BACTERIA CORROSION OF MILD AND MEDIUM CARBON STEELS

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CERTI ION

I certify that this work "Bacteria Corrosion of Mild and Medium Carbon Steels" was carried out by **Okeahialam Solomon IFEANYI** (20064549658), in partial fulfillment for the award of the degree of (M.ENG. in Materials Engineering in the Department of Materials and Metallurgical Engineering) of the Federal University of Technology, Owerri, Nigeria.

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DEDICATION

This work is dedicated to the most high God and also to my beloved family especially my parents friends who contributed in one way or the other to make this work a success.

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ABSTRACT

Investigations were carried out to determine the corrosion effect of sulphur-reducing bacteria on mild and medium carbon steels. Specimens were exposed to anaerobic, aerobic and distilled water environments. The corrosion rates were evaluated at intervals of seven days using weight loss and electro-chemical methods for a period of forty two days. The specimens were also subjected to visual examination and the result indicated uniform corrosion in all the environments. In all the environments, mild steel was most corrosive (6.43×10^{-4}mpy) due to high rate of depassivation of the oxide film by the corrosion inducing agents. Also, medium carbon steel recorded the least corrosion rate (5.30×10^{-4}mpy) due to low rate of depassivation of the oxide film by corrosion-inducing agents. An average potential of -0.93mV was observed for mild steel in anaerobic environment, -0.89mV in Aerobic, -0.77mV in control. While an average potential of -0.91mV, was recorded for medium carbon steel in anaerobic environment, -0.84mV in aerobic, -0.74mV in control.Mild steel recorded the highest electrode-potential.

Key Words: Corrosion, SRB; pH, Bacteria Concentration, Electrode Potential, Mild Steel, Medium Carbon Steel, Aerobic and Anaerobic Environment.

CHAPTER ONE

1.0 INTRODUCTION

The problem of corrosion pervades all facets of life in the home, transportation system, air, naval, paper and pulp industries and in the oil/allied industries. Metals and their alloys especially stainless steels and refractory metals have been used in hostile environments (Borode and Okpala, 1999). Several factors are known to accelerate the corrosion of metal and alloys. Such factors include the composition of the metals and alloys and their surface finish to mention just a few. Corrosion in an aqueous environment and in an atmospheric environment is an electrochemical process. The energy stored in the metal during the refining process makes corrosion possible and this energy supplies the driving force for corrosion.

It is in recognition of the technical and economical importance of the oil platform as a must in the crude oil exploration and production, particularly in harsh oceanic environments, that it became necessary to study the process and the driving force for corrosion of the given structures (Umezurike, 1998). Control measures implemented in some oil and gas industries include; chemical injection (biocides), pigging, coating and cathodic protection. Most developed nations spend 6% of their total gross domestic product in addressing corrosion-related issues. In United States, this amounts to about $550 billion (Donald and Pradeep, 2006).

Sulphur-reducing bacteria (SRB) are a group of ubiquitous, diverse anaerobes that reduce oxidized sulphur compounds, such as sulphate as well as sulphur to H_2S. Although, SRB are strictly anaerobic (obligate anaerobes), some genera tolerate oxygen and are even able to grow at low oxygen concentrations. Oil gas and shipping industries are seriously affected by the sulphide generated by SRB. Biogenic sulphide production leads to health and safety problems, environment hazards and severe economic losses due to reservoir souring and corrosion of equipment.

Microbially Influenced Corrosion (MIC) has become the "joker" in cases where there is no plausible electrochemical explanation for a given corrosion case. (Iwona and Christine, 2002). This research is carried out to evaluate the corrosion behaviour of SRB on mild steel and medium carbon steels and also to know the effect of carbon content on corrosion of steels.

1.1 PROBLEM STATEMENT

SRB as a type of microbial influenced corrosion (MIC) has so far been viewed with skepticism, particularly among engineers and chemists with little appreciation of the behaviour of microorganisms and so the corrosion effect is lacking.

Obviously, no much work has been reported in the corrosion studies of SRB.

1.2 RESEARCH OBJECTIVES

Against the background of the problem stated above, and in pursuit of the remedies, the objectives of this research are to:

(i) Investigate the corrosion effect of sulphur reducing bacteria on steels used in ship walls, storage tanks, drilling pipe, to convey crude and finished oil products etc in order to establish an idea of the basic concept of SRB on steels;

(ii) To know the effects of carbon compositions, pH, concentration of bacteria on corrosion of steels;

(iii) Determine an experimental data base on the corrosion behaviour of SRB which shall be of practical use to engineers and other workers involved in oil and gas operations;

(iv) Proffer necessary and acceptable control measures for SRB corrosion.

1.3 JUSTIFICATION OF RESEARCH

This research finds wide application to all workers, engineers and professional associated with exploration in oil and gas industries.

The research will serve as data base to all who wish to embark on corrosion research and to students handling related study on SRB corrosion.

1.4 RESEARCH SCOPE AND LIMITATION

This work is limited to SRB in anaerobic and aerobic environment using medium and mild steels. The corrosion rates were measured using weight loss and electrochemical methods.

The extent to which the finding of this research can be applied is basically restricted to SRB corrosion on oil and gas exploration equipments as well as in tanks. The test sites were biotechnology laboratory and materials and metallurgical engineering laboratory, FUTO.

CHAPTER TWO

2.0 LITERATURE REVIEW

Biological organisms which influence the corrosion of metals include microscopic forms, such as bacteria and macroscopic forms, such as algae and barnacles (Anyakwo, 1993). Corrosion occurs when materials made of pure materials and/or their mixtures undergo a chemical change from the ground state to an ionized species. (Iwona and Christine, 2002).

The extent to which a corrosion process will proceed is determined by a number of factors which may be biotic (living) or abiotic (non living).The abiotic factors include scratches, abrasion on metal surfaces, and presence of salt and corrosives in the surrounding medium. The biotic factors involve the activities of microorganisms such as microbiological influenced corrosion (MIC) or biological corrosion (Anyakwo, 1993).

Under favorable condition, bacteria can multiply every 10-60 minutes and it is the metabolic (chemical) activities associated with their growth and reproduction that lead to the corrosion and bio-deterioration of materials. In one day alone, assuming a multiplication period of 30 minutes, one organism could, theoretically produce 2.8×10^{14} organisms. Fortunately, this cannot happen as after first bloom, conditions become progressively inhibitory, predators become evident, and so on. It does explain, however, how once condition are right, a considerable quantity of bacteria debris quickly accumulate (Anyakwo, 1993). SRB could survive in aerobic environment with the assistance of oxygen depletion bacteria. (Zhu, Riskowski, and Mackie, 1995).

2.1 SULPHUR CYCLE

Sulphur and its compounds are an essential part of the metabolic processes of the most important bacteria involved in microbial corrosion. Together with animal's plants, these micro-organisms play important role in the progressive large scale transformation of sulphur nature (Ringas and Robison, 1987).

The main reservoirs of sulphur and sulphur compounds in nature are the deposits of sulphidic minerals and elemental sulphur. Dissolved sulphates occur mainly in marine environments. Hydrogen sulphide is produced in both soil and aquatic by the decay of sulphur containing biological materials and SRB. The hydrogen sulphide is either precipitated as metal sulphide, or it enters the water, soil, or air, and may then be oxidized spontaneously, either chemically or biologically (Ringas and Robison, 1987).

Bacteria may oxidize sulphide or hydrogen sulphide to sulphur and further microbial oxidation may yield to sulphate. To complete the full cycle, plants or bacteria's, or both, reduce the sulphate to the original starting material, viz sulphide. It is important to bear in mind that the bacteria corrosion processes involving steel are part of this general sulphur cycle. Corrosion occur either because of attack initiated by bacteria end product or during the metabolism of the bacteria. The oxidation of elemental sulphur to sulphate is affected by a group of aerobic bacteria of the genus Thiobacilus. These are also the main organisms with aerobic microbial corrosion, often with some preliminary assistance from group of organisms capable of converting sulphide to sulphur via polythionates and thiosulphate (Ringas and Robison, 1987).

The important organism in anaerobic conditions is the SRB of the genera Desulfovibrio and Desulfotomacillum. These bacteria successfully reduce sulphate to sulphide. (Ringas andRobison, 1987).

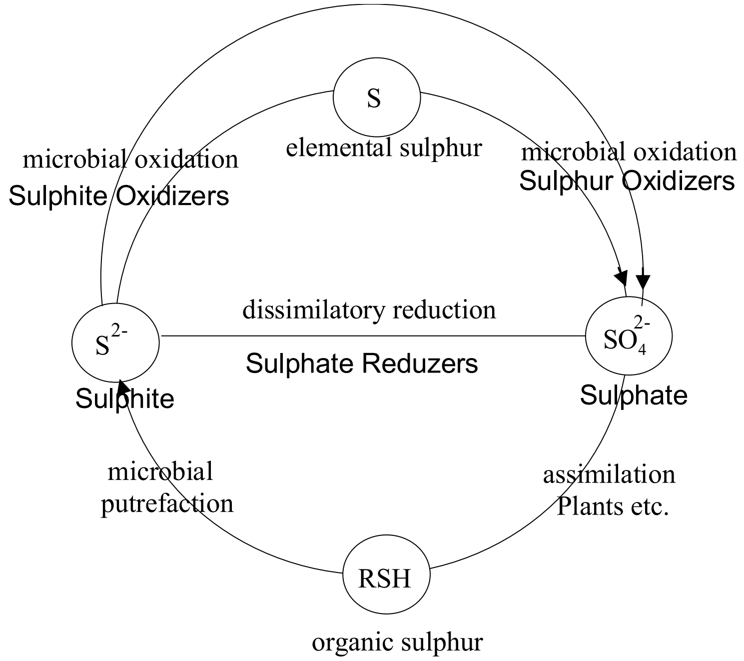

Fig. 2. 1. The sulphur cycle

Source: Ringas and Robison. (1987), P.427

2.2 MICROBIAL-INFLUENCED CORROSION

MIC is the acronym for "Microbial Influenced Corrosion". It refers to the possibility that microorganisms are involved in the deterioration of metallic materials (Iwona and Christine, 2000). However, the number of attached micro-organisms does not necessary correlate with the extent of corrosion, a fact that has long been known for suspended cells. It is the metabolic statue of the cells that is believed to be the relevant parameter, but to date no clear consensus has been reached linking specific bacteria metabolic rate to observe corrosion rate (Iwona and Christine, 2002).

MIC, as significant phenomenon, has thus been viewed with skepticism, particularly among engineers and chemists with little appreciation for the behavior of microorganisms. The slow process in establishing the importance of MIC in equipment damage is also the result of the paucity of analytical techniques to identify, localize and control corrosion reactions on metal surface with surface association microbial process.

2.3 SULPHATE-REDUCING BACTERIA (SRB)

SRB are a group of diverse anaerobs which carry out dissimilatory reduction of sulphur compound such as sulphate, sulphite, thiosulphate and even sulphur itself to anaerobic, some genera tolerate oxygen and at low dissolve oxygen concentration certain SRB are able to respire with Fe^{3+} or even oxygen with hydrogen acting as electron donor (Iwona and Christine, 2000). SRB act as a catalyst in the reduction reaction.

Oil, gas and shipping industries are seriously affected by the SRB. Biogenic sulphide production leads to health and safety problems, environmental hazard and sever economic losses due to reservoir souring and the corrosion of equipment (Yuzwa, 1991). Since the beginning of the investigation into the effect of SRB on corrosion of cast iron in 1930, the role of those bacteria in pitting corrosion of various metals and their alloys in both aquatic and terrestrial environment under anoxic as well as oxygenated conditions has been confirmed. Several models have been proposed to explain the mechanism by which SRB can influence the corrosion of steel. These have included cathodic deplorization by the enzyme hydroganase, anodic deplorization, production of corrosive iron sulphides, release of exopolymer capable of binding Fe-ions, sulphide-induced stress-corrosion cracking, and hydrogen induced cracking or blistering (Iwona and Christine, 2002).

The two main-type of SRB involved in corroision are the genus Desulfovibio and Desulfotomaculum (Ringas Robison, 1987). There is uptake of gaseous hydrogen by non-growing bacteria supplied with a small quantity of sulphate according to the following equation.

$$So_4^{2-} + 4H_2 = S^{2-} + 4H_2O \text{ ------------------------- } (2.0.1)$$

2.4 CLASSIFICATION OF MICROORGANISMS THAT INFLUENCE CORROSION:

This classification is linked to their ability to carry out their growth and reproductive activities in the presence or absence of oxygen. Those which require oxygen in their metabolic processes are termed aerobic; they grow only in nutrient medium containing dissolved oxygen (Anyankwo, 1993). Other organisms, organisms called anaerobic, grow most favorably in environment containing little or no oxygen.

2.5 EFFECT OF ANAEROBIC BACTERIA

In anaerobic conditions (no oxygen or air present) some bacteria can thrive. These bacteria can provide the reducible chemicals that allow corrosion to occur (www.micscan.com) From the presence of iron sulphide, which was found as an adherent corrosion product and also in the vicinity of oil pipes, it was deducted and eventually confirmed that SRB were present (Anyakwo, 1993).

Sulphide reduced from sulphate reacts with available hydrogen and iron to form hydrogen sulphide and ferrous sulphide. The tying up of hydrogen in this fashion leaves an excess of hydroxyl ions, which produce a characteristic alkaline environment.SRB can thrive in condition with pH range of 5 to 9.5

Equations to describe SRB Corrosion:

Electrolytic dissolution of water

$8H_2O = 8OH^- + 8H^+$ ……………………………….(2.0.2)

Anodic Reaction $4Fe = 4Fe^{2+} + 8e^-$ ……………………..(2.0.3)

Cathodic reaction $8H^+ + 8e^- = 8H$ ……………………..(2.0.4)

Cathodic deplorization by bacteria

$SO_4^{2-} + 8H = S^{2-} + 4H_2O$ ……………………………………….. (2.0.5)

Corrosion Product $Fe^{2+} + S^{2-} = FeS$ …………………..(2.0.6)

Corrosion product $3Fe^{2+} + 6OH^{-} = 3Fe(OH)_2$ …………(2.0.7)

Overall reaction

$4Fe + SO_4^{2-} + 4H_2O = FeS + 3Fe(OH)_2 + 2(OH)^{-}$ …….. (2.0.8)

Source: Ringas and Robison (1987), p.431

Under anaerobic condition as in wet clay, boggy soil marshes, corrosion of iron and steel (e.g., buried steel structure) is usually caused by sulphate reducing bacteria (SRB) which are anaerobes of the genera Desulphovibrio and Desulphotomaculum. The most abundant is Desulphovibrio which flourishes in the pH range 5-9.

2.6 THE ROLE OF BIOFILM

In principles, corrosion is an interfacial process. The kinetics of corrosion are determined by the physico-chemical environment at the interface, e.g. by the concentration of oxygen, salt, pH value, redox potential and conductivity. All these parameters can be influenced by microorganisms growing at interfaces. The organisms can attach to surface, embed themselves in slime, so called extracellular polymeric substances (EPS) and form layers which are called "biofilm". These can be very thin (monolayer) but reach the thickness of centimeters, as it is the case in microbial materials. It is well known that the metabolic activity of clusters of biofilm organisms can change the pH value for more three units locally (Iwona and Christine, 2000).

The role of biofilm in enhancing corrosion in a biologically condition metal-solution interface can be diverse, and may proceed through simultaneous or successive mechanism including:

(a) Alteration of transport of chemical species from or towards the metal surface. The biofilm accumulate and form a significant diffusion barrier for certain chemical species. For instance, a mature biofilm composed of microbial cells and their EPS prevent the diffusion of oxygen to cathodic area and the diffusion of aggressive anion such as chloride to anodic sites. Outward diffusion of metabolites and corrosion products is also impeded.

(b) Facilitate the removal of protective films when the biofilm detaches. Inducing differential aeration effect as a consequence of a patchy distribution of the biofilm. Non uniform or patchy colonization by microbial biofilm results in the formation of differential aeration cells, where areas under respiring colonies are depleted of oxygen relative to surrounding non-colonized area. These effect gives rise to potential differences and, consequently, to corrosion currents. The area under respiring colonies becomes anodic and there, metal dissolution occurs. Altering the structure of inorganic passive layers, and increasing their dissolution, and removal from the metal surface. Some metabolic activities of microorganism within the biofilm may markedly affect MIC. An example is the reducing capacity of ferric to ferrous ions inherent to certain bacteria (Hector, 2005).

Table 2.1: Prerequisite for the growth of microorganisms

Prerequisite	Provided by	Kind of growth
Energy source	Light, Chemical substances	Phototrophic Chemotropic
Carbon Source	CO_2 Organic substances	Autotrophic Heterotrophic
Electron donor (which is Oxidized)	Inorganic Substances Organic substances	Lithotrophic Organotrophic
Electron acceptor (which is reduced)	Oxygen NO_2^-, NO_3^- SO_4^{2-}, CO_2	Aerobic Anoxic Anaerobic

Source: Iwona and Christine (2000), P.184

Light is very important energy source as it promotes photosynthesis. This process has been invented by microorganisms some three billion years ago and led to the existence of molecular oxygen in the atmosphere (Iwona and Christine, 2000).

2.7 TYPES OF BACTERIA CORROSION

2.7.1 Metal-Reducing Bacteria

Microorganisms are known to promote corrosion of iron and its alloy through reactions leading to the dissolution of corrosion-resistance oxide film on the metal surface. This results in the protective passive layers on e.g. stainless steel surface being lost or replaced by less stable reduced metal films that allow further corrosion to occur (Iwona and Christine, 2002).

Numerous types of bacteria, including those from the genera pseudomonas and shewanella are able to carry out manganese and/or iron oxide reduction and have been shown to influence corrosion reaction. (Iwona and Christine, 2002).

2.7.2 Metal-Depositing Bacteria (MDB)

Many bacteria of different genera participate in the biotransformation of oxide of metals such as iron and manganese. Iron-depositing bacteria oxidize Fe^{3+}.Bacteria of manganese ions with concomitant deposition of manganese dioxide. Dense accumulations of MDB on the metal surface are thought to promote corrosion reactions by the deposition of cathodically reactive ferric and manganese oxide and the local consumption of oxygen caused by bacteria respiration in the deposit. (Iwona and Christine, 2000).

2.7.3 Sulphur –Oxidizing Bacteria

In general, we may expect corrosion by organisms producing acids, the most effective being, of course, those that are not only acid producers, but also acidophilic or at least acid tolerant. These organisms are active at very low pH values, and will be effective in the dissolution of metals and other materials such as concrete (Bos and Kunen, 2006).

The detrimental effect of fungi and especially sulphur oxidizing bacteria, such as member of the genus Thiobacilus, on metals and concrete have been described in this literature. The corrosive effect of the thiobacilus can mainly be attributed to their ability to produce sulphuric acid from the oxidation of inorganic reduced sulphur compounds or elemental sulphur and occurs especially in environments characterized by low pH. Obvious examples of this type of corrosion are those involving acid mine effluent or acid soils (Bos and Kunen, 2006).

2.8 MICROBIAL CORROSION UNDER AEROBIC CONDITION

Microbial corrosion under aerobic conditions involves the colonization of material by microbial growths and deposits, or the formation of tubercles. Organisms that colonize a surface may lead to formation of an oxygen concentration cell. As the organism grow, they consume oxygen until eventually the region below colony depleted of oxygen. However, the periphery of the colony has a higher concentration of oxygen, and a differential oxygen concentration is thus set up. The different in oxygen may lead to the formation of anode in the centre with the corresponding oxygenated periphery functioning as the cathode. These conditions can be created through colonization on the metal by microbial growth such as slime-forming bacteria, or through the production of tubercles by iron bacteria.

Where tubercles are formed, the outer shell consist of a hard layer of magnetite (Fe_3O_4) overlaying a mixture of hydrated ferrous oxide and iron sulphides. The latter are produced by the activity of sulphate-reducing bacteria. The outer skin of the tubercles in contact with the water is covered by a thin layer of goethite. (FeO.OH) mixed with compounds that that have been absorbed by the tubercles from the water, particularly silica, manganese, and organic matter. Siderite ($FeCO_3$) has also been identified, as well as 5% of the sulphur as sulphide. According to Schaschl, the bacteria population of sulphate reducer is higher on the outer surface of the tubercle than in the interior. This is considered due to inhibitive properties of the sulphide. Hence under these conditions it is suggested the sulphate reduction takes place at or near the surface of the tubercle, and the sulphide produced diffuses back into the nodules to react with ferrous ions to precipitate more iron sulphide (Ringas and Robison, 1987).

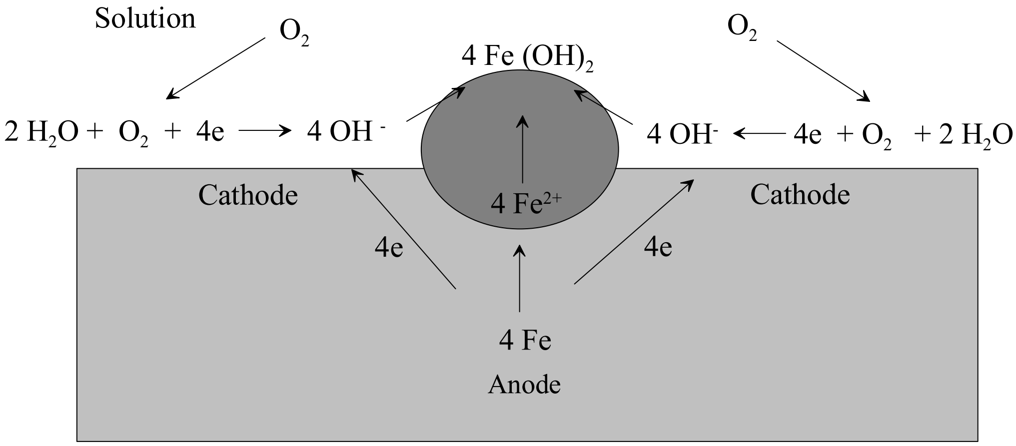

Fig 2.2 Differential Oxygen Concentration Cell

Source: Ringas and Robison, (1987), P.428

2.9 DEPOLARIZATION BY HYDROGEN SULPHIDE

Hydrogen sulphide is known to be corrosive as regards metallic materials. Costello investigated the corrosive action of SRB on ferrous metals. Using electrochemical and biological theory, he critically evaluated the cathodic depolarizing theory and showed theoretically that, if depolarization occurred that way, it is unlikely to affect corrosion rates. His experimentally results indicated that the cathodic depolarization phenomenon was due to the cathodic activity of dissolve hydrogen sulphide produced by the organisms. He demonstrated this phenomenon experimentally by showing that growing cells of the genus Desulfovibrio do lead to stimulation of iron cathodes exposed to them, but that this stimulation is retained in cell-free centrifugates of active cultures. Furthermore, the depolarization can be removed if an inert gas is bubbled through the bacteria solutions. Hence cathodic depolarization is caused by some species produce by SRB rather than by the organisms themselves (Ringas and Robison, 1987).

2.10 THE EFFECTS OF SULPHUR-REDUCING BACTERIA

2.10.1 Pollution of Water:

Canals, harbors, estuaries and stagnant waters at or near industrialized regions are prone to become anaerobic as the detritus of human activities increases their biological demand for oxygen. All such water contain sulphate and, particularly warm climates or seasons, sulphate reduction ensures, and a smell of hydrogen sulphide develops, with consequent nuisance to those living in a region and damage to metal and paintwork (Ringas and Robison, 1987).

2.10.2 Infection of Sand and Soil:

Very often, sand and mud's contain black products that impart a dark colour to them. If this type of formation is exposed to air, it turns brown after certain period of time. In a certain instances, the change in colour is accompanied by the odour of hydrogen sulphide. The interpretation is that black ferrous oxides and sulphates on being exposed to air. Such colour change serves as warming that metal and stone installation in the environments are threatened by microbial corrosion. This is reflected by the damage suffered by marble and stone statues in Europe and in Asia. Soil totally free of SRB occurs very rarely, but the SRB are inactive if the soils are aerobic. Soil showing pronounced blackening or clay showing ‘graying’ are anaerobic and often heavily infected. These are potential initiators of metallic corrosion (Ringas and Robison, 1987).

2.10.3 Paper Industry

Blackening of paper and pulp can occur as a result of activity of SRB. The presence of SRB leads to disposal problem, highlighted by the example of a plant that disposed paper-pulp wastes into river, which led to sulphide pollution (Ringas and Robison, 1987).

2.10.4 Gas Industry.

Town gas in gas holders is always underlain by a layer of water. The growth of SRB in the gas-holder water leads to the formation of hydrogen sulphide contaminating the gas and causing serious corrosion of the vessel (Ringas and Robison, 1987).

2.10.5 Concrete Corrosion

Microbial induced corrosion is important biological or chemical phenomenon that is having extreme effect on the infrastructure of our cities. It is found that aerobic heterotrophy and neutrophilic and acidophilic sulphur oxidizer are dominant microbes. There are also SRB, aerobic hetertrophs, nitrate reducing bacteria, and ammonia oxidizing bacteria present in some sample (File://c/users/solo/Document/microbial induced corrosion.

The corrosion of concrete pipes is a consequence of a cyclic process caused by microbial sulphur metabolism. Two types of sulphur metabolism are involved in the cycle of sulphur in the environment. One is anaerobic process in which H_2S is produced by anaerobic bacteria, the other is an aerobic process in which in which the H_2S is oxidized to elemental sulphur (S) or sulphuric acid (H_2SO_4), this cyclic process exists as a natural method for the cyclic of sulphur compounds in the environment and may also exist in sewage collection systems.

During the transport of raw sewage from the top of the sewage collection system to the treatment plants, the organism in the sewage start to degrade the abundant organic compounds present in the raw sewage. This often results in the depletion of O_2 from the sewage. This results in the creation of anaerobic or anoxic condition which allow the growth of sulphur of sulphate reducing bacteria (SRB) which grow only in the absence of O_2 and obtain energy by utilizing small organic compounds or H_2 as energy sources and transferring the electrons produced to sulphate, thus reducing it to sulphide (File://c/users/solo/Document/microbial induced corrosion).

2.11 BRIEF REVIEW OF CORROSION TYPES

Corrosion processes occur in so many other forms which include, crevice corrosion, pitting corrosion, Galvanic corrosion, erosion corrosion, Stress corrosion cracking, inter-granular Corrosion, Leaching corrosion and general or uniform attack (Onyemaobi and Amaghaghi, 1998).

2.11.1 Uniform or General Attack

This is the most common form of corrosion and includes rusting of iron, high temperature oxidation, tarnishing of silver and brass. It is characterized by chemical or electrochemical reaction and the reaction proceeds uniformly over the entire surface. (Onyemaobi and Amaghaghi, 1998).

2.11.2 Crevice Corrosion

This is intense localized corrosion which frequently occurs within crevices and shielded area on the metal surface. This type of attack is associated with small volume stagnant solution which is found in little holes and in gaskets and around deposits. It occurs commonly under bolts and rivets heads (Onyemaobi and Amaghaghi, 1998).

2.11.3 Pitting Corrosion

This is extremely localized attack that results in holes in metal. The materials that show this type of attack are the stainless steels, chromium alloys and aluminum and its alloys. The pits can vary in depth – shallow or deep. Sometimes pitting factor, p, is the ratio of the deepest pit to the average metal penetration as determined by weight loss (Onyemaobi and Amaghaghi, 1998).

2.11.4 Galvanic Corrosion

When two different metals are joined together and immersed in a corrosive solution, a potential difference giving rise to a flow of electrons between the metals occurs. The less resistant metals, corrodes significantly and becomes anodic (Onyemaobi and Amaghaghi, 1998).

It is difficult to see that much of the corrosion which afflicts buried metal work is of the galvanic types already discussed, such as rusting, or at joints, or where stones lumps of clay or chalk rest against the metal causing crevice corrosion. There are however, certain particular varieties of corrosion to which buried metals are particularly prone, and the conditions under which corrosion commences also need comment. Galvanic cell causing severe rusting and pitting may be set up where a pipe from one soil to another, especially if one of the soil is acidic or contain sulphides, or if one soil has much higher oxygen content. In fact the principle of differential aeration, varying oxygen content can cause galvanic corrosion even where only one soil is present. The electrical conductivity of the soil is also important; the higher the conductivity the further apart anodic and cathodic regions may be spaced and still give rise to corrosion (Umezurike, 2008).

2.11.5 Stress Corrosion Cracking

This is the failure of a metal when subjected to tensile stress in a specific corrosive environment. The tensile stress can be static or residual. Brasses for example are susceptible to this type of attack in ammonia solution (Onyemaobi and Amaghaghi, 1998).

2.11.6 Intergranular Corrosion

This occurs at the grain boundaries resulting in loss of strength. This can be caused by impurities at the grain boundaries, depletion of alloying element, and enrichments of alloying element and so on (Onyemaobi and Amaghaghi, 1998).

It also occurs when there is precipitation of a second phase or segregation at grain boundaries produces a galvanic cell. In zinc alloys, for example, impurities such as cadmium, tin, and lead segregate at the grain boundaries during solidification. The grain boundaries are anodic compared with the remainder of the grains, and corrosion of the grain boundaries occurs. In austenite stainless steels, chromium carbides can precipitate at grain boundaries. The formation of the carbides removes chromium from the austenite adjacent to the boundaries. The low-chromium (<12% Cr) austenite at the grain boundaries is anodic to the remainder of the grain and corrosion occurs at the grain boundaries (Scully, 1988).

2.11.7 CO_2 Corrosion

Carbon dioxide systems are one the most common environments in the oil field industry where corrosion occurs. Carbon dioxide forms a weak acid known as carbonic acid (H_2CO_3) in water, a relatively slow rate. However, CO_2 corrosion rates are greater than effect of carbonic alone. Cathodic depolarization may occur, and other attack mechanisms may also be at work. Corrosion rates in a CO_2 system can reach very high level, but it can be effectively inhibited. Velocity effects are very important in the CO_2 systems; turbulence is often a critical factor in pushing system into corrosive regime (Omodafe and Ovri, 2004).

CO_2 with water will give Carbonic acid.

$$CO_2 + H_2O = H_2CO_3 = H^+ + HCO_3^{2-} \text{-----------} (2.0.9)$$

Carbonic acid with steel gives

$$2Fe + H_2CO_3 = Fe_2CO_3 + H_2 \text{--------------------} (2.1.0)$$

Reaction with Oxygen:

$$4Fe + 3O_2 + 6H_2O = 4Fe(OH)_3 \text{----------------} (2.1.1)$$

And corrosion with carbonic acid

$$Fe + 2H_2CO_3 = Fe(HCO_3)_2 + H_2 \text{---------------} (2.1.2)$$

$$2Fe(HCO_3)_2 + 1/2O_2 = Fe_2O_3 + 4CO_2 + 2H_2O \text{ -- } (2.1.3)$$

Source: Anita, (2004) PP.12

2.11.7 Hydrogen Sulphide Corrosion H_2S

Hydrogen sulphide (H_2S) is produce when manure undergoes anaerobic (absence of oxygen) fermentation. Hydrogen sulphide is produced continuously in all un-aerated manure storage systems, including shallow barn gutters; underground storage tanks (Anita, 2004).

Hydrogen sulphide is often found in natural gas or dissolved in crude oil, and in addition, it may be formed by the decomposition of organic sulphur compound at high temperature. It rapidly attacks steel parts that are exposed to the gas. Equipment that suffers by this corrosion comprises storage tanks and gas line, and at temperature exceeding 200ċ, pipestill tube, evaporators and fractionators (Umezurike, 2008).

Molecules of H_2S are acidic and poisonous gas, every possible precaution must be taken to protect any person working in environment containing it, even in small quantity. Because H_2S is acidic, it reacts with steel (iron) to form soluble iron sulphides (file://G:/ONGC print.htm).

$$H_2S + Fe^{2+} = FeS_X + H_2 \text{ ----------------------(2.1.4)}$$

2.12 HYDROGEN EMBRITTLEMENT

The embrittlement of metal or alloys by atomic hydrogen involves the ingress of hydrogen into a component even that can seriously reduce the ductility and load-bearing capacity cause cracking and catastrophic brittle failure at stresses below the yield stress of susceptible materials. Hydrogen embrittlement occurs in a number of forms but the common features are an applied tensile stress and hydrogen dissolved in the metal (Anita, 2004).

Examples of hydrogen embrittlement are cracking of weldment or hardened steel when exposed to conditions which inject hydrogen into the component. Presently this phenomenon is not completely understood and hydrogen embrittlement detection, in particular, seems to be one of the most difficult aspects of the problem. Hydrogen embrittlement does not affect all metallic materials equally. The most vulnerable are high- strength steels, titanium alloys and aluminum alloys (Anita, 2004).

2.13 SOURCES OF HYDROGEN

Sources of hydrogen causing embrittlement have been encountered in the steel making, in processing parts, in welding, in storage or containment of hydrogen gas, and related to hydrogen as a contaminant in the environment that is often a by-product of general corrosion. It is the latter that concerns the nuclear industry. Hydrogen may be produced by corrosion reactions such as rusting, cathodic protection, and electroplating. Hydrogen may be added to reactor coolant to remove oxygen coolant systems (Anita, 2004).

AS a by-product of corrosion reaction such as in circumstances when the hydrogen production reaction described here acts as the cathodic reaction since some of the hydrogen produced may enter the metal in atomic form rather than be all evolved as a gas in the surrounding environment. In this situation, cracking failure can often be thought of as a type of stress corrosion cracking. If the presence of hydrogen sulphide causes entry of hydrogen into the component, the cracking phenomenon is often termed "sulphide stress cracking (SSC)". The use of cathodic protection for corrosion protection if the process is not properly controlled (Anita, 2004).

2.14 CORROSION IN AEROSPACE INDUSTRIES

In itself, the hard vacuum of space does not cause corrossion. The severe corrosion problems are due to liquids such as oxidizers and fuels and also the high temperature encountered in blast nozzle and during reentry. Refractory metals such as tungsten are used for nozzles because of their strength at very high temperature (Fontana, 1987).

Cleanliness and careful inspection of all parts during fabrication and assembly are paramount to avoid contamination. Rusting of high-strength steel due to resident water can cause stress corrosion and hydrogen Embrittlement. Hydrogen charging of steel during electroplating can cause brittle fracture. Extensive corrosion of missiles stored in underground silos is caused by excessive moisture and inadequate coatings (Fontana, 1987).

2.15 CORROSION IN PETROLEUM INDUSTRIES

Corrosion problems occur in the petroleum industry in at least three areas: (1) production (2) transportation and storage, and (3) refinery operations. The petroleum refining industry is one of the largest manufacturing industries in the world. Huge amount are spent each year on capital equipment, modernization and maintenance, the major microbial problem in the industry is contamination of stored products, which lead to loss of product quality, formation of sludge and deterioration of pipe work and storage tanks, both in the refinery and at the end-user (Gaylarde, 1995).

2.16 ENVIROMENTAL EFFECTS OF CORROSION ON ELECTRICAL FACILITES

Electrical facilities are used in various environmental ranging from highly resistive soil buried underground power distribution facilities which include pipes cables employing coated steel pipes with oil as a coolant and lead sheath cable exposed to the soil or buried duct. Another major facility commonly used is direct burial concentric neutral construction where the neutral wire of the system is commonly unprotected by conventional coatings and is exposed directly to the soil. Other environments in which electrical facilities are used are the atmosphere, marine with different salinity. Freshwater, acidic,bacteria and Hydrogen sulphide (H_2S) and carbon-dioxide (CO_2) environment. When these facilities are in contact with the environment and water and oxygen are available, corrosion is bound to occur (Obah, 1998).

2.17 CARBON AND LOW ALLOY STEELS

These are used in the construction of the bodies of most electrical infrastructures such as generators and transformer bodies, casing and housing. These classes of steels are expected to corrode in every environment and are expected to fail from corrosion related factors. Their corrosion can be monitored with some degree of accuracy since the form of corrosion is usually uniform. Pitting corrosion is also observed in this grade of steels. They corrode in almost all environment and their corrosion tendencies are more pronounced in acidic environment (Obah, 1998).

2.18 STAINLESS STEEL

Stainless steels are commonly used in areas where corrosion resistance is of prime concern. They are therefore used in transformers, generators, electrical motors, compressor pumps etc. Stainless steels with high chromium content have high corrosion resistance. This high corrosion resistance is due primarily to a thin film of chromic oxide formed on the surface of the steel. This oxide is about 10nm thick. In the absence of this oxide, stainless steel corrodes at rate comparable to carbon steels. The major corrosion observed in stainless is stress corrosion cracking (SSC) and intergranular corrosion. When the chromium content is less than 12%, the corrosion resistance is enhanced and it is insensitive to most mild steel corroding.

Pitting corrosion is the major problem with this grade of steel. Pitting results from the localized break down of the oxide film. Stainless steel when used in sea water, brackish and acid polluted waters pitting is bound to occur. The corrosion resistance of stainless steel is not as good in most industrial and marine atmosphere. I.e. for austenitic and martensitic types but the ferric type is generally corrosion resistant in atmospheric environments in rural and urban area (Umezurike, 2008).

2.19 CONTROLLING MICROBIAL CORROSION

According to Samant (file://G:/ONGC print.htm), biocides are those chemicals which kill the micro-organisms completely while bactericides are chemicals that suppress the growth of biological activity up to a permissible limit.

For effective control of microbial corrosion, the biocides should be used in conjunction with thorough physical cleaning because it has been observed that once a biofilm of sludge is formed over a surface, it will be difficult to control with biocides.

The majority of industrial biocides used to control MIC are manufactured from fuels such as petroleum or natural gas. Apart from their high costs, these biocides are extremely toxic to most living organisms including man. Organic compounds such Chlorinated phenols and aldehydes e.g para formaladehyde, glutaraldhyde appear to be most suitable biocides.

2.20 FACTORS AFFECTING CORROSION:

Temperature: As water depth increases temperature decreases, this decrease in temperature affects the ability to form calcareous deposits to form. Calcareous deposits are a result of the cathodic protection polarization process. These deposits are critical in the cathodic protection process as they act like crude coating system to reduce the current required from the anode thus; it is possible to provide cathodic protection for a very long life with relatively small anodes. At low temperatures the deposits form much more slowly and when formed are generally less dense than deposits formed under equivalent conditions in shallow water. The slower formation leads to higher levels of cathodic protection current being required to sustain protection, and thus more anodes being required (Gelling, 1976).

The Deep Water Environment

To understand how the mechanisms vary in deep water, it is necessary to appreciate how the deep water environment differs from shallow water areas. There is common misconception that steel does not corrode in very deep water.”Look at titanic, the dam thing’s as good as new and it’s been down there for a hundred of years.” We have all heard this at one time, in the truth the titanic is a crumbling wreck, corrosion will eventually destroy every trace of the vessel, but the initial attack is at galvanic couples, just as it would be on an unprotected pipeline. It is true that the corrosion rate is less in deep water, but it is far activation (2) concentration (3) resistance polarization (Umezurike, 2008).

2.21 DETECTION OF SRB IN A WATER SYSTEM

General

The presence of sulphate reducing bacteria in a water system may be determined by three methods. These include sensory perception, pH level determination, and biological analysis (Yuzwa, 1991).

Sensory Perception

Since hydrogen sulphide is a by-product of their metabolism, the "rotten egg" odour associated with this sulphur compound is an indication that sulphur reducing bacteria may be present in the water system (Yuzwa, 1991).

PH Level Determination

Since hydrogen sulphide is a by-product of their metabolism, SRB can also cause the pH level of the water system to fall to as low as pH 5.0. Therefore, if repeated caustic additions are required in order to maintain the pH level of a closed water system within prescribe control limits, and then sulphate reducing bacteria are most likely present in the system (Yuzwa, 1991).

Biological Analysis

Biological analysis of a water or deposits sample collected from the system may be performed either by laboratory analysis or by field analysis. The basic procedure for both of these techniques involves the addition of the water or deposits into a container to which nutrient have been added, and incubation of the sample.

The laboratory procedure is costly, the sample must be collected in a sterilized bottle, and the sample should be delivered to the laboratory within 24 hours after collection.

The analysis procedure, however, is substantially cheaper, and it does not require a great deal of training or expertise. The field test kit contains a prepared medium. The water sample is simply injected into a vial, and incubated either at 32-37C or at room temperature. If a quantitative analysis is required, an incubation temperature of 32-37C must be maintained; however, if a qualitative analysis is required, the sample may be incubated at room temperature. If SRB's are present in the sample, they will reduce the medium to sulphate, which in turn reacts with the iron in the solution to produce a black ferrous sulphide film will on the sides of the vial within a 28 days period (Yuzwa, 1991).

2.22 METHODS OF CONTROLLING CORROSION

2.22.1 Cathodic Protection

The need to save the Nations through adequate protection of oil and gas industry facilities and pipelines from agents of degradation such as corrosion cannot be over stretched. (Okoroafor, 2004). Corrosion is a major agent of waste. Cathodic protection (CP) remains popular, cost-effective and probably the most acceptable method of mitigating corrosion of buried and submerged structures. Therefore, the need to save the nation’s income through corrosion mitigation cannot ignore cathodic protection. However, for cathodic protection system to result into income saving it must be effective. Cathodic protection of our oil and gas industry facilities and pipelines if effectively applied can save the nation a lot of income. However, even through Cathodic Protection (CP) technology is vital but common method of corrosion mitigation of buried or submerged metal structure, its state in Nigerian petroleum industry operation is still below international standard in term of design and monitoring. Design and monitoring obsolescence has denied some Nigerian operators the benefit of modern CP systems provides. Based on the principle first discovered over two centuries ago by Luigi Galvani of Italy, its application by oil and gas industry started only in 1930; and the technology introduced by them has remained in use, but with significant modification and improvement in the area of design, survey and monitoring .These modification and improvements have resulted in the long-term integrity of cathodic protection system, guaranteeing continuous protection (Okoroafor, 2004). The most significant factor influencing corrosion in the Nigeria petroleum industry today is “ageing process”. Most of the nation’s oil and gas facilities and pipeline are over 40 years old. This ageing process coupled with ineffective protection, results in coating disbandment and accelerated corrosion, necessitating premature rehabilitation, waste of crude oil and products, environmental damage, etc.

Cathodic protection can be achieved in two ways:

By the use of galvanic (sacrificial) anode, or

By “impressed” current.

Galvanic anode system employs reactive metals as auxiliary anode that is directly electrically connected to the steel to be protected. The difference in the natural potential between the anode and the steel, as indicated by their relative position in the electro-chemical series, causes a positive current to flow in the electrolyte, from the anode of the steel. Thus, the whole surface of the steel becomes more negatively charged and becomes cathode. The metals commonly used, as sacrificial anode are aluminum, zinc and magnesium. These metals are alloyed to improve the long-term performance and dissolution characteristics. (Umezurike, 2008).

Impressed-current systems employ inert (zero or low dissolution) anode and use an external anode onto the cathode surface.

The connection is similar for the application of cathodic protection to metallic storage tanks, jetties offshore structures and reinforced concrete structure. Structures that are commonly protected by cathodic protection are the exterior surface of:

Pipeline

Ships' hull

Storage tank bases

Jetties and harbors structure

Steel sheet, tabular and foundation pilings

Offshore platform, floating and subsea structure.

Cathodic protection is also used to protect the internal surface of:

Large diameter pipeline

Ship's tanks (product and ballast)

Storage tanks (oil and Water)

Water-circulating systems.

However, since an internal anode will seldom spread the protection for a distance of more than two to five pipediameters, the method is not usually practical, or suitable, for the protection of small-bore pipe work (Umezurike, 2008).

Cathodic protection can be applied to control the corrosion of steel embedded in reinforce concrete structure (bridges, buildings port and harbor structure, etc)

2.22.2 Anodic Protection or Passivation

Metals near the anodic end of the galvanic series are active and serve as anode in most electrolyte cells. However, if these metals are made passive or more cathodic, they corrode at slow rate than normal. Passivation is accomplished by producing strong anodic polarization, preventing the normal anode reaction; thus term anodic protection (Donald and Pradeep, 2006).

We cause passivation by exposing the metal to highly concentrated oxidizing solution. If iron is dipped in very concentrated nitric acid, the iron rapidly and uniformly corrode to form a thin protective iron hydroxide coating. The coating protects the iron from subsequent corrosion in nitric acid. Metals such aluminum, chromium, titanium and zirconium naturally develop surface oxide films which confer remarkable resistance to further corrosion. All metals, however can certain conditions of wet corrosion become immune by the formation of oxide films; in this state the metal is said to be passive, and will remain unattached indefinitely as long as the condition remain unchanged (Umezurike, 2008).

We can also cause passivation by increasing the potential on the anode above a critical level. A passive film forms on the metal surface, causing strong anodic polarization, and current decreases to a very low level (Donald and Pradeep, 2006).

Weakly alkaline conditions promote passivity in most metals, whereas acid condition stimulates corrosion; the presence of chloride and sulphate ions is particularly damaging to passive films. In neutral solution both results are possible simultaneously, and the result is usually a scattered galvanic attack. The balance between attack and passivity depends on the acidity of the corrodant and the magnitude of the galvanic potential acting on the metal; charts plotting the relation between these variables have now been prepared for all engineering metals and are known as pourbaix diagram (Umezurike, 2008).

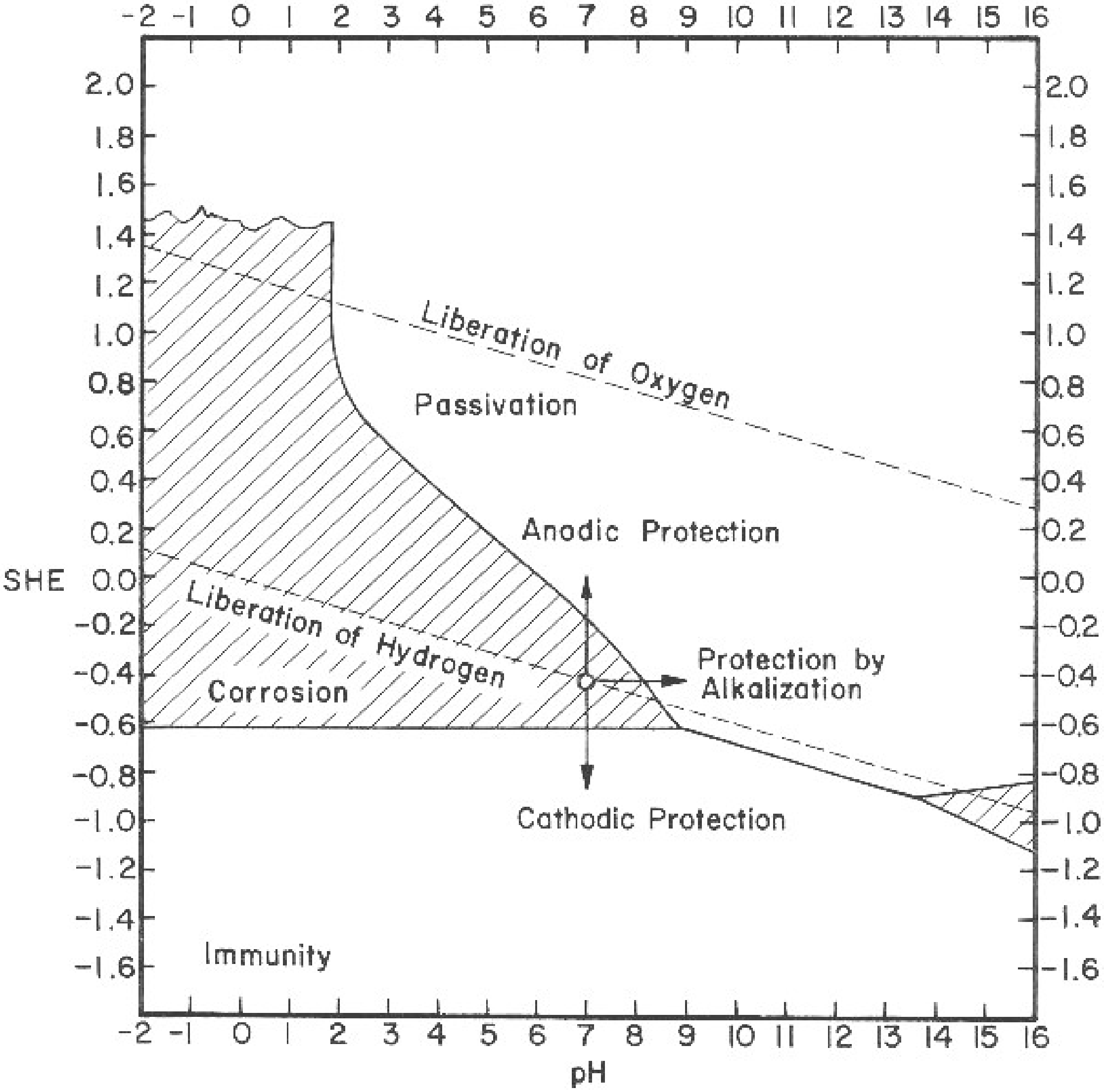

Fig. 2.2: Pourbaix Diagram

Source: Umezurike, C (2008),P.382

2.22.3 Coating

Coatings are used to isolate the anode and cathode regions. Coatings also prevent diffusion of oxygen or water vapor that initiates corrosion or oxidation. Temporary coatings, such as grease or oil, provide some protection but easily disrupted. Organic coating, such as paint, or ceramic coating, such as enamel or glass, provides better protection. However, if the coating is disrupted, a small anodic site is exposed that undergoes rapid, localized corrosion (Donald and Pradeep, 2006).

Pretreatment of Metals for Coating

Before considering the various protective coatings which may be applied to metals it is necessary to stress the importance of adequate cleansing of the metal surface. Surface preparation may show quickly (as in galvanizing or electroplating) or slowly (as frequently in painting) but in the long run the quality of preparation makes or mars the quality of protection as much as the nature of coating itself (Umezurike, 2008).

The major sources of trouble on metal surface are grease and oil films, rust and mill scale on steel surfaces, and moisture (where paint is not applied). Moisture is perhaps the commonest of the three, together with rust; it is also fairly simple to remove, but on large structures its avoidance is largely a matter of common sense. Ideally, paint should be applied when the temperature is above 4.4C. and the relative humidity below 86%; therefore wherever possible, especially in the winter months, painting should be done indoors, whilst outdoor painting should be done in dry weather and preferably the latter part of the day to allow the metal to warm up and any dew to evaporate (Umezurike, 2008).

Mill scales, the relatively thick adherent layer of oxide on hot mild steel, and rust have always been a problem. In theory a perfect overall layer of scale might provide reasonable base for painting; in practice, however, the brittle nature of mill scale leads to cracks and imperfections so that the only safe course is its entire removal.

Flame cleaning is also employed quite extensively oxyacetylene flames are passed over the surface of the metal, whereupon differential expansion of scale and steel causes the former to flake off. Rust patches are also dried out; making for easier removal by brushing and the procedure leaves a warm dry surface which is advantageous if the undercoat can be applied straight away (Umezurike, 2008).

Metallic Coating

Protective metallic coating can be applied in two ways: by dry, or diffusion coating in which article is dipped, sprayed, clad or heating in a powder of the protective metal, and by wet, electrodeposited coatings (Umezurike, 2008).

In general terms, the advantages of metallic coatings are that they are strong , and insensitive to light and moderate heat; for the most part they are more wear resistant than paint, and emendable to soldering. On the other hand, if corrosion once starts it will proceed faster because of the galvanic conditions which are set up and because it is not possible to impregnate metallic coatings with the inhibitive compounds that are present in paints. The following techniques are employed in metallic coating (Umezurike, 2008).

(i) Hot Dipping

In this technique, the material to be coated is lowered into a bath of molten protective metal and withdrawn carrying a film of the protective metal on its surface. The commonest instances are coating steel with zinc (galvanizing) and tin (tin plate). Adhesion results from alloying at the interface and as usual is dependent on complete cleanliness of the metal surface. To this end, after the standard cleansing procedure has been carried out, the article is passed through a layer of flux which is maintained on the surface of the molten dip. However, since some of the alloy phases developed is brittle, the time of this immersion must be kept to the minimum necessary for an adequate thickness coating, in order to prevent excessive growth of brittle intermetallic phases. The addition of a very small amount of aluminum to the molten zinc has been found beneficial in suppressing diffusion of zinc into the steel and thereby maintaining a reasonable ductile coating. Galvanizing steel is used for sheeting in building, for wire-mesh fencing and for water systems and storage tanks (Umezurike, 2008).

Aluminum may also be applied to steel surface by hot dipping, although the commonest method of application is by spraying. It is not as popular as zinc for coating steels, but weight for weights it has better general corrosion resistance, except in marine conditions. The higher temperature of the dipping bath also means that the process is unsuitable for work-hardened steels. Painting (as with zinc coatings) helps to prolong the life of the coating (Umezurike, 2008).

(ii) ELECTROPLATING

This afford excellent (and frequent decorative) protection if carried out with due care, and can be used for laying down all the common metals, (Except aluminum), and a wide varieties of alloys. Unfortunately the need for high purity, cleanliness and careful monitoring of the process makes it unsuitable as a large scale protective technique for civil engineering structures. It is however, valuable as a finishing process for smaller components, particularly since a number of plating is abrasion as well as corrosion resistant.

2.22.4 MATERIAL SELECTION AND TREATMENT

Corrosion can be prevented or minimized by selecting appropriate materials and heat treatments. In casting, for example, segregation causes tiny, localized galvanic cells that accelerate corrosion. We can improve corrosion with a homogenization heat treatment. When metals are formed into finished shapes by bending, difference in the amount of cold work and residual stresses causes local stress cells. These may be minimized by a stress-relief anneal or a full recrystallization (Donald and Pradeep, 2006).

2.22.5 DESIGN

Proper design of metals structures can slow and even avoid corrosion in the following ways;

1).Design components so that fluids systems are closed, rather than open, and so that stagnant pools of liquids do not collect. Partly filled tanks water-line corrosion. Open systems continuously dissolve gas, providing ions that participate in the cathode reaction and encourage concentration cells (Donald and Pradeep, 2006).

2). In some cases, the rate of corrosion cannot be reduced to a level that will not interfere with the expected lifetime of the component. In such cases, the assembly should be designed in such manner that the corroded part can easily and economically replace (Donald and Pradeep, 2006).

3). Avoid crevice between assembled or joined materials. Welding may be a better joining technique than brazing, soldering, or mechanical fastening. Galvanic cells develop in brazing or soldering, since the filler metals have difference composition from the metal being joined. Mechanical fasteners produce crevices that lead to concentration cells. However, if the filler metal closely matched to the base metal, welding may prevent these cells from developing (Donald and Pradeep, 2006).

4). Prevent the formation of galvanic cells. This can be achieved by using similar metals or alloys. For example, steel pipe is frequently connected to brass plumbing fixture, producing a galvanic cell that causes the steel to corrode. By using intermediate plastic fittings to electrically insulate the steel and brass, this problem can be minimized (Donald and Pradeep, 2006).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 MATERIALS/APPARATUS.

In carrying out this research, the materials/apparatus used include:

(i) Digital electronic weighing machine (ConTech)

(ii) Bench Type pH meter (mac)

(iii) Colony Counter

(iv) High Impedance Digital Multimeter (DT 9205)

(v) Copper/Copper sulphate reference electrode potential

(vi) Medium carbon steel coupons

(vii) Mild steel coupons

(viii) Distilled water

(ix) Acetone (analar grade)

(x) Anaerobic and aerobic sulphur reducing bacteria environments.

3.2 DESCRIPTION OF SAMPLES

Two grades of the test specimens used in this research were medium carbon steel and mild steels. Each of the rectangular shaped coupons of mild steel has a thickness of

5.0mm and dimension of 73.0mm by 22.0mm as was obtained from Shell Petroleum Development Company (SPDC) Port - Harcourt. The rod shaped medium carbon steel was obtained from Delta steel Company Limited, Oviwian-Alaja, Delta State. It was shaped to dimensions similar to that of mild steel using shaping machine and grinded to produce a good surface finish using emery cloths of different grades. Two separate and close holes of diameter 7.0mm each were drilled on the steel coupons to enhance easy suspension in the different environments.

The chemical compositions of the mild and medium carbon steels as supplied by the manufactures are given in table 3.1 and 3.2 below:

Table 3.1: Chemical composition of steel used:

Steel Grade	**C**	**Si**	**Mn**	**Cu**	**P**	**S**	**Cr**	**Ni**	**Sn**	**Fe**
MS	0.18	0.23	0.80	0.20	0.03	0.04	0.05	0.55	0.02	Bal
MCS	0.40	0.25	0.52	0.05	0.03	0.02	-	-	-	bal

Key:

MS = Mild Steel

MCS = Medium Carbon Steel

Table 3.2: Compositions of nutrient algae used:

Compound	Nacl	$MgSO_47H_20$	KCl	KH_2PO_4	Na_2HPO_4	$NaNO_3$	Agar
Composition	10g	0.3g	0.29g	0.83g	1.25g	0.42g	12.5g

3.3 ENVIRONMENTS

Two environments were used in this research, viz

(i) Sulphur reducing Bacteria in aerobic and anaerobic environment

(ii) Distilled water (control).

3.4 HOW TO ISSOLATE SULPHUR REDUCING BACTERIA FROM THE SOIL.

5g of sulphur was measured and buried in the soil for seven days. The sulphur powder mixed with soil sample was collected after seven days. Then, 1g of the soil was weighed and serially diluted. Nutrient agar medium was prepared by mixing the compositions in table 3.2 and was added to 1g of sulphur and allowed to solidify. 0.1ml of the fifth serially diluted soil sample was pipette on the nutrient agar plate. It was spread with a spreader and incubated anaerobically. The bacterial of the genera Desulphurvibrio was isolated from anaerobic incubation.

3.5 PROCEDURE FOR DATA COLLECTION AND ANALYSIS.

3.5.1 Experimental Procedure

The corrosion rate of the coupons was monitored by total immersion/weight loss technique and electropotential method. The coupons were cleaned and dried in acetone before immersion.

The initial weights of the coupons were taken with a digital electronic weighing machine (contech) to the nearest 0.001g and were noted. The samples were then totally exposed to the environments containing aerobic and anaerobic sulphur reducing bacteria.

Suspension was done with the aid of a rubber thread which passes through the hole in each coupon. The initial electro-potential of each of the coupons was taken using the copper/copper sulphate ($Cu/CuSO_4$) reference electrode connected to a digital multi-meter of the model DT 9205, and the results were noted. A coupon was removed from each media each week till the end of the experiment.

3.5.2 Electrochemical Methods

Electrochemical corrosion monitoring is based on the premise that corrosion is essentially an electrochemical process that can be monitored through the measurement of the electrical properties of the material (potential, current and resistance). The corrosion potential measurement was made on each mild steel and medium carbon steel coupons exposed to anaerobic, aerobic and control environments using reference electrode which was connected to a digital multi-meter. The reading was taken at intervals of seven days for a period of six weeks. The negative lead of the meter was made to touch the coupons in the solutions while the positive lead of the multi-meter was connected to the test lead of the reference electrode which was immersed freely in the solution.

3.5.3 Weight Loss Technique

The coupons were removed from the environments at interval of seven days. The oxide film formed on the surface of the coupons were examined visually, brushed with a sponge in tap water and then dipped in acetone and then dried.

The final weight of the test specimen removed from the control and other environments was taken and recorded using electronic weighing machine. The coupons were then discarded. The procedure was repeated at intervals of seven days for a total period of six weeks.

3.5.4 Visual Examaintion

Samples were carefully examined visually during each monitoring day with the aim of identifying:

(1) The type of substances or the nature of the oxide scales on the surface of the specimens

(2) The type of corrosion occurring
(3) Any changes in the colour of the corrosion products

3.5.5 Chemical Test

Chemical test was carried out to indicate the type of corrosion. This was done by gently scrapping the corroding surface and putting it in a test tube. Concentrated hydrochloric acid (HCl) was then poured on it. The mixture was heated in a gas burner.

3.5.6 Bacteria Concentration and pH of the Environment.

The bacteria concentrations in colony forming units per milliliter (cfu/ml) were taken at an interval of seven days for a period of six weeks using colony counter. Bacterial concentration increases with exposure time (days).

The pH of the environment was taken along each time potential readings were taken. The pH readings were made using a pH meter (MAC Type).

CHAPTER FOUR

4.1 RESULTS AND DISCUSSION

4.1.1 WEIGHT LOSS

The corrosion behavior of mild and medium carbon steels in aerobic, anaerobic environments and in distilled water which serves as a control was studied by monitoring the electro-potential and weight loss of the specimens at intervals of seven days.

The results of the weight losses of the steel coupons were converted to corrosion rate in penetration per year and are given in Table 4.1 and plotted in Figures 4.1-4.5.

Table 4.1: Weight loss (g), Corrosion rate (mpy) and potential (mV) in various environments.

	Weight Loss Method														Electrode Potential Method						
	0 day		7 days		14 days		21 days		28 days		35 days		42 days		0 days	7 days	14 days	21 days	28 days	35 days	42 days
	Wt Loss (g)	CR (mpy)	Wt Loss (g)	CR (mpy)	Wt Loss (g)	CR (mpy)	Wt Loss (g)	CR (mpy)	Wt Loss (g)	CR (mpy)	Wt Loss (g)	CR (mpy)	Wt Loss (g)	CR (mpy)	EP (mV)	EP (mV)	EP (mV)	EP (mV)	EP (mV)	EP (mV)	EP (mV)
Control MCS	0.00	0.00	0.030	2.94	0.051	2.50	0.076	2.35	0.076	1.86	0.076	1.49	0.074	1.21	-0.47	-0.65	-0.70	-0.74	-0.74	-0.72	-0.73
Control MS	0.00	0.00	0.042	4.15	0.069	3.41	0.076	2.60	0.082	2.03	0.080	1.58	0.078	1.29	-0.55	-0.67	-0.73	-0.76	-0.77	-0.74	-0.74
Anaerobic MCS	0.00	0.00	0.054	05.30	0.088	4.31	0.125	4.08	0.136	3.33	0.132	2.59	0.128	2.09	-0.66	-0.77	-0.83	-0.90	-0.91	-0.83	-0.82
Anaerobic MS	0.00	0.00	0.065	6.43	0.098	4.84	0.140	4.61	0.152	3.76	0.150	2.95	0.140	2.31	-0.70	-0.83	-0.87	-0.95	-0.93	-0.86	-0.85
Aerobic MCS	0.00	0.00	0.49	5.00	0.076	3.72	0.089	2.91	0.098	2.40	0.083	1.76	0.085	1.40	-0.54	-0.70	0.77	-0.82	-0.84	-0.76	-0.75
Aerobic MS	0.00	0.00	0.053	5.24	0.084	4.15	0.105	3.46	0.130	3.21	0.120	2.37	0.116	1.91	-0.62	-0.75	-0.81	-0.88	-0.89	-0.79	-0.79

Key: Envt. - Environment Wt. Loss - Weight Loss
C.R - Corrosion Rate Ep - Electro potential

TABLE 4.2: Results for pH measurement in control, anaerobic and aerobic environments

pH	**0-day**	**7-day**	**14-day**	**21-day**	**28-day**	**35-day**	**42-day**
Control	6.90	6.72	6.40	5.78	5.78	6.32	6.80
Anaerobic	6.80	6.05	5.50	5.00	4.50	5.50	6.00
Aerobic	6.85	6.40	6.35	5.25	5.00	6.00	5.85

Table 4.3: Results for bacterial concentration of steel coupons exposed to anaerobic and aerobic environments.

Bac.Conc	0-day	7-day	14-day	21-day	28-day	35-day	42-day
Anaerobic (cfu/ml)	300	350	400	450	500	530	550
Aerobic (cfu/ml)	150	200	250	280	320	350	420

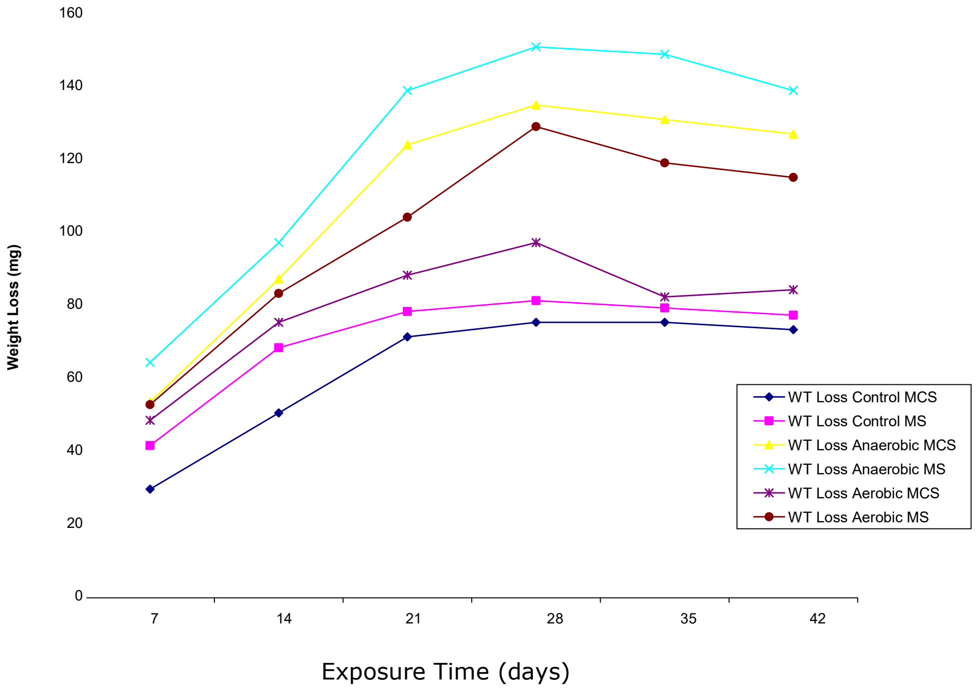

Fig. 4.1 variation of Weight Loss in (mg) with Exposure time in (days) for steel coupons exposed to Aerobic, Anaerobic and Control.

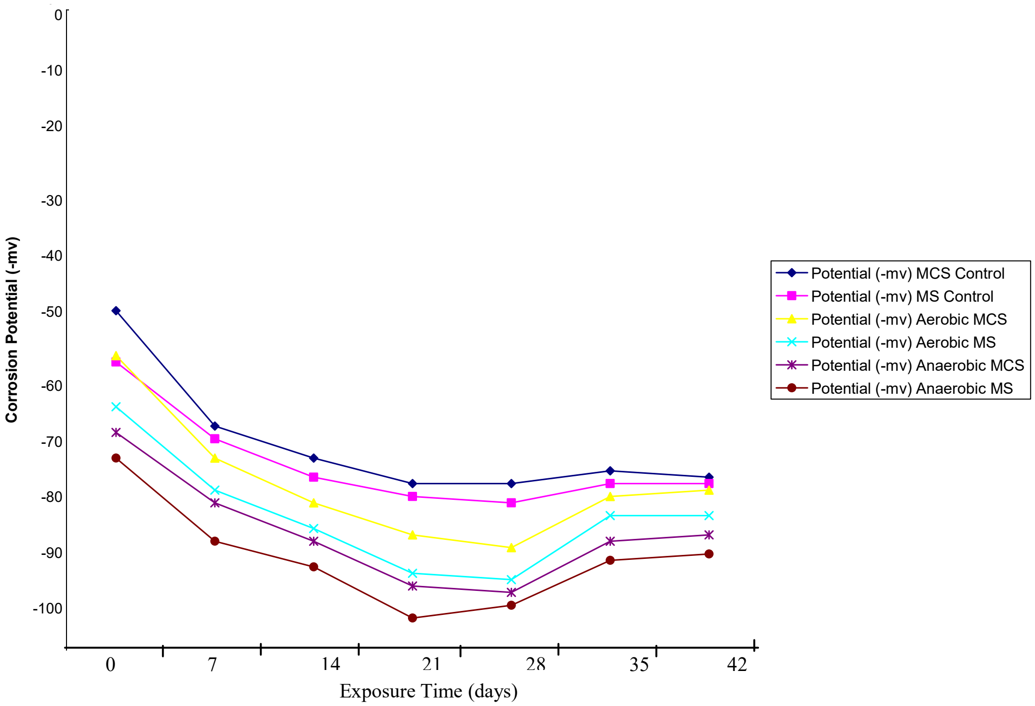

Fig. 4.2 Variation of Potential (-mV) with Exposure Time with (days) for Steel Coupons exposed to Aerobic, Anaerobic and Control.

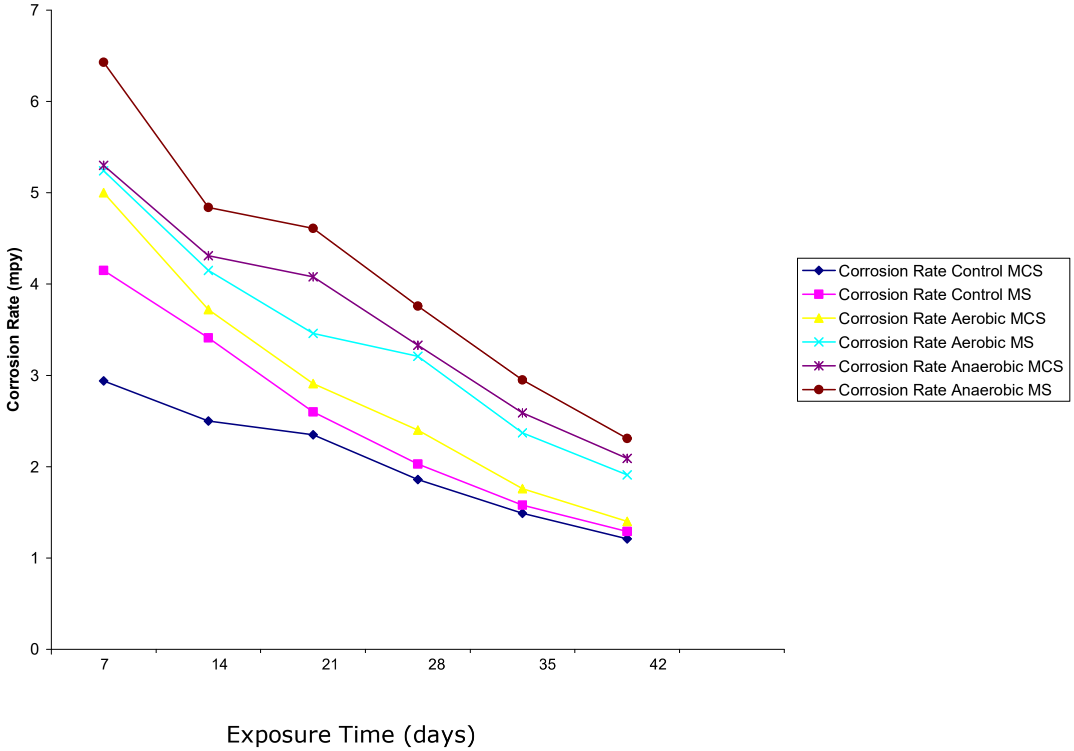

Fig. 4.3 Variation of Corrosion rate in (mpy) with Exposure Time (days) for Steel Coupons exposed to Aerobic, Anaerobic and Control.

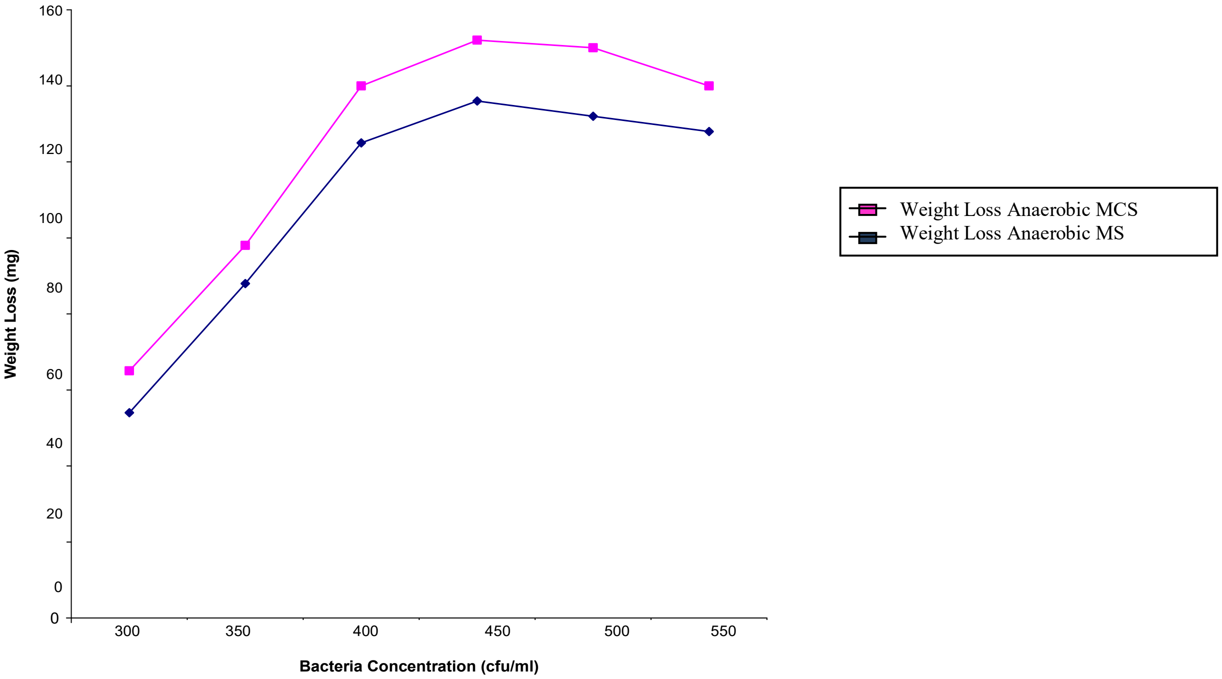

Fig. 4.4 Variation of Weight Loss in (mg) with Bacteria concentration (cfu/ml) for Steel Coupons exposed to anaerobic environment

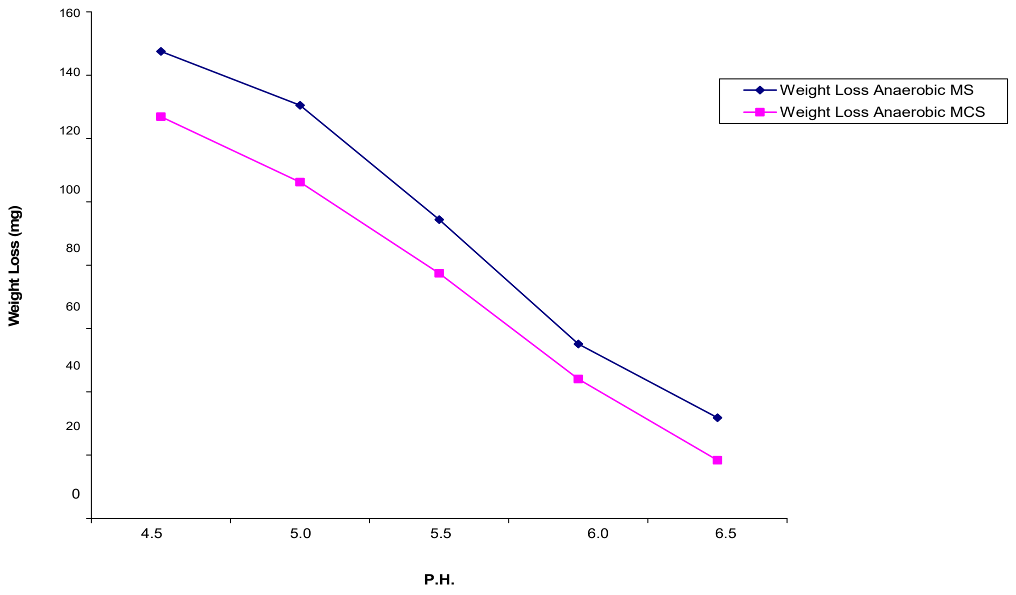

Fig. 4.5: Variation of Weight Loss with pH for Steel Coupons exposed to anaerobic environment.

4.1.2: CORROSION RATE

The corrosion rates of steels using weight loss method in the various environments were calculated using the formula. (42)

CR = 534W/DAT

Where, CR= corrosion rate in mill per year (mpy)

W= weight loss in grams (g)

D= Density of steel (g/cm^3)

A= Total surface area (cm^2)

T= Exposure Time in hours (hrs)

The results are given in column 2 of table 4.1 for each week.

Details of calculation are shown in appendix A

4.1.3 POTENTIAL MEASURMENT

The corrosion rate measurement was made using the electrical properties of the corroding system. For a corroding system the electrical potential and consequently the current and resistance are affected (Ovri, 1998a).

Using Ohm's law i.e.

V = IR

Where V = Potential in voltage

R = Resistance in ohms

I = Current in Amperes

The voltage decreases as the resistance increase due to the corrosion product formed on the steel surface. Hence, the lower the potentials, the more the corrosion (Ovri, 1998).

4.1.4 CHEMICAL TEST RESULT

A colourless gas with a rotten egg odour evolved with a black residue of iron II chloride. The rotten egg odour of H_2S indicated that SRB is responsible for the corrosion.

$$2HCl + FeS = H_2S + FeCl_2 \quad \text{-------------------------} \quad (4.1.1)$$

4.1.5 VISUAL EXAMINATTION

The steel samples exposed to the various environments were examined visually. General (uniform) corrosion and pitting were observed for all the steel samples exposed to aerobic, anaerobic and the control.

4.2 DISCUSSION OF RESULTS

The corrosion rate of mild steel and medium carbon steels depends on several corrosion parameters such as chemical composition, surface finish, and pH. Anaerobic, aerobic and distilled water contain corrosion inducing ions such OH^- and SO_4^{2-}. Therefore these environments are considered aggressive and toxic to most engineering materials including steel.

Relating between laboratory test, chemical analysis, and visual examination, the results of the investigation were discussed under the following headings: weight loss of sample, and corrosion rate measurement.

4.2.1 WEIGHT LOSS OF SAMPLES

Figure 4.1 shows the weight loss of the steel samples as a function of the environment and exposure time (days). Mild steel and medium carbon steel were found to corrode in different environment containing SRB investigated, and this was evidenced by the decrease in the original weight (weight loss).

Mild steel has the highest weight loss in all the environments investigated; recorded (156mg) in anaerobic, (130mg) in aerobic environment and (82mg) in the control. As could be seen in Table 4.1 and Fig 4.1, the weight loss of mild steel coupons in all the environments increased with in the first 28th days. This observation was attributed to the fact that the rate of a chemical reaction increased with time (18). However, between the 35th and 42nd days of the test, mild steel in the entire environment showed a sharp decrease in weight loss with time. This behaviour could be explained from the concept of passivation of oxide (Donald and Pradeep, 2006).

Medium carbon steel has the least weight loss, recorded (136mg) in anaerobic, (98mg) in aerobic environment and (76mg) in the control. It was generally observed in Table 4.1 and Fig 4.1 that the weight loss of medium carbon steel coupons in the entire environment increased with time in the first 28th days. Also, between the 35th and 42nd day of the test, medium carbon steel in the entire environment showed sharp decrease in weight loss with time. These observations are attributed to the same facts stated in mild steel above.

The highest weight loss associated with anaerobic environment was due to high rate of diffusion of corrosion-inducing agents such as OH^- and SO_4^{2-} ions through the barrier oxide film, while in aerobic environment the rate of diffusion of these corrosion-inducing ions is slow.

The presence of SO_4^{2-} ion which is reduced by SRB to produce H_2S, ferrous sulphide and other corrosion products is illustrated in the equations below:

Electrolytic dissolution of water $8H_2O = 8OH^- + 8H^+$ --- (4.1.2)

Anodic reaction $4Fe = 4Fe^{2+} + 8e^-$ ---- (4.1.3)

Cathodic Reaction $8H^+ + 8e^- = 8H$ ---- (4.1.4)

Cathodic Deplorization by Bacteria $SO_4^{2-} + 8H = S^{2-} = 4H_2O$ ---- (4.1.5)

Corrosion Product $Fe^{2+} + S^{2-} = FeS$ ----- (4.1.6)

Corrosion Product $3Fe^{2+} + 6OH^- = 3Fe(OH)_2$ ---(4.1.7)

Overall Reaction becomes

$4Fe + SO_4^{2-} + 4H_2O = FeS + 3Fe(OH)_2 + 2(OH)^-$ --- (4.1.8)

The corrosion products such as Fes and $3Fe(OH)_2$ do not protect layer as stated earlier hence continuation in the corrosion process.

4.2.2 CORROSION RATE MEASURMENT

(i) Weight Loss Method:

The corrosion rate was highest in mild steel, followed by medium carbon steel. It was generally observed in Figure 4.2 that corrosion rate decreases with exposure times in all the environments. This experimentally observed behaviour was due to the formation of an impermeable protective oxide film on the surface of the steel. In this state, the steel is said to be passive, (Borode and Okpala, 1996; Ovri, 1998) and does not corrode easily.

Mild steel corroded more than medium carbon steel in the first 28th days due to high rate of depassivation and diffusion of corrosion inducing agents such as OH^- and SO_4^{2-} , while after 28th days the aggressive ions in the various environments could not be absorbed by the protective oxide film, hence the decrease in the corrosion rate with higher exposure times for all the environments studied.

(ii) Electro-Chemical Method:

The plot of the electrode potentials with exposure times of the steel coupons in all the environments investigated is given in Figure 4.2. It was observed that the electrode potential of the steel exposed to all the environments decreased with time during the first 28th days of the test and later increased till the end of the experiment. The electrode potential (voltage) decreased as resistance increased due to corrosion product formed on the steel surface (Ovri, 1998). Hence, the lower the potential, the more the corrosion.

Mild steel in anaerobic environment recorded highest decrease in electrode potential in the first 28th days of the test. It had initial potential of -0.47(mV) in the first day and -0.93(mV) in the 28th days. This decrease in electrode potential shows increase in corrosion rate and weight loss. However, a sharp increase in electrode potential occurred from the 35th to 42nd days (-0.86mV to -0.85mV), showing a decrease in corrosion rate. This effect is similar to all results obtained for mild steel in aerobic environment and the control.

Medium carbon steel in anaerobic environment was next after mild steel. It had -0.66(mV) in the first day and -0.91(mV) in the 28th day which is an indication of increase in corrosion rate. However, the electrode potential increased from -0.83mV to -0.82mV in the 35th to 42nd days respectively, showing decrease in corrosion rate and weight loss. This effect is similar to all results obtained for medium carbon steels in aerobic environment and the control.

The observed increase in electrode potential after 28 days of the test was attributed to the concept of passivity. This was caused by the formation of protective oxide film on the surface of the steels. Due to chemical, physical and electronic properties of these oxide films, metal dissolution is lowered resulting to the decrease in corrosion rate. The mild steel in anaerobic environment exhibited lowest electrode potential (highest negative potentials) indicating both high weight losses and corrosion rate, followed by aerobic and control respectively.

The results are in agreement with those reported by Owate, Osarolube, and Oforka, (2008) for the corrosion of mild and high carbon steels.

(iii) The pH

The pH decreased in the first 28th days indicating high corrosion rate and weight loss. It could be seen in Figure 4.6 that weight loss increased as the p.H is decreased (lowered) making the environment more acidic and consequently more corrosive. However, between the 35th and 42nd days, the pH increased. This is due to the presence of protective oxide film that passivate the steel surface. The passivity of steel is reduced as the pH is increased (Ovri 1998).

CHAPTER FIVE

5.0 CONCLUSION AND RECOMANDATIONS

5.1 CONCLUSION

The following conclusion can be drawn from this investigation:

(1) Mild steel was observed to be more corrosive in the entire environments (6.43×10^{-4} mpy). This is due to high rate of depassivation and diffusion by corrosion inducing agents such as OH^- and SO_4^{2-} through the oxide film. This was followed by medium carbon steel (5.30×10^{-4} mpy) with low rate of depassivation and diffusion of the corrosion agents.

(2) General (uniform) corrosion was observed for mild and medium carbon steels in the entire environments investigated.

(3) The passivity of the steels is reduced as the pH is lowered.

(4) It has been shown that corrosion rate tends to decrease with increasing carbon content.

(5) Based on these results, medium carbon steel is suggested for use in oil industries when the environment contains SRB.

5.2 RECOMMENDATIONS

For the past centuries, science, technology and engineering process are dynamic, the following variables are recommended for further study.

(1) Temperature is an important variable in corrosion studies. It is therefore suggested that periodic temperature measurement of the entire environment be carried out for further studies.

(2) Further investigation using more steels of variable chemical compositions would be useful.

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APPENDIX A

The total surface area (A) of the rectangular steel coupons used in the investigation was calculated using the following relationship.

$A = 2[LW + LH + WH] - 2(\pi d^2/4)$

Where, A = Total surface area of coupons (cm^2)

L = Length (cm) = 7.30cm

W = Width (cm) = 2.20cm

H = Thickness = 0.5cm

D = Diameter of holes (cm) = 0.7cm

$A = 2[7.3 \times 2.2 + 7.3 \times 0.5 + 2.2 \times 0.5]$

$- (3.142 \times (0.7)^2/4)$

$= 2[16.06 + 3.65 + 1.10] - 2(0.385)$

= 40.85cm2

The corrosion rate (CR) is calculated using the relationship.

C.R = 534W/DAT

W = Weight loss (g)

D = Density of metal (g/cm^3)

A = Total surface area of coupons (cm^2)

T = Exposure Time (hrs)

C.R (Control 7days mcs) = $534 \times 0.030/7.87 \times 40.85 \times 168$

$= 16.02/54010.24$

$= 2.94\times10^{-4}$mpy

C.R (Control 7 days ms) = $534 \times 0.042/7.87 \times 40.85 \times 168$

$= 4.15 \times 10^{-4}$mpy.