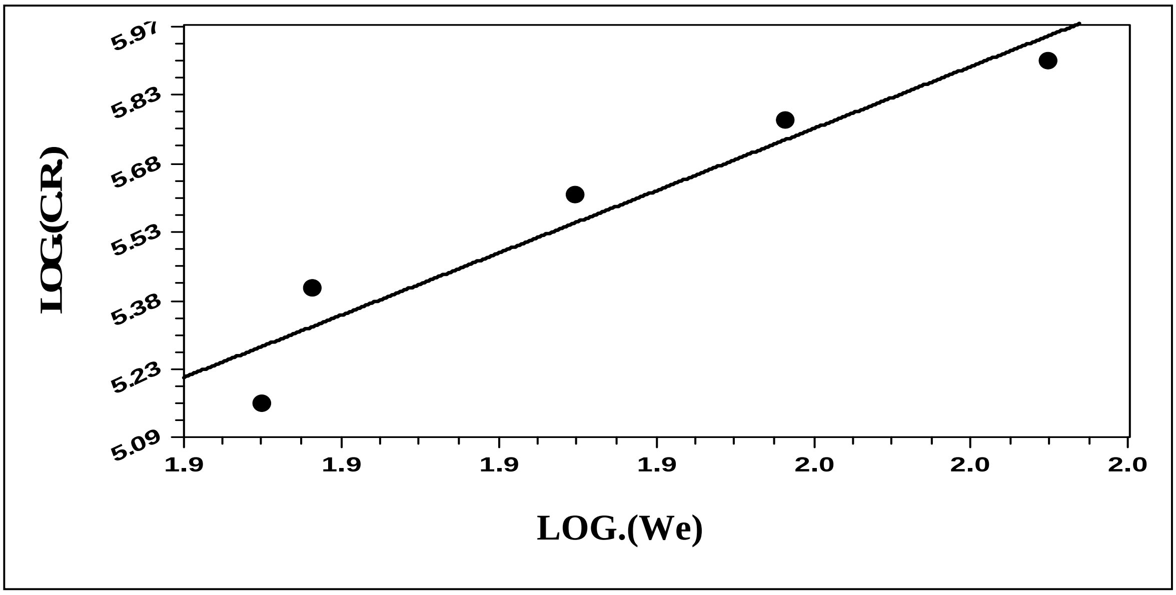

Fig.(6.19)Relation Between LOG.(C.R) vs. LOG.(We) in Two- Phase of 16.4%vol. Aqueous Solution 1%wt.NaCl /83.6% vol. kerosene(T=40^{o}C, C.R. in gmd).

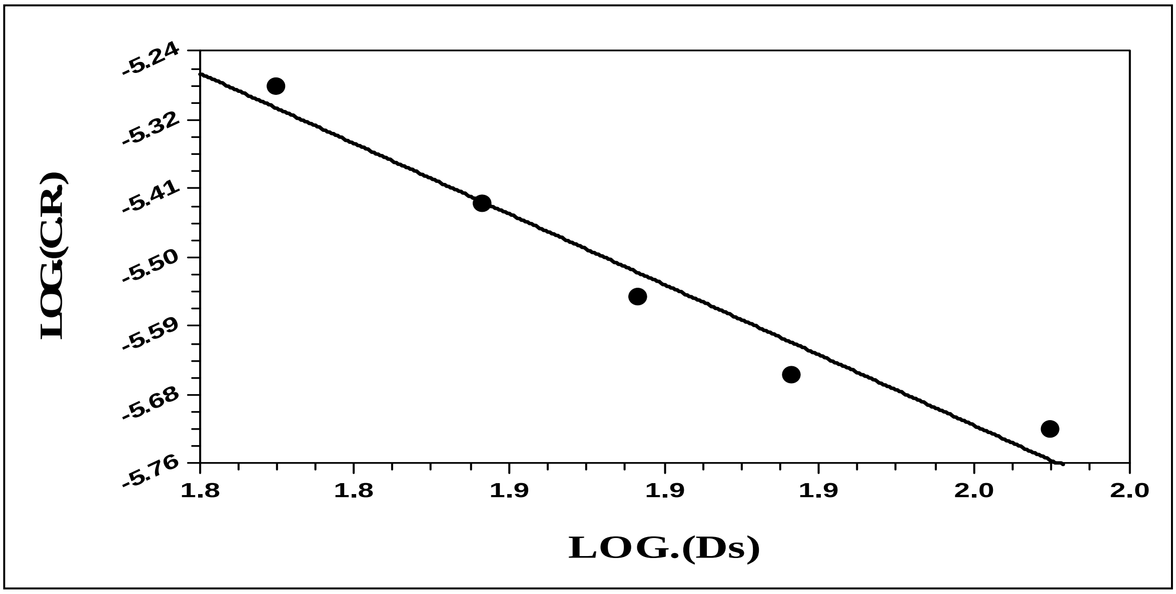

Fig.(6.20)Relation Between LOG.(C.R)vs. LOG.(Ds) in Two- Phase of 8%vol. Aqueous Solution 1%wt.NaCl /92% vol. kerosene(T=40^{o}C, C.R. in gmd and D_s in m).

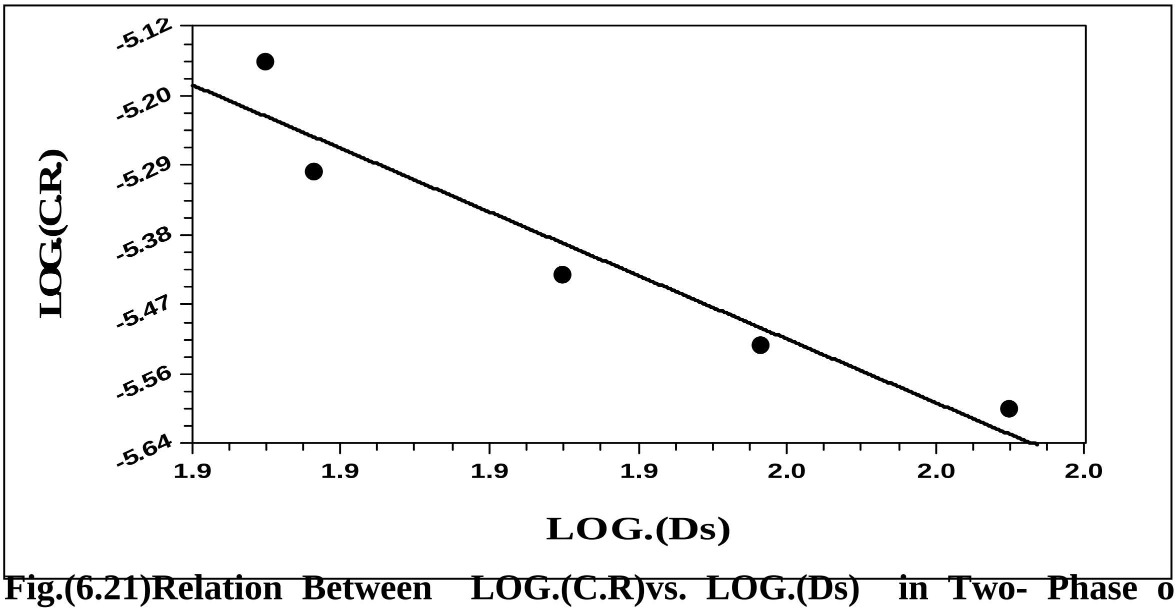

Fig.(6.21)Relation Between LOG.(C.R)vs. LOG.(Ds) in Two- Phase of 16.4%vol. Aqueous Solution 1%wt.NaCl /83.6% vol. kerosene(T=40^{o}C, C.R. in gmd and D_s in m).

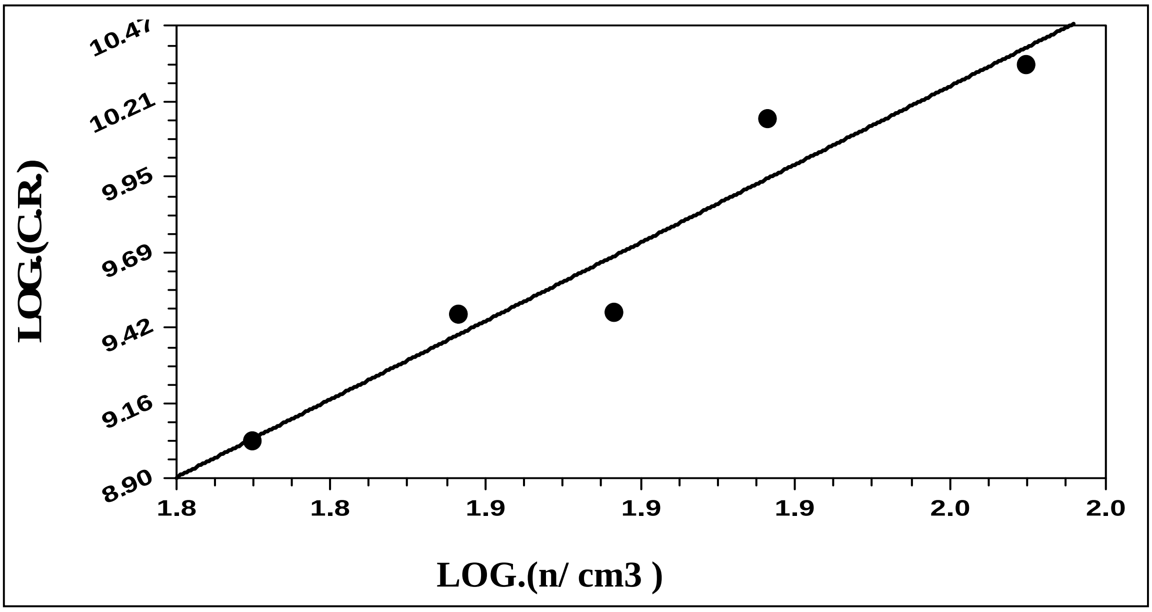

Fig.(6.22)Relation Between LOG.(C.R)vs. LOG.(n/ cm3) in Two- Phase of 8%vol. Aqueous Solution 1%wt.NaCl /92% vol. kerosene(T=40^{o}C, C.R. in gmd).

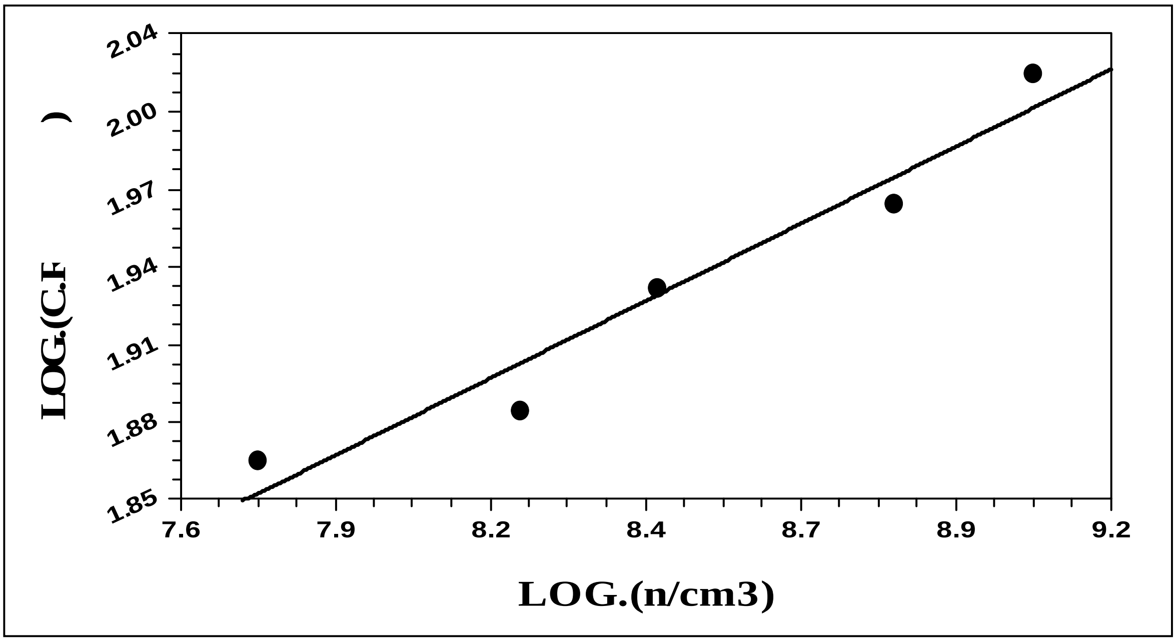

Fig.(6.23)Relation Between LOG.(C.R)vs. LOG.(n/ cm3) in Two- Phase of 16.4%vol. Aqueous Solution 1%wt.NaCl /83.6% vol. kerosene(T=40^{o}C, C.R. in gmd).

6.4 Effect of Phase Concentration on Corrosion Rate:

The hydrocarbon phase has a marked influence on corrosion rate; one hand it prevents the metal to be wetted by the aqueous phase and on the other hand it supplies the aqueous phase with oxygen since its content is higher than that of the aqueous phase, the results indicated that the corrosion rate increased with increased aqueous phase (%vol.), this finding was also seen in the resulting of Slaiman and Kaffy (63).

Tables 5.3, 5.5, 5.7and 5.9 show that at a particular Re increasing percentage volume of aqueous phase leads to increase the corrosion rate for the whole range of Re and volume percentages. The presence of aqueous phase leads to increase the corrosion rate in spite of the fact that water contains less dissolve O_2 concentration (main cathodic reaction), i.e. the oxygen dissolved in kerosene is six times higher than water , but the electrical conductivity of aqueous phase increases when the quantity of aqueous phase increases which lead to increase corrosion rate. Micro-turbulence and impact of droplets on metal specimen surface are main reasons for increased corrosion rates in agitated two-phase systems.

Generally the corrosion rate in single aqueous phase is higher than that in two phases (1%vol. & 5%vol.) at the same or equivalent Re values and lower than two phases (8, 16.4%vol.) of aqueous phase.

6.5 Corrosion Inhibition:

Sodium nitrite is used as inhibitor in two phases (8 %vol. aqueous phase). This inhibitor absorbs oxygen (de aerator or oxygen scavenger), which removes dissolved oxygen from aqueous solution according to the reaction:

$$NaNO_2 + O^- \rightarrow NaNO_3 \qquad (6.9)$$

When the quantity of sodium nitrite is doubled the percentage of protection is increased because of the increased quantity absorbed oxygen from aqueous solution.

Sodium hexapolyphosphate acts as inhibitor in two phases (8 %vol. aqueous phase), due to the formation on the metal surface of a layer of insoluble or slightly soluble corrosion products. However, in all cases, a preliminary stage of adsorption of the inhibitor can be envisaged and to the extent, the adsorption theory has fulfilled its purpose (1).

Another theory says that these inhibitors are adsorbed on the metal surface forming protective layer. The adsorption is considered either as physical adsorption or chemisorption (1).

Sodium hexapolyphosphate is better than sodium nitrite (1) as shown in Figs. (6.24&6.25). Generally the presence of inhibitors lead to decrease the corrosion rate for the whole investigated range of Re as the concentrations of inhibitor increased the corrosion rate decreased at any particular value of Re, when speed of rotational was increased the percent protection decreased and the average corrosion rate decreased when the concentration of inhibitors increased.

Furthermore increased micro turbulence and impact of droplets, on the metal specimens, with increasing Re destroys the protective layer and reducing percent inhibition (76). This relevant in Figs.(6.24&6.25) as the reduction in average corrosion rate is less with increasing values of Re.

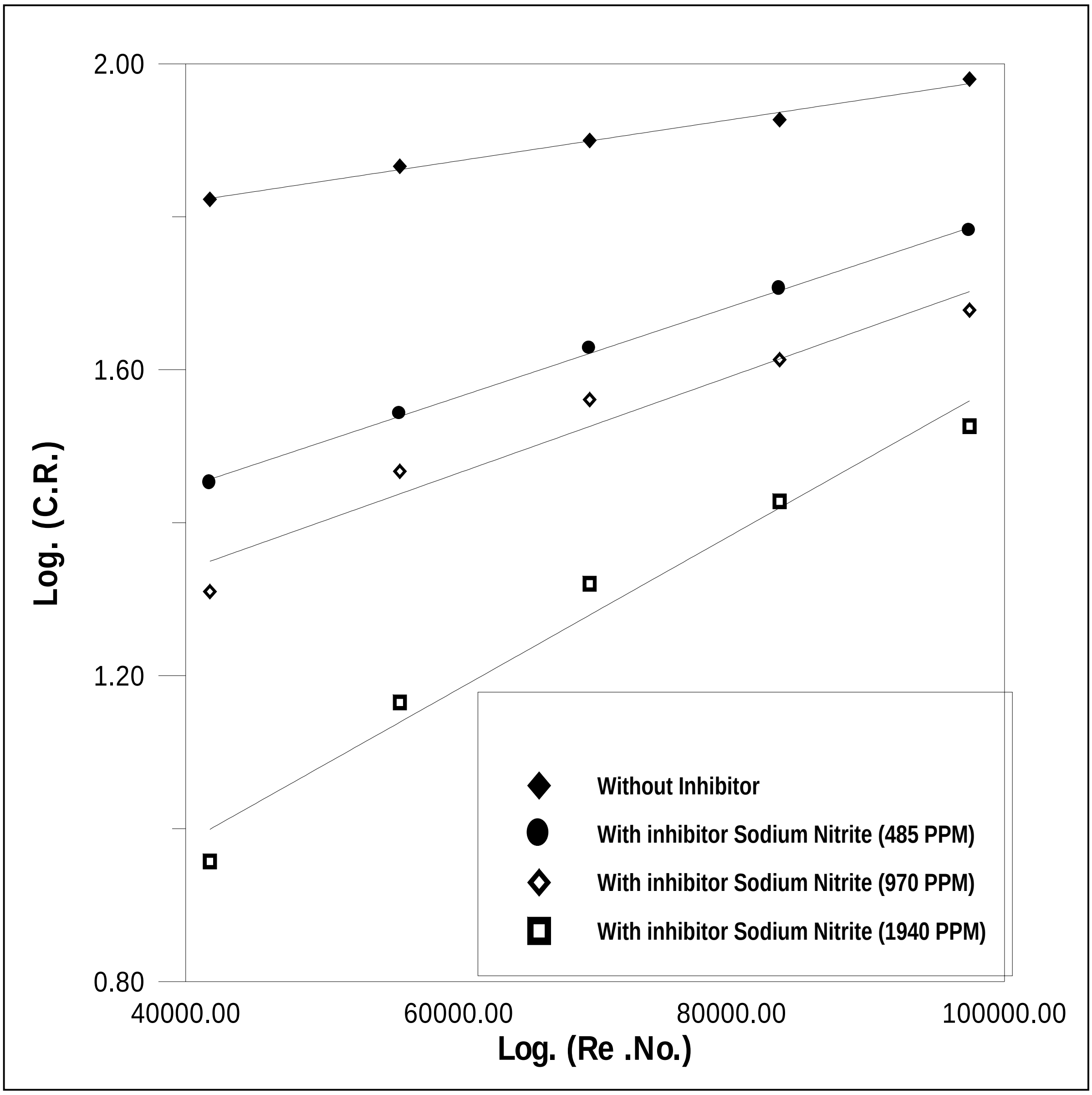

Fig.(6.24) Relation Between LOG.(C.R.) vs. LOG.(Re) in 8%vol. Aqueous Solution with and without Inhibitor(sodium nitrite), C.R. in gmd .

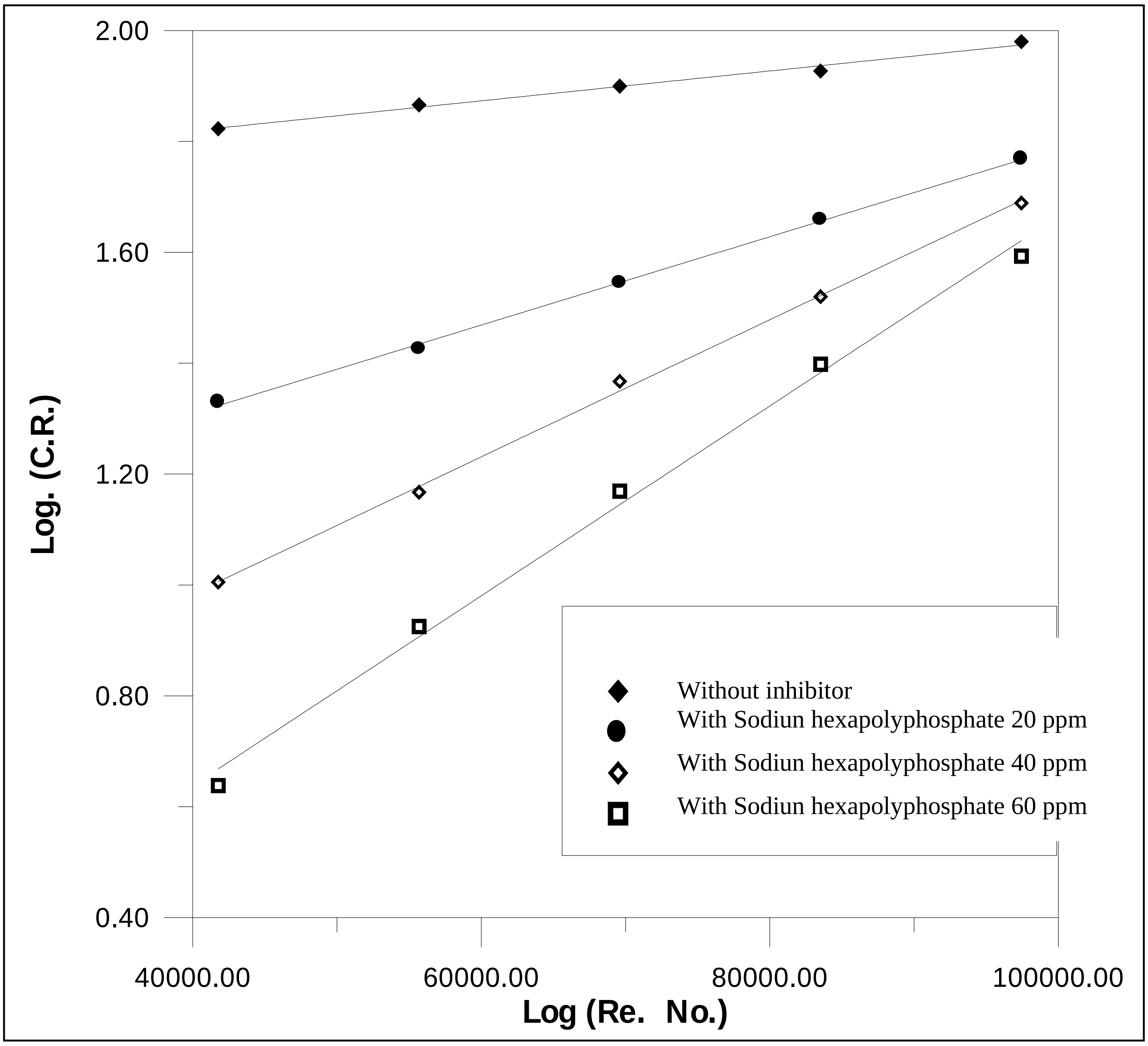

Fig.(6.25) Relation Between LOG.(C.R.) vs. LOG.(Re) in 8%vol. Aqueous Solution with and without Inhibitor (sodium hexapolyphosphate), C.R. in gmd.

Chapter Seven

Conclusions and Recommendations of Future Work

7.1 Conclusions:

1. In single phase (1%wt. NaCl solutions) the average corrosion rate in agitation system increased with increasing impeller Reynolds number.
2. In Two- phases 1%wt. NaCl solution/ kerosene the average corrosion rate in agitation system increased with increasing aqueous phase concentration.
3. In Two- phases 1%wt. NaCl solutions /Kerosene the average corrosion rate in agitation system increased with increasing Re (or We) and decreasing droplet size.
4. In Two- phase 8%vol. of 1%wt. NaCl solution/kerosene the percent inhibition decreased with increasing impeller Reynolds number (rotational speed) and the average corrosion rate decreased when the concentration of inhibitor increased.

7.2 Recommendations for Future Work:

The present investigation should be future work carried out in the following directions

1. The influence of agitation and flow geometries.
2. More definite simulation of oil field or process conditions, e.g., flow pressure, temperature, presence of gaseous phase, etc.
3. The use of mixed inhibitors for single and two phases.
4. Experimental investigation in presence of a third gaseous phase,

e.g. hydrocarbon containing CO_2 or H_2S.

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Appendix-A-

Table -A.1-Expermintal Corrosion Results in Single Phase at Rotational Velocities of 262, 349, 438, 525, 600, 612, 800,1000,1200 and 1400 rpm (T=40 ^{o} C).

Revolution per min. (rpm)	Avearge weight loss. $(\Delta W)\times10^4$ (g)	Avearge corrosion rate (C.R.) (gmd)	Reynold number (Re)	Sherwood number (Sh)	Current density (i_L) (A/m^2)	Mass transfer coffcient $(K)\times10^5$ (m/s.)
262	36	35.2658	41814.62	470.1661	1.4065	1.7690
349	43	42.1231	55699.62	561.5940	1.6800	2.1130
438	49	48.0007	69903.83	639.9466	1.9144	2.4078
525	57	55.8376	83788.33	744.4518	2.2270	2.8010
600	64	62.6948	95758.673	834.8704	2.5005	3.1412
612	64	62.6948	97673.84	834.8704	2.5005	3.1412
800	69.5	68.0827	127678.23	906.6049	2.7153	3.4111
1000	78	76.4093	159597.79	1017.4086	3.0474	3.8280
1200	84	82.2870	191517.35	1095.7608	3.2819	4.1228
1400	86	84.2462	223436.90	1121.8605	3.3600	4.2210

Table -A.2- Expermintal Results in Two –Phase 1%vol. Aqueous Phase/ Kerosene at Rotational Velocities of 600, 800, 1000, 1200,1400 rpm (T=40 ^{o} C).

Revo. Per min. (rpm)	Ave. weig. loss. (ΔW) $\times 10^4$ (g)	Ave. Corr. rate (C.R.) (gmd)	Reynolds number (Re)	Sherwood number (Sh)	Current density ($i_C = i_L$) (A/m^2)	Mass tran. Coffc. (K) $\times 10^6$ (m/s.)
600	9.5	9.3062	38428	124	0.3711	4.6676
800	14.5	14.2043	51238	189.4	0.5665	7.1253
1000	19.5	19.1023	64047	254.7	0.7618	9.5817
1200	22.5	22.0411	76856	293.9	0.8790	11.0558
1400	30.5	29.8780	89666	398.4	1.1916	14.9876

Table -A.3- Expermintal Results in Two –Phase 1%vol. Aqueous Phase/ Kerosene at Rotational Velocities of 600, 800, 1000, 1200,1400 rpm (T=40 ^{o} C).

Revo. Per min. (rpm)	Weber number (We)	Sauter mean diameter (Ds) $\times 10^6$ (m)	Number of drops per cm^3 of two-phase mixture (n/cm^3)
600	147344	3.8757	3.2824×10^8
800	261946	2.7443	9.2407×10^8
1000	409290	2.0996	2.0634×10^9
1200	589378	1.6870	3.9770×10^9
1400	802209	1.4021	6.9289×10^9

Table -A.4- Expermintal Results in Two –Phase 5%vol. Aqueous Phase/ Kerosene at Rotational Velocities of 600, 800, 1000, 1200,1400 rpm ($T=40\,^{o}C$).

Revo. per min. (rpm)	Ave. weig. loss. $(\Delta W) \times 10^4$ (g)	Ave. corr. rate (C.R.) (gmd)	Reynolds number (Re)	Sherwood number (Sh)	Current density ($i_C=i_L$) (A/m^2)	Mass tran. Coffc. $(K) \times 10^6$ (m/s.)
600	17	16.6533	38428	222	0.6641	8.3529
800	20.5	20.0819	51238	267.7	0.8009	10.073
1000	24.5	24.0003	64047	319.9	0.9572	12.039
1200	26.5	25.9595	76856	346	1.0353	13.021
1400	33.5	32.8168	89666	437.5	1.3088	16.461

Table -A.5- Expermintal Results in Two –Phase 5%vol. Aqueous Phase/ Kerosene at Rotational Velocities of 600, 800, 1000, 1200,1400 rpm ($T=40\,^{o}C$).

Revo. per min. (rpm)	Weber number (We)	Sauter mean diamter. $(Ds) \times 10^6$ (m)	Number of drops per $cm^3$of two-phase mixture. (n/cm^3)
600	147344	4.6700	1.8752×10^8
800	261946	3.3067	5.2822×10^8
1000	409290	2.5298	11.7962×108
1200	589378	2.0327	22.7395×10^8
1400	802209	1.6894	39.6099×10^8

Table -A.6- Expermintal Results in Two –Phase 8%vol. Aqueous Phase/ Kerosene at Rotational Velocities of 600, 800, 1000, 1200,1400 rpm ($T=40\ ^{o}C$).

Revo. Per min. (rpm)	Ave. weig. loss. (ΔW) $\times 10^4$ (g)	Ave. corr. rate (C.R.) (gmd)	Reynolds number (Re)	Sherwood number (Sh)	Current density ($i_C = i_L$) (A/m^2)	Mass tran. Coffc. (K) $\times 10^5$ (m/s.)
600	68	66.6133	38428	888.1	2.6567	3.3415
800	75	73.4705	51238	979.5	2.9302	3.6855
1000	81	79.3482	64047	1057.9	3.1647	3.9804
1200	86	84.2462	76856	1123.2	3.3600	4.2261
1400	97	95.0219	89666	1266.9	3.7898	4.7667

Table -A.7- Expermintal Results in Two –Phase 8%vol. Aqueous Phase/ Kerosene at Rotational Velocities of 600, 800, 1000, 1200,1400 rpm ($T=40\ ^{o}C$).

Revo. Per min. (rpm)	Weber number (We)	Sauter mean diamter. (Ds) $\times 10^6$ (m)	Number of drops per cm^3 of two-phase mixture. (n/cm^3)
600	147344	5.2657	1.3080×10^8
800	261946	3.7285	3.6846×10^8
1000	409290	2.8526	8.2277×10^8
1200	589378	2.2920	15.862×10^8
1400	802209	1.9049	27.6302×10^8

Table -A.8- Expermintal Results in Two –Phase 16.4%vol. Aqueous Phase/ Kerosene at Rotational Velocities of 600, 800, 1000, 1200,1400 rpm ($T=40^{o}$ C).

Revo. per min. (rpm)	Ave. weig. loss. (ΔW) $\times10^4$ (g)	Ave. corr. rate (C.R.) (gmd)	Reynolds number (Re)	Sherwood number (Sh)	Current density ($i_C= i_L$) (A/m^2)	Mass tran. Coffc. (K) $\times10^5$ (m/s.)
600	75	73.4705	38428	979.5	2.9302	3.6855
800	78	76.4093	51238	1018.7	3.0474	3.8329
1000	88	86.2054	64047	1149.3	3.4382	4.3244
1200	95	93.0627	76856	1240.7	3.7116	4.6683
1400	107	104818	89666	1397.5	4.1805	5.2581

Table -A.9- Expermintal Results in Two –Phase 16.4%vol. Aqueous Phase/ Kerosene at Rotational Velocities of 600, 800, 1000, 1200,1400 rpm ($T=40^{o}$ C).

Revo. per min. (rpm)	Weber number (We)	Sauter mean diameter. (Ds) $\times10^6$ (m)	Number of drops per $cm^3$of two-phase mixture (n/cm^3)
600	147344	6.9337	05729×10^8
800	261946	4.9095	1.6139×10^8
1000	409290	3.7562	3.6037×10^8
1200	589378	3.0180	7.0032×10^8
1400	802209	2.508	12.106×10^8

Appendix-B-

Table (B-1) The Best Amount of Inhibiter (Hexamine) Added to a Liter of 20% HCl Is 60g, the Weight Loss Was Zero.

Exp.No.	L(cm)	W_1(g)	W_2(g)	ΔW(g)
1	3.250	5.0394	5.0394	0
2	3.250	5.0286	5.0286	0
3	3.250	4.8765	4.8765	0
4	3.250	5.0143	5.0143	0
5	3.250	5.1580	5.1580	0
6	3.250	5.3451	5.3451	0
7	3.250	5.0146	5.0146	0
8	3.250	5.0261	5.0261	0
9	3.250	5.1458	5.1458	0
10	3.250	4.9854	4.9854	0

Appendix- C-

C.1 **Properties for Water .**

C.1.1 Physical Properties for Water .

Table C.1.1: Physical Properties of Water at Atmosheric Pressure (59).

T (^oC)	Cp (KJ/Kg. ^oC)	ρ (Kg/m^3)	μ x 10^4 (Kg/m.s.)
0.00	**4.225**	**999.8**	**17.9**
4.44	**4.208**	**999.8**	**15.5**
10.0	**4.195**	**999.2**	**13.1**
15.56	**4.186**	**998.6**	**11.2**
21.11	**4.179**	**997.4**	**9.80**
26.67	**4.179**	**995.8**	**8.60**
32.22	**4.174**	**994.9**	**7.65**
37.78	**4.174**	**993.0**	**6.82**
43.33	**4.174**	**990.6**	**6.16**
54.44	**4.179**	**985.7**	**5.13**
60.0	**4.179**	**983.3**	**4.71**
65.55	**4.183**	**980.3**	**4.30**
71.11	**4.186**	**977.3**	**4.01**
82.22	**4.195**	**970.2**	**3.47**
93.33	**4.204**	**963.2**	**3.06**

C.1.2 Diffusivity of Oxygen in 0.1N NaCl Solution.

Audin and Jhon (60) showed that the diffusivity of oxygen in the electrolyte solution is generally lower than that in pure water, and it is proportionality decreased with increasing electrolyte concentration according to the following general correlation

$$D = D_o \times (1 - k \times C^{0.5}) \qquad \text{(C.1)}^{(60)}$$

where D and D_o are the diffusivity of oxygen in the electrolyte solution and in pure water respectively, k is constant and equal to about 0.482 for range (0.1-1 N) NaCl and C is the normality of NaCl solution. The values of diffusion coefficients of oxygen are tabulated below.

Table C1.2: Values of oxygen Diffusivity (60)

$T(^oC)$	$D_o \times 10^9$ (m^2/s.) (pure water)	$D_o \times 10^9$ (m^2/s.) (0.17 N NaCl solution)
10.0	**1.54**	**1.233**
15.0	**1.66**	**1.329**
16.0	**1.87**	**1.497**
20.0	**2.01**	**1.609**
22.0	**2.24**	**1.793**
25.0	**2.41**	**1.929**
29.6	**2.49**	**1.993**
30.0	**2.80**	**2.241**
37.0	**3.0**	**2.040**
40.0	**3.55**	**2.842**
50.0	**4.20**	**3.362**
55.0	**4.50**	**3.603**
60.0	**5.70**	**4.563**

C.1.3: Solubility of Oxygen

Table C.1.3: Oxygen Solubility at atmospheric Pressure (59, 61).

T (^oC)	Solubility (mg/l) Distilled Water	Solubility (mg/l) 0.1 N NaCl
30	**7.559**	**7.500**
35	**6.625**	**6.95**
40	**6.401**	**5.990**
45	**6.001**	**5.399**
50	**5.477**	**4.490**
60	**4.501**	**4.389**

C.2: physical properties for kerosen (55).

1. API=42.6,

SP.gr=0.8127

ρ=805.79 kg/m^3 at T= 40 C^o

2. Viscosity (μ=1.342 $\times 10^{-3}$ kg/m.s. at T= 40 C^o).

3. Bulk concentration (51). ($(C_{b)\ O2=}$ 0.572 mol. /m^3)

4. Diffusivity (oxygen solute) in (kerosen solvent). (58)

By using Wilke-chang correlation

$$D_{AB} = 1.173 \times 10^{-16} \times (\theta \times M_B)^{0.5} \times (\frac{T}{\mu_B \times (V_A)^{0.5}}) \qquad \textbf{(C.2)}^{(51)}$$

where:

θ: is associated parameter (θ=1 for benzene and kerosene)

$M_{B:}$ molecular weight of species B (kerosen solvent).

μ_B: viscosity of species B (kerosen solvent).

T: temprature of solution (K^O).

V_A:molar volume (m^3/mol.)

T=313.15 K^o, Ø=1, M_B=13.9,. μ=1.342 $\times 10^{-3}$ kg/m.s. at T= 40 ^oC, , V_A=14.8$\times 10^{-6}$

That lead to (D_{o2}) =1$\times 10^{-9}$ m^2 /s.

4. Interficial tension (50) (σ) =28$\times 10^{-5}$ N/m

Appendix-D-

Polarization Data of single phase

RPM	Area of cathodic(m^2)	Conc. (%wtNaCl
600	0.00049	1%Wt.

RPM	Area of cathodic(m^2)	Conc. (%wtNaCl)
800	0.00049	1%Wt.

E(V)vs. SCE	Current density(A/m^2)
-1.211	6.09
-1.19	5.73
-1.165	5.38
-145	5.17
-1.123	4.87
-1.154	4.59
-1.123	4.36
-1.076	3.9
-1.054	3.81
-1.032	3.62
-1.007	3.31
-0.982	3.09
-0.96	2.96
-0.935	2.84
-0.913	2.71
-0.891	2.64
-0.87	2.31
-0.845	2.12
-0.825	2.02
-0.8	1.91
-0.776	1.76
-0.749	1.3
-0.723	0.84
-0.698	0.004

E(V)vs. SCE	Current density(A/m^2)
-1.194	6.86
-1.173	6.51
-1.145	6.12
-1.11	5.87
-1.093	5.61
-1.070	5.36
-1.049	5.17
-1.031	4.71
-1.001	4.52
-0.974	4.41
-0.949	4.17
-0.929	3.89
-0.908	3.71
-0.891	3.6
-0.863	3.52
-0.851	3.44
-0.814	3.24
-0.789	2.92
-0.756	2.82
-0.73	2.74
-0.71	2.53
-0.681	2.27
-0.663	1.63
-0.61	0.0012

RPM	Area of Cathodic(m^2)	Conc. (% wt. NaCl)
1000	0.00049	1%Wt.

RPM	Area of Cathodic(m^2)	Conc. (% wt. NaCl)
1200	0.00049	1% Wt.

E(V)vs. SCE	Current density(A/m^2)
-1.17	7.61
-1.151	7.24
-1.125	6.53
-1.083	6.32
-1.062	6.04
-1.048	5.84
-1.025	5.49
-1.01	5.24
-0.981	5.1
-0..952	4.86
-0.928	4.52
-0.903	4.4
-0.889	4.24
-0.871	4.16
-0.841	4.02
-0.830	3.92
-0.79	3.7
-0.764	3.54
-0.739	3.41
-0.706	3.2
-0.684	2.97
-0.653	2.61
-0.639	1.78
-0.584	0.0017

E(V)vs.SCE	Current density(A/m^2)
-1.149	8.23
-1.131	7.73
-1.09	7.31
-1.054	7.02
-1.031	6.8
-1.016	6.54
-0.989	6.31
-0.954	6.01
-0.91	5.78
-0.882	5.62
-0.864	5.36
-0.843	5.09
-0.81	4.9
-0.794	4.74
-0.764	4.66
-0.738	4.52
-0.708	4.41
-0.688	3.98
-0.656	3.72
-0.601	3.6
-0.59	3.3
-0.569	2.96
-0.504	2.87
-0.47	0.0014

RPM	Area of Cathodic(m^2)	Conc. (% wt. NaCl)
1400	0.00049	1%Wt.

RPM	Area of Cathodic(m^2)	Conc. (% wt. NaCl)
262	0.00049	1%Wt.

E(V)vs. SCE	Current density(A/m^2)
-1.12	8.12
-1.101	7.64
-1.07	7.21
-1.033	6.9
-1.009	6.7
-0.987	6.34
-0.964	6.2
-0.923	5.91
-0.887	5.66
-0.834	5.51
-0.821	5.26
-0.790	4.9
-0.768	4.87
-0.734	4.63
-0.704	4.51
-0.698	4.41
-0.664	4.31
-0.631	3.88
-0.598	3.62
-0.57	3.5
-0.54	2.86
-0.487	2.76
-0.47	1.7
-0.44	0.002

E(V)vs. SCE	Current density(A/m^2)
-1.39	3.46
-1.373	3.31
-1.356	2.87
-1.331	2.64
-1.299	2.54
-1.281	2.41
-1.253	2.29
-1.231	2.17
-1.213	2.
-1.199	1.87
1.181	1.73
-1.16	1.49
-1.097	1.3
-1.081	1.1
-1.031	1.02
-1.006	
0.987	0.98
-0.943	0.8
-0.921	0.75
-0.897	0.36
-0.851	0.12
-0.84	.09
-0.827	0.04
-0.799	0.010

RPM	Area of Cathodic(m^2)	Conc. (% wt. NaCl)
349	0.00049	1%Wt.

RPM	Area of Cathodic(m^2)	Conc. (% wt. NaCl)
438	0.00049	1%Wt.

E(V)vs. SCE	Current density(A/m^2)
-1.351	3.56
-1.326	3.36
-1.306	2.91
-1.287	2.74
-1.254	2.61
-1.254	2.53
-1.236	2.4
-1.203	2.2
-1.186	2.03
-1.174	1.93
-1.154	1.81
-1.139	1.53
-1.116	1.36
-1.094	1.16
-1.08	1.07
-0.994	1.01
-0.988	0.87
-0.956	0.84
-0.919	0.41
-0.893	0.19
-0.876	0.13
-0.847	0.09
-0.836	0.05
-0.817	0.008
-0.795	0.0001

E(V)vs. SCE	Current density(A/m^2)
-1.301	3.69
-1.269	3.61
-1.253	3.41
-1.236	3.02
-1.204	2.81
-1.181	2.76
-1.151	2.59
-1.136	2.44
-1.120	2.29
-1.096	2.1
-1.066	2.09
-1.031	1.97
-1.01	1.66
-0.996	1.41
-0.981	1.31
-0.964	1.26
-0.934	1.16
-0.909	0.96
-0.89	0.46
-0.86	0.24
-0.831	0.16
-.811	0.016
-0.793	0.00014
-0.763	

RPM	Area of Cathodic(m^2)	Conc. (% wt. NaCl)
525	0.00049	1%Wt.

RPM	Area of cathodic(m^2)	Conc. (%wt. NaCl)
600	0.00049	1%Wt.

E(V)vs. SCE	Current density(A/m^2)
-1.241	3.91
-1.209	3.8
-1.196	3.61
-1.17	3.29
-1.152	3.06
-1.123	2.91
-1.096	2.84
-1.081	2.69
-1.064	2.53
-1.037	2.4
-1.006	2.31
-0.994	2.12
-0.964	1.96
-0.942	1.74
-0.921	1.6
-0.904	1.53
-0.875	1.465
-0.851	1.03
-0.831	0.98
-0.801	0.65
-0.779	0.43
-0.751	0.26
-0.721	0.063
-0.703	0.0001

E(V)vs. SCE	Current density(A/m^2)
-1.211	6.09
-1.19	5.73
-1.165	5.38
-145	5.17
-1.123	4.87
-1.154	4.59
-1.123	4.36
-1.076	3.9
-1.054	3.81
-1.032	3.62
-1.007	3.31
-0.982	3.09
-0.96	2.96
-0.935	2.84
-0.913	2.71
-0.891	2.64
-0.87	2.31
-0.845	2.12
-0.825	2.02
-0.8	1.91
-0.776	1.76
-0.749	1.3
-0.723	0.84
-0.698	0.004

الخلاصة

ان التآكل في الحديد الكربوني في نظام خلط ذو طور واحد (1% نسبة وزنية محلول مالح) ونظام ذو طورين (1% وزنية محلول مالح / نفط ابيض) تم التحري عنه بواسطة فقدان الوزن والاستقطاب في نظام الطور الواحد أجريت تجارب فقدان الوزن بسرع مختلفة (262، 349، 438، 525، 600، 612، 800، 1000، 1200، 1400) دورة / دقيقة باستخدام مزاجة دائرية بقطر 8 سم . إن معدل التآكل يزداد بزيادة سرعة التدوير. أما في طريقة الاستقطاب أجريت بنفس السرع فقدان الوزن. أن التيار المحدد (بمعنى آخر معدل التآكل) وجد انه يسند النتائج التي حصلنا عليها بفقدان الوزن بمعنى آخر يزداد معدل التآكل بزيادة سرعة التدوير.

في نظام طورين (1% وزنية محلول مالح / نفط ابيض) تم اجراء التجارب باستخدام فقدان الوزن فقط وذلك لكون مقاومة كهر بائية عالية في المحاليل الممزوجة. هذه التجارب اجريت عند تراكيز المحاليل المائية (1، 5، 8، 16.4 % حجمية) من 1% محلول مالح ممزوج مع النفط الأبيض عند سرع تدوير 600، 800، 1000، 1200، 1400 دورة / دقيقة. أن معدل التآكل يزداد بزيادة سرعة التدوير عند جميع التركيز. بالإضافة وجد أن معدل التآكل يزداد بزيادة عدد رينولد وعدد ويبر وعكسيا مع قطر ساوتر.

تاثير تركيز الطور قد لوحظ يعتمد على تركيز الطور للمحلول الملحي فعند التركيز الواطئ للطور الملحي (1% وزنية محلول مالح) عند تركيز 1% حجمية و 5% حجمية أن

معدل التآكل يزداد بزيادة تركيز الطور المالح عند عدد رينولد 38428 و 51238 و 64047 و 76856 و 89666. بالإضافة لذلك أن معدل التآكل يكون اقل في محلول ذي طور واحد (1% وزنية محلول مالح) عند عدد رينولد المكافئ أما عند التركيز العالي للطور الملحي 1% وزنية محلول مالح عند تركيز 8% حجمية و 16.4% حجمية وجد ان معدل التآكل يزداد بزيادة تركيز الطور ويكون اعلى من محلول ذي طور واحد (1% وزنية محلول مالح) عند عدد رينولد المكافئ.

ان تأثير المادة المقللة من شدة التآكل حيث اجريت التجارب باستخدام نوعين من المواد المقللة من شدة التآكل (نترات الصوديوم وفوسفات الصوديوم) عند 8% حجمية محلول مالح ممزوج مع نفط ابيض. بوجود تلك المادتين عند زيادة سرعة التدوير تقل نسبة الحماية وكذلك معدل سرعة التآكل يقل عند زيادة تركيز المواد المقللة من شدة التآكل.

أن فوسفات الصوديوم وجدت أكثر فعالية من نترات الصوديوم. عند تركيز 20 و 40 و60 جزء من المليون لفوسفات الصوديوم وجدت كفاءة الحماية 67.43 – 58.71 % و 84.79 – 48.8 و 93.46 – 58.75 على التوالي عند سرع تدوير من 600 – 1400 دورة بالدقيقة. وبنفس الظروف أجريت تجارب على نترات الصوديوم عند تركيز 485 و 970 و 1940 جزء من المليون وجدت أن نسبة الحماية 57.35 – 36.41 % و 69.32 – 49.78 % و 86.4 – 94.58 % على التوالي.

شكر و تقدير

اود ان اعبر عن خالص شكري وتقديري وامتناني العميق للمشرف الأستاذ الدكتور قاسم جبار السليمان والدكتور باسم عبيد حسن لما بذلوه من جهد كبير وإرشادات سديدة وقيمة طوال فترة إعداد الرسالة.

اود ايضا ان اشكر السيد رئيس القسم وموظفي قسم الهندسة الكيمياوية لإبدائهم المساعدة اللازمة أثناء فترة البحث.

ولا أنسى إن أتقدم بالشكر والامتنان إلى من لازمني طوال فترة البحث وخلال أصعب الظروف عائلتي والى أعز من في الوجود أبي وأمي فلهم جزيل الشكر والتقدير.

التآكل عند طوري ماء / نفط ابيض باستخدام أنظمة مضطربة الخلط

رسالة

مقدمة إلى كلية الهندسة في جامعة النهرين
وهي جزء من متطلبات نيل درجة ماجستير علوم
في الهندسة الكيمياوية

من قبل

حسين عزيز محمود العنبكي
بكالوريوس 2000

جمادى الأولى	1427
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