PINEAPPLE *(ANANAS COMOSUS L.)* PEELS AS CORROSION INHIBITOR FOR CARBON STEEL IN HYDROCHLORIC ACID SOLUTION

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ABSTRACT

Corrosion in steel has been identified as one of the major problem in chemical industry which responsible for substantive plant shutdown that contributes to high maintenance costs especially in pipelines system. In addition contamination of products and process streams, and external corrosion leaks due to internal corrosion failures can create unfortunate safety, manpower and environmental jeopardy. In order to overcome this problem, certain techniques have been applied and one of the most practical ways is using inhibitor to protect metals against corrosive environment. Commercial and synthetic inhibitors are commonly used and have been proved to be effective in inhibiting corrosive attack on metal but most of these inhibitors are toxic and expensive thus become major setback. To alleviate this issues, researcher were focused on eco – friendly corrosion inhibitor using natural and biodegradable compound which is effective, low cost and low environmental impact. Pineapple peels is cheap abundant resource in Malaysia, and hence this work presents corrosion inhibitor studies using pineapple (*Ananas comosus L.*) peels extract. Corrosion rates were determined using weight loss method for three parameters; concentration of inhibitor, acid concentration and exposure time. Pineapple peels extract was analysed by Gas Chromatography-Mass Spectrometer to determine the chemical composition in the extracts which has the inhibition functions. The extract proved to contains oleic acid and octadenoic acid which have carbonyl group and double bonds. These characteristics mostly found in plant extract which can inhibit corrosion. The weight loss method was conducted according to the standard provided by ASTM. The corrosion rate of steel was found to be dependent on acid concentration and also extract concentration. Another factor is exposure time which contributes to the value of corrosion rate. Results from this work may be useful to study the efficiency of this inhibitor using more parameters as this will become alternative for commercial inhibitor.

Key words: corrosion inhibitor, pineapple peels, weight loss, GCMS

ABSTRAK

Kakisan pada keluli telah dikenalpasti sebagai salah satu masalah utama dalam industri kimia yang bertanggungjawab untuk penutupan loji - loji yang menyumbang kepada kos penyelenggaran yang tinggi terutamanya dalam sistem talian paip. Selain itu pencemaran produk dan proses aliran serta kebocoran kakisan luar kerana hakisan dalaman merbahaya kepada tenaga manusia dan alam sekitar. Untuk mengatasi masalah ini, teknik-teknik tertentu telah digunakan dan salah satu cara yang paling praktikal ialah menggunakan perencat untuk melindungi logam daripada persekitaran mengakis. Perencat komersil dan sintetik yang biasa digunakan telah terbukti berkesan dalam menghalang hakisan logam namun kebanyakan perencat ini bersifat toksik dan mahal menjadikan ia salah satu masalah utama. Untuk mengatasi masalah ini, penyelidik telah memfokuskan kajian terhadap perencat mesra alam yang menggunakan sumber alam dan terbiodegradasi, yang berkesan, murah dan tidak berbahaya kepada alam sekitar. Kulit Nanas adalah sumber banyak dan murah di Malaysia, dan dengan itu kajian ini membentangkan tentang perencat kakisan daripada ekstrak kulit Nenas (Ananas comosus L.). Kadar kakisan ditentukan menggunakan kaedah kehilangan berat berdasarkan tiga pembolehubah; kepekatan perencat, kepekatan asid dan masa. Ekstrak kulit nenas dianalisis menggunakan *Gas Chromatography- Mass Spectrometry* untuk menentukan komposisi kimia dalam ekstrak yang berfungsi untuk merencat kakisan. Ekstrak kulit nenas terbukti mengandungi asid oleik dan asid octadenoic yang mempunyai kumpulan carbonyl dan ikatan berganda. Ciri-ciri ini kebanyakannya ditemui di ekstrak tumbuhan yang boleh menghalang hakisan. Kaedah kehilangan berat telah dijalankan mengikut piawaian yang disediakan oleh ASTM. Kadar kakisan keluli didapati bergantung pada kepekatan asid, kepekatan perencat dan masa pendedahan. Hasil dari kerja-kerja ini mungkin berguna untuk mengkaji keberkesanan perencat dengan berpandukan kepada pembolehubah – pembolehubah yang lain sebagai alternative kepada perencat sedia ada.

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LIST OF ABBREVIATIONS

A	cross-sectional area of the sample of eq. (3.1)
D	density in g/cm^3 eq. (3.1)
K	corrosion constant in mm/yr. of eq. (3.1)
T	time of exposure in hour eq. (3.1)
W	mass loss in grams eq. (3.1)
W_o	initial weight in grams eq. (3.1)
W_a	final weight in grams eq. (3.1)

Subscripts

a	after
o	initial

LIST OF ABBREVIATIONS

ASTM	American Standard for Testing Material
DSCLE	*Dendrocalmus sinicus Chia et* J.L Sun
DPC	Diphenylcarbonzone
GCMS	Gas Chromatography- Mass Spectrometry
MBT	Mercaptobenzotriazole
PGB	Petronas Gas Berhad
PGU	Peninsular Gas Utilization
TOD	Transmission Operating Division

1 INTRODUCTION

1.1 Motivation and statement of problem

Pipeline is the major medium in transportation of liquid, gas, water and other substances between regions or countries. According to the Field-Listing of the World Factbook statistical calculation until 2010, there are over 1 million kilometers of pipeline transporting oil, gas, crude oil, water and other substances across the world. This number expected to be increasing through another years ahead as pipelines systems are the most efficient transportation to supply substances or product from one plant to another and have been used in various kinds of industries such as water treatment, oil and gas, chemical or even some of the electrical industries used pipeline to secure their cable under the ground. But the biggest usage was to transport oil, gas and also water.

The Peninsular Gas Utilization (PGU) project which had been completed in 1998 is one of the most extensive natural gas pipeline networks in Asia. PGU systems can transport the capacity of 2 billion cubic feet per day (Bcf/d) of natural gas (Energy Information Administration, 2011). Currently, Malaysia has over 2,554 km of high pressure gas pipeline across the country that has been buried in several types of soil environments for many years. This pipeline was monitoring by one of the PETRONAS Gas Berhad (PGB) operating division that is Transmission Operating Division (TOD) for over 24 years and had shown the great achievement in pipeline safety (Nazmi, 2008). The TOD need to ensure that the transmission of the gas reached the certain place safely as natural gas is one of the major energy source that been used to generate electricity in Malaysia. The condition of the pipeline and its railways must always been inspected to ensure the pipelines do not have any leaks or ruptures.

Most of the chemical industry use carbon steels for the pipelines materials because of the high availability of carbon. One major problem for pipelines system is corrosion of metallic materials in acidic medium and the high risk of corrosion attacks on pipeline become more serious as the pipelines were used for decade to transporting the chemical, liquid or gas. Pipelines that was buried underground transport whether crude oil, gas or water will facing various environment such seawater (offshore) and soil (onshore) that may lead into the corrosion attack and finally leaking situation. The corrosion of pipelines will bring a lot of loss especially in maintenance cost.

In order to reduce the corrosion of metals, several techniques have been applied and of the most practical methods are using inhibitors. Inhibitors can be inorganic, organic or mixed material (Ebenso *et al.*, 2008) and (organic) commercial inhibitors have been proved as successful inhibitors but the usage of these inhibitors to control corrosion should be well considered based on several factors such as cost, availability, toxicity and environmental friendliness are very important. The interest of using of plant extract is greatly expanded because of the fact that they are cheap, readily available, ecologically friendly, biodegradable and renewable source of materials. The study of efficient and economical natural corrosion inhibitor is necessary to avoid more losses and hazardous effect to the environment and for this project, pineapple peel (wastes) is chosen as natural inhibitors.

Pineapple (*Ananas comosus* L. Merr) is a member of the Bromeliaceae family (monocotyledons) and comprises about 2000 species with an annual worldwide production of over 14 million tons; it is eighth most abundantly produced fruit in the world (Brat *et al.*, 2004). It is grown rapidly in Hawaii, Philipines, Caribbean area, Malaysia, Taiwan, Thailand, Australia, Mexico, Kenya, South Africa and Hainan province of China (Xie *et al.*, 2006). Previous study on inhibition of aluminium corrosion in 0.1 M HCl solution using pineapple leaves extract by Ating *et al.*, 2009 showed that the plant extract is an effective inhibitor with the highest inhibition efficiency of 96.09% obtained at extracts concentration 0.5g/L at 60°C.

There are many corrosion inhibitors that have been proven effectively retarded the corrosion mechanism and mostly the inhibitors are organic compounds. But, according to (Raja and Suthuraman, 2008) most of these compounds are not only expensive but also toxic to living beings and the study of efficient and economical plant extract corrosion inhibitor is necessary to avoid more losses and hazardous effect to the environment. For this project, pineapple peel (wastes) is chosen as a material for corrosion inhibitor due to these facts:

1.1.1 The Availability of Pineapple Peels in Malaysia and Cost

In Malaysia, pineapple peels become the major waste in pineapple canning industry (Hajar *et al.*, 2012) and the abundant of this fruit peels can provide a very high availability for this project. The cost to prepare the material for this project can be minimized due to the availability of pineapple peels which exist as wastes.

1.1.2 Toxicity and Environmental Impact

Pineapple peels are considered as agricultural waste which is a renewable resource of great variety of biotechnological potential and should be non - toxic, abundant, totally biodegradable, non – exotic, and cheap (Dhanassekaran *et al.*, 2011). Pineapple waste might have a potential for recycling to get raw material or for conversion into useful product of higher value added products, or even as raw material for other industries. Pineapple wastes which is not utilized and is discharged as wastage can cause disposal problems and maybe harmful to the environment. This project will have to reduce the environmental pollution by recycling the wastes.

1.1.3 Natural inhibitors as the Replacement for Synthetic Organic Inhibitors

The use of plant extract as inhibitor has continued to receive attention as replacement for synthetic organic inhibitors (Saleh *et al.*, 1983). The study is based on several factors such as cost, availability and the most important is the effect of the inhibitors to the environment. It is not yet known whether the pineapple peels can give higher inhibition efficiency compared to commercial inhibitors and hence this study conducted based on the research objective and scopes.

1.2 Objectives

The following are the objectives of this research:

- To study the inhibition effect of pineapple peels (*Ananas comosus*) on the corrosion mechanism of carbon steel in HCL solution by using weight loss method (ASTM G1 – 90, ASTM G1 – 72.)

1.3 Scope of this research

The following are the scope of this research:

i) Extraction of inhibitor and GCMS analysis

ii) Corrosion rate will be determined by weight loss method

iii) Influence of parameters to the inhibitor performance; inhibitor concentration, acid concentration and exposure time

1.4 Main contribution of this work

The following are the contributions:

i) To identify the methods for inhibitor extraction and GCMS analysis for chemical constituents present in the extract.

ii) The methods and analysis may assist another further study using pineapples or any others plant extracts.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides the information of the corrosion type and mechanism. A general description on the prevention method for corrosion, inhibitors types and organic inhibitors are also presented. A summary of previous experimental work related to corrosion inhibitor using plants extracts is also being discussed.

Chapter 3 gives a review of the method approach applied for inhibitor extraction, chemical analysis of the inhibitor, and weight loss methods. The corrosion rates were compared in experimental data by three factors namely inhibitor concentration, acid concentration and exposure time. The results of experiments are presented and compared with previous study of natural inhibitors using plants extracts.

Chapter 4 discuss the results from experimental work where the inhibitor extraction and steel coupon preparations are done for weight loss method to calculate corrosion rate. Discussion and comparison of various analysis of corrosion rate based on three different parameters: inhibitor concentration, acid concentration and exposure time are also presented.

Chapter 5 draws together a summary of the thesis and outlines the future work which might be used from the analysis of inhibitor performance using pineapple peels.

2 LITERATURE REVIEW

2.1 *Introduction*

This paper presents the information of the corrosion type and mechanism, prevention method for corrosion, and past research related to natural corrosion inhibitor using plants material. Besides that, this chapter will include the past research on corrosion inhibitor using pineapple.

2.2 *Corrosion Mechanism*

2.2.1 *Basic principle of corrosion*

Basically, people are familiar with corrosion in the form of physical destruction that can be seen such as rusting of fence, corroded pipe valves, rusting on automotive body panels, exhaust components, etc. Corrosion is a natural process and defined as the deterioration and unintentional attack of metal by electrochemical reactions with its environment and ordinarily begins at the surface. Electrochemical is a chemical reaction in which there is electrons transfer from one chemical molecule to another.

When metallic surface exposed to an aqueous electrolyte usually possesses sites for an oxidation (anodic reaction) where metal atoms characteristically lose or give up electrons (oxidation) at less stable sites and a reduction (cathode reaction) that consumes the electrons produced by the anodic reaction (Adeloju, 1993), the anodic and cathode reaction together make up a corrosion cell. The anodic reaction is the dissolution of the metal atoms to the metal ions. These ions form either soluble ionic products or an insoluble compound of the metal, usually an oxide for example; the hypothetical metal M that has n valence electrons may experience oxidation according to the reaction:

$$\mathrm{M} \rightarrow \mathrm{M}^{n+} + ne^-$$

which M becomes an n+ positively charged ion and in the process loses its valence electrons; *e-* is used to symbolize an electron. Examples in which metals oxidize are

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

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

The common corresponding cathode reactions involved in corrosion process, at the cathode sites at the metal/solution interface are:

(1) Reduction in neutral or basic solution containing dissolved oxygen;

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

(2) Reduction reaction in acid solution containing dissolved oxygen;

$$O_2 + 4H^+ + 4e^- \rightarrow 2H2O$$

(3) Reduction of hydrogen ions in acidic solution;

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

2.3 Prevention Methods for Corrosion

In most industrial situations, it is very impossible to "prevent" corrosion because this mechanism occur naturally (Jones, 1996). The general startegy is to use method that can reduce the corrosion rate to an economically sustainable level. The most important corrosion preventantion prcedures are as follows:

2.3.1 Selection of Materials and Design

The selection of materials for the working environment is based on mechanical and physical properties, availability, method of fabrication and overall cost of component or structure. It must be decided whether or not an expensive corrosion – resistant alloy is more economical than a cheaper metal that requires protection or possible periodic replacement (Shreir, 1974).

2.3.2 Changing Interfacial Potential

The metal will be protected cthodically by making interfacial (metal/solution) potential sufficiently negative by means of either (i) sacrificial anode or (ii) impressed current, i.e by cathodic protection (Jones, 1996). The other way is protecting metal by making interfacial potential sufficiently positive to cause passivation (formation of a protective film on the metal).

2.3.3 Protective Coatings

In this method, the metal reaction products is formed, e.g., anodic oxide films on Al, phosphate coatings on steel, chromate films on light metals (Zn, Al, Cd). The metallic coatings that form protective barriers (Ni, Cr) is generated or protect the substrate by sacrifical action (Zn, Al, Cd on steel) (Shreir, 1974). Another way is to use inorganic glasses and ceramics or organic coatings such as paint, plastic and greases.

2.3.4 Changing the Environment

For aqueous corrosion, the environment is change to be less aggressive by removing constituents or modifying conditions that facilitate corrosion such as decreasing the temperature, velocity and also preventing the access of water and moisture (Shreir, 1974). For atmospheric corrosion, the air is de - humidify and the solid particles is removed.

2.3.5 Corrosion Inhibitor

Corrosion inhibition means the reduction of the corrosion rate of metal by the addition of a chemical compound to the solution in contact with the metal (Uhlig and Winston, 1985). In general, an inhibitor forms a protective film by reaction with the corroding surface. As a result, the rate of anodic and/ or cathode corrosion reactions are retarded (Sadtri, 1998). Normally, only a small quantity of the inhibiting compound is needed to be effective.

Corrosion inhibition is reversible and a minimum concentration of the inhibiting compound is required to maintain the inhibiting surface film. Over the years many compounds have been tested and efficiently used as corrosion inhibitors for different materials and different environments. However the recently increasing concern toward environmental and health consideration is likely to restrict inhibitor choices. Many effective inhibitors such as chromate and nitrites will eventually abandoned due to the new regulations. Thus there is a need for testing and developing corrosion inhibitors that are effective and in addition being environmentally accepted. Because of the limited range of inorganic compounds, organic ones are most likely to meet those requirements.

2.4 *Corrosion Inhibitors*

2.4.1 *Introduction*

The use of chemical inhibitors to decrease the rate of corrosion processes is quite varied. In the oil extraction and processing industries, inhibitors have always been considered to be the first line of defence against corrosion. A great number of scientific studies have been devoted to the subject of corrosion inhibitors. However, most of what is known has grown from trial and error experiments, both in the laboratories and in the field. Rules, equations, and theories to guide inhibitor development or use are very limited. By definition, a corrosion inhibitor is a chemical substance that, when added in small concentration to an environment, effectively decreases the corrosion rate (Stern, 1958). The efficiency of an inhibitor can be expressed by a measure of this improvement:

$$\text{Inhibitor efficiency (\%)} = \frac{(CRuninhibited - CRinhibited)}{CRuninhibited} \, x \, 100$$

where $CR_{\text{uninhibited}}$ = corrosion rate of the uninhibited system
$CR_{\text{inhibited}}$ = corrosion rate of the inhibited system

In general, the efficiency of an inhibitor increases with an increase in inhibitor concentration (e.g., a typically good inhibitor would give 95% inhibition at a concentration of 0.008% and 90% at a concentration of 0.004%). The selection of inhibitors type would be based on factors; cost, toxicity, availability, and environmental friendliness.

2.4.2 Classifications of Inhibitors

Inhibitors are chemicals that react with a metallic surface, or the environment this surface is exposed to, giving the surface a certain level of protection. Inhibitors often work by adsorbing themselves on the metallic surface, protecting the metallic surface by forming a film. Inhibitors are normally distributed from a solution or dispersion. Some are included in a protective coating formulation. Inhibitors slow corrosion processes by:

i. Increasing the anodic or cathode polarization behaviour
ii. Reducing the movement or diffusion of ions to the metallic surface
iii. Increasing the electrical resistance of the metallic surface

Inhibitors have been classified differently by various authors. Some authors prefer to group inhibitors by their chemical functionality, as follows (Jones, 1988):

i. *Inorganic inhibitors.* Usually crystalline salts such as sodium chromate, phosphate, or molybdate. Only the negative anions of these compounds are involved in reducing metal corrosion. When zinc is used instead of sodium, the zinc cation can add some beneficial effect. These zinc-added compounds are called mixed-charge inhibitors.

ii. *Organic anionic.* Sodium sulfonates, phosphonates, or mercaptobenzotriazole (MBT) are used commonly in cooling waters and antifreeze solutions.

iii. *Organic cationic.* In their concentrated forms, these are either liquids or wax like solids. Their active portions are generally large aliphatic or aromatic compounds with positively charged amine groups.

However, by far the most popular organization scheme consists of regrouping corrosion inhibitors in a functionality scheme as follows (Hackerman, 1984).

Table 2-1: Corrosive system and inhibitor

SYSTEM	INHIBITOR	METALS	CONCENTRATION
	Acids		
HCL	Ethylaniline	Fe	0.5%
	MBT*	..	1%
	Pyridine + phenylhydrazine	..	0.5% + 0.5%
	Rosin amine + ethylene oxide	..	0.2%
H_2SO_4	Phenylacridine	..	0.5%
H_3PO_4	NaI	..	200 ppm
Others	Thiourea	..	1%
	Sulfonated castor oil	..	0.5-1.0%
	As_2O_3	..	0.5%
	Na_3AsO_4	..	0.5%
	Water		
Potable	$Ca(HCO_3)_2$	Steel, cast iron	10 ppm
	Polyphosphate	Fe, Zn, Cu, Al	5 -10 ppm
	$Ca(OH)_2$	Fe, Zn, Cu	10 ppm
	Na_2SiO_3	..	10 – 20 ppm
Cooling	$Ca(HCO_3)_2$	Fe, Zn, Cu	10 ppm
	Na_2CrO_4	..	0.1%
	NaH_2PO_4	Fe	0.05%
	NaH_2PO_4	..	1%
	Morpholine	..	0.2%
Boilers	NaH_2PO_4	Fe, Zn, Cu	10 ppm
	Polyphosphate	..	10 ppm
	Morpholine	Fe	Variable
	Hydrazine	..	O2 scavenger
	Ammonia	..	Neutralizer
	Octadecaylamine	..	Variable
Engine coolants	Na_2CrO_4	Fe, Pb, Cu, Zn	0.1-1%
	$NaNO_2$	Fe	0.1-1%
	Borax	..	1%
Glycol/water	Borax + MBT*	All	1% +0.1%
Oil field brines	Na_2SiO_3	Fe	0.01%
	Quaternaries	..	10-25 ppm
	Imidazoline	..	10-25 ppm
Seawater	Na_2SiO_3	Zn	10 ppm
	$NaNO_2$	Fe	0.5%
	$Ca(HCO_3)_2$	All	pH dependent
	NaH_2PO_4 + $NaNO_2$	Fe	10 ppm + 0.5%

*MBT = Mercaptobenzotriazole.

2.4.3 *Corrosion Inhibition Mechanism*

The majority of inhibitor applications for aqueous, or partly aqueous, systems are concerned with four main types of environment (Huger, 1960):

i. Aqueous solutions of acids as used in metal-cleaning processes such as pickling for the removal of rust or mill scale during the production and fabrication of metals or in the post service cleaning of metal surfaces

ii. Natural waters, supply waters, and industrial cooling waters in the near-neutral pH range (5 to 9)

iii. Primary and secondary production of oil and subsequent refining and transport processes

iv. Atmospheric or gaseous corrosion in confined environments, during transport, storage, or any other confined operation

The following sections describe corrosion mechanisms in terms of these four main environments:

2.4.3.1 *Inhibitors for Acid Solutions*

The corrosion of metals in acid solutions can be inhibited by a wide range of substances, such as halide ions, carbon monoxide, and many organic compounds, particularly those containing elements of Groups V and VI of the Periodic Table (i.e., nitrogen, phosphorus, arsenic, oxygen, sulphur, and selenium). Organic compounds containing multiple bonds, especially triple bonds, are effective inhibitors. The primary step in the action of inhibitors in acid solutions is generally agreed to be adsorption onto the metal surface, which is usually oxide-free in acid solutions. The adsorbed inhibitor then acts to retard the cathode and/or anodic electrochemical corrosion processes.

Inhibitors of corrosion in acid solution can interact with metals and affect the corrosion reaction in a number of ways, some of which may occur simultaneously. It is often not possible to assign a single general mechanism of action to an inhibitor because the mechanism may change with experimental conditions. Thus, the predominant mechanism of action of an inhibitor may vary with factors such as its concentration, the pH of the acid, the nature of the anion of the acid, the presence of other species in the solution, the extent of reaction to form secondary inhibitors, and the nature of the metal. The mechanism of action of inhibitors with the same functional group may additionally vary with factors such as the effect of the molecular structure on the electron density of the functional group and the size of the hydrocarbon portion of the molecule (Mercer *et al.*, 1994).

2.4.3.2 Inhibitors in near– neutral Solution

Corrosion of metals in neutral solutions differs from that in acid solutions in two important respects. In air-saturated solutions, the main cathode reaction in neutral solutions is the reduction of dissolved oxygen, whereas in acid solution it is hydrogen evolution. Corroding metal surfaces in acid solution are oxide-free, whereas in neutral solutions metal surfaces are covered with films of oxides, hydroxides, or salts, owing to the reduced solubility of these species (Thomas *et al.*, 1994). Because of these differences, substances that inhibit corrosion in acid solution by adsorption on oxide-free surfaces do not generally inhibit corrosion in neutral solution.

Typical inhibitors for near-neutral solutions are the anions of weak acids, some of the most important in practice being chromate, nitrite, benzoate, silicate, phosphate, and borate. Passivating oxide films on metals offer high resistance to the diffusion of metal ions, and the anodic reaction of metal dissolution is inhibited. These inhibitive anions are often referred to as anodic inhibitors, and they are more generally used than cathode inhibitors to inhibit the corrosion of iron, zinc, aluminium, copper, and their alloys in near-neutral solutions. The action of inhibitive anions on the corrosion of metals in near-neutral solution involves the following important functions:

i. Reduction of the dissolution rate of the passivating oxide film

ii. Repair of the oxide film by promotion of the reformation of oxide

iii. Repair of the oxide film by plugging pores with insoluble compounds

iv. Prevention of the adsorption of aggressive anions

2.4.3.3 Inhibitors for Oil and Gas Systems

Even in early days, oil producers applied numerous chemical compounds, sometimes with success, to minimize corrosion damage in the oil wells themselves and in surface handling equipment. Once amines and imidazolines came into use, corrosion inhibition in oil wells became dramatically more effective. Modern inhibitors are applied in the field, continuously or by periodic batch, at concentrations of 15 to inhibitor chemistry is available today for combating oil-field corrosion than existed only a decade ago (French, 1993). In recent years, organic molecules containing sulphur, phosphorus, and nitrogen in various combinations have been developed. These inhibitor types have extended the performance of oil-field inhibitors, particularly in the directions of being tolerant of oxygen contamination and of controlling corrosion associated with high CO_2, low H_2S conditions (French, 1993).

Most of the inhibitors currently used in producing wells are organic nitrogenous compounds. The basic types have long-chain hydrocarbons (usually C18) as a part of the structure. Most inhibitors in successful use today are either based on the long-chain aliphatic diamine or on long carbon chain imidazolines. Various modifications of these structures have been made to change the physical properties of the material (e.g., ethylene oxide is commonly reacted with these compounds in various molecular percentages to give polyoxy-ethylene derivatives that have varying degrees of brine dispersibility). Many carboxylic acids are used to make salts of these amines or imidazolines. Inhibitors in general petroleum production can be classified as follows (Lahodny-Sarc, 1994):

i. Amides/imidazolines

ii. Salts of nitrogenous molecules with carboxylic acids

iii. Nitrogen quaternaries

iv. Polyoxyalkylated amines, amides, and imidazolines

v. Nitrogen heterocyclics and compounds containing P, S, O

2.4.3.4 Atmospheric and Gaseous Corrosion

VCIs represent a very economical and powerful tool in combating the atmospheric or gaseous corrosion damage done to metals and alloys. Volatile corrosion inhibition is based on conditioning of the environment with trace amounts of inhibitive material to achieve a protective effect (. A VCI compound, in addition to being volatile, is required to promote electrochemical effects such as change of the potential in the diffuse part of the double layer that controls the migration of components of the electrode reactions ((Fiaud, 1994). The first condition for good efficiency of a vapour phase inhibitor is its capability to reach the metallic surface to be protected. The second is that the rate of transfer of the molecule should not be too slow to prevent an initial attack of the metal surface by the aggressive environment before the inhibitor can act. These two conditions are related partly to the vapour pressure of the inhibitor, partly to the distance between the source(s) of the inhibitor and the metal surfaces, and partly to the accessibility of the surfaces.

The vapour pressure of a chemical compound will depend upon the structure of the crystal lattice and the character of the atomic bonds in the molecule. In this respect, organic components of the molecule will generally ensure its volatility. A convenient volatile inhibitor should not have too high a vapour pressure, because it will be lost as a result of the fact that enclosures are generally not airtight; protection will then drop. A convenient partial vapour pressure for efficient compounds will lie between 10^{-5} and 10^{-1} mm Hg (i.e., 10^{-3} to 10 Pa).