KINETICS AND THERMODYNAMICS OF CARBON STEEL CORROSION IN DIFFERENT TYPES OF SOIL SOLUTION

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For my beloved...

Mom and Dad - thanks for your support, understanding and concern. I will always love you.

Brothers and Sisters- thanks for your advice and support.

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Even thousand words could not express my gratitude...

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ABSTRACT

The fundamental cause of deterioration of buried pipeline is soil corrosion. Factors that influence soil corrosion includes soil type, moisture content, supply of oxygen, redox potential, pH value, soil resistivity, and microbial activity. This study investigated the effect of soil types on the corrosion of carbon steel. Three types of soil namely, laterite, yellow soil, and kaolin were taken as soil of interest. The corrosion rates of carbon steel in various types of soil solutions were studied by applying weight loss method in the temperature range of $30^{\circ}C - 90^{\circ}C$ for 1-5 days and electrochemical method based on Tafel polarization measurements. The results obtained from weight loss method and Tafel polarization measurement revealed that yellow soil has the highest corrosion rate. High corrosion rate is due to the low pH and high conductivity of yellow soil solution. The corrosion rates also increased with increasing temperature and decreased with increasing immersion time. Kinetic functions in terms of activation energy, E_a indicates that yellow soil solution has the lowest activation energy followed by laterite and kaolin which is 3.33 kJ mol⁻¹, 5.48 kJ mol⁻¹, and 8.82 kJ mol⁻¹ respectively. The positive value of heat of reaction, ΔH indicates that the process of interaction of chemical species in the solution of soil samples on the steel surface is endothermic. The negative value of entropy of reaction, ΔS implies that the system is less disorder and decrease in randomized motion. The positive values of Gibbs free energy, ΔG suggested that the corrosion reactions by chemical species in the soil solutions did not occur spontaneously. This investigation showed that the corrosion of laterite soil solution on carbon steel surface can be described as pitting corrosion which follows the Frumkin adsorption isotherm.

ABSTRAK

Punca utama berlakunya pengaratan paip bawah tanah ialah kakisan tanah. Faktor yang mempengaruhi kakisan tanah termasuk jenis tanah, kandungan kelembapan, bekalan oksigen, keupayaan redoks, nilai pH, kerintangan tanah, dan aktiviti mikrob. Kajian ini dijalankan untuk mengkaji kesan pelbagai jenis tanah terhadap kakisan keluli karbon. Tiga jenis tanah iaitu laterit, tanah kuning, dan kaolin telah dipilih. Kadar kakisan keluli karbon dalam pelbagai jenis larutan tanah telah dikaji dengan menggunakan kaedah kehilangan berat dalam julat suhu 30°C – 90°C untuk tempoh masa 1-5 hari dan kaedah elektrokimia berdasarkan pengukuran pengutuban Tafel. Keputusan yang diperolehi daripada kaedah kehilangan berat dan pengukuran pengutuban Tafel menunjukkan bahawa tanah kuning mempunyai kadar kakisan tertinggi. Kadar kakisan yang tinggi adalah disebabkan oleh nilai pH yang rendah dan kekonduksian larutan tanah kuning yang tinggi. Kadar kakisan juga meningkat dengan peningkatan suhu dan menurun dengan peningkatan masa rendaman. Fungsi kinetik dari segi tenaga pengaktifan, E_a menunjukkan bahawa larutan tanah kuning mempunyai tenaga pengaktifan terendah diikuti oleh laterit dan kaolin iaitu 3.33 kJ mol⁻¹, 5.48 kJ mol⁻¹, dan 8.82 kJ mol⁻¹ masing-masing. Nilai positif haba tindak balas, ΔH menunjukkan bahawa proses interaksi spesies kimia dalam larutan sampel tanah pada permukaan keluli adalah endotermik. Nilai negatif entropi tindak balas, ΔS menunjukkan bahawa sistem tersusun dan kerawakan sistem menurun. Nilai-nilai positif tenaga bebas Gibbs, ΔG mencadangkan bahawa kakisan oleh spesis kimia dalam larutan tanah tidak berlaku secara spontan. Kajian ini juga mendapati bahawa kakisan larutan tanah laterit di atas permukaan keluli karbon adalah jenis kakisan liang yang mematuhi isoterma penjerapan Frumkin.

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LIST OF SYMBOLS

А	-	Pre-exponential factor
А	-	Ampere
Al	-	Aluminium
Au	-	Gold
С	-	Carbon
Cl	-	Chlorine
Cr	-	Chromium
C_R	-	Corrosion rate
Ea	-	Activation energy
F	-	Fluorine
Fe	-	Iron
J	-	Joule
К	-	Potassium
K	-	Kelvin
L	-	Liter
Mg	-	Magnesium
0	-	Oxygen
R	-	Universal gas constant
R^2	-	Correlation coefficient
S	-	Surface area
S	-	Sulfur
Si	-	Silica
Т	-	Temperature
Ti	-	Titanium
V	-	Volt

cm	-	Centimeter
g	-	Gram
m	-	Meter
mL	-	Milliliter
mm	-	Millimeter
E_{corr}	-	Corrosion potential
K _{ads}	-	Equilibrium constant of the corrosion process
N	-	Avogadro's number
b_{a}	-	anodic
$b_{\rm c}$	-	cathodic
f	-	Factor of energetic in homogeneity
h	-	Plank constant
<i>i</i> _{corr}	-	Current density
t	-	Immersion period
Wo	-	Moisture content
%	-	Percent
ΔG	-	Gibbs free energy
ΔH	-	Heat of reaction
ΔS	-	Entropy of reaction
°C	-	Degree Celsius
θ	-	Surface coverage
Ω	-	Ohm

LIST OF ABBREVIATIONS

AC	-	Alternate Current
ASTM	-	American Society for Testing and Materials
EDX	-	Energy Dispersive X-ray Spectrometer
FESEM	-	Field Emission Scanning Electron Microscopy
GDS	-	Glow Discharge Spectrometer
GPES	-	General Purpose Electrochemical System
MIC	-	Microbiological Influenced Corrosion
PVC	-	Polyvinyl Chloride
SCE	-	Saturated Calomel Electrode
SEM	-	Scanning Electron Microscopy
SRB	-	Sulfate-reducing Bacteria
XRD	-	X-ray Diffraction
XRF	-	X-ray Fluorescence

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Corrosion can be defined in a number of ways but the chemical or electrochemical reaction of a metal or an alloy with its environment provides a reasonable explanation of the term corrosion. It is one of the common causes of metal deterioration, the other being the mechanical loss of the metal by erosion, and abrasion or wear. Sometimes there is a joint action of corrosion and erosion (Chandler, 1985). Corrosion and cracking on the external or internal surfaces of inservice pipes, tanks, or other industrial assets reduce the integrity of the material and potentially reduce the service life of the equipment. Defects may have various forms and may be initiated by one or more mechanisms potentially resulting in corrosion and cracking. These factors affect a wide range of materials in many industries including industrial, aerospace, pipeline, power generation, and marine (Ginzel and Kanters, 2002).

Many structures affected by soil corrosion around the world, such as crude oil, natural gas, and water mains pipelines. Pipelines are widely used as engineering structures for the transportation of fluid from one place to another. In many instances pipelines are placed underground, under runways, railways, and roadways (Ahammed and Melchers, 1997). The deterioration of buried pipeline is commonly caused by soil corrosion (Ismail and El-Shamy, 2009). Underground steel structures are designed to have a long working life. Continuous inspection and maintenance are required in order to secure the lifetime and reliability. Failure in underground structures can have severe consequences economically and environmentally (Li *et al.*, 2007). Therefore, corrosion prevention and control is a matter of options to fit in with the many other requirements to be taken into account by the design team.

Soil type, moisture content, supply of oxygen, redox potential, pH value, soil resistivity, and microbial activity are some factors that influence corrosion in soil (Rim-rukeh *et al.*, 2006). From engineering aspects, an increase in soil water content has a number of disadvantages such as swelling, shrinkage, and cohesion decreases which affected directly on the interaction of pipelines, causing deterioration of pipelines materials and also caused damage on the top soil due to the occurrence of general and localized corrosion which was present in different sites of steel structures (Ismail and El-Shamy, 2009).

Carbon steels are widely used as constructional material due to its excellent mechanical properties, high strength, low cost, and weldability (Abdallah *et al.* 2006). The response of carbon steel to soil corrosion depends primarily on the nature of the soil and other environmental factors, such as moisture and oxygen. These factors can lead to extreme variations on corrosion (Rim-rukeh *et al.*, 2006).

1.2 Problem Statement

Carbon steel is a common material for many industrial units because of its low cost and excellent mechanical properties. However carbon steel suffers severe attack in service particularly in oil and gas production systems. Although corrosion inhibitors are the most effective and flexible mean of corrosion control in oil and gas production systems, the selection and application of inhibitors are actually complicated because of variable corrosive environment in these systems. Corrosion occurred widely through all specific types of pipeline.

Corrosion in soil is the fundamental cause of the deterioration of metal structures in soil. Metal structures corrode in soil by complex electrochemical processes due to the presence of different types of electrolyte. Soils with high moisture content, high electrical conductivity, high acidity, and high dissolved salts will be most corrosive. Many industries tend to expose to various type of soil in Malaysia that can cause corrosion.

To date, there is no report in the literature regarding the effect of laterite, yellow soil and kaolin on the corrosion of carbon steels. On account of this reasons, the corrosion study of carbon steel in different types of soil was carried out by using weight loss and electrochemical method to measure the corrosion rate in terms of temperature and time.

1.3 Research Objectives

The objectives of this research are:

- 1. To study the kinetic and thermodynamic aspects of corrosion caused by different types of soil solutions.
- 2. To investigate the effects of temperature and immersion time on the corrosion rate of carbon steel in different types of soil solutions.

1.4 Scope of the Study

The scope of this study is to identify the kinetic and thermodynamic parameters on corrosion of carbon steel in three different types of soil solutions (laterite, yellow soil, kaolin). The measurement technique for corrosion rate has been studied using weight loss method and electrochemical method based on Tafel polarization measurements. The effect of temperature on the corrosion rate of carbon steel in soil solution was studied in the temperature range of 30°C-90°C for 1-5 days of immersion time. The effect of concentrations of soil solution on corrosion rate was focused on laterite at temperature 30°C for 3 days of immersion time. The kinetic and thermodynamic parameters are determined based on the Arrhenius based equation.

1.5 Significant of Research

Corrosion of metals is a serious problem related to material application. There are numerous factors that influence metal corrosion in soil such as the degree of oxidation, pH of the corrosion environment, soluble salts, and the water content of soil (Wang, 2009). These make the prediction of corrosion rates very complex. Hence, the study of kinetics and thermodynamics of the corrosion would give a better understanding of corrosion of carbon steel in particularly the soil solution samples studied.

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