TO STUDY THE CORROSION TENDENCY OF API X-70 IN BASE OIL ENVIRONMENTS

By

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Abstract

In this research work the corrosion tendency of different surfaces of API X-70 petroleum pipeline steel in Base oil emulsion and Base oil extract has been evaluated by Potentiodynamic Tafel scan. The results demonstrated that formation of an oily film on the surface of material decrease anodic dissolution of steel that ultimately increase polarization resistance. Corrosion rate in base oil extract was higher than oil/water emulsion due to the absence of oily film at ground and polished surfaces by promoting of oxygen reduction reactions at a limiting current density in Base oil extract which controlled corrosion phenomenon at ground surface with minor influence on polished steel surface. It was also revealed that the polished surface of X-70 has lower value of I_{corr} compared to rough surface in both Base oil extract and emulsion. Hence accelerated degradation of rough surface compared to polished surface in base oil will occur.

Key Words: - Corrosion; Potentiodynamic; Steel; Base oil; Polarization;

1. Introduction

Base oil is a lubrication grade oil that is produced initially from refining crude oil (mineral base oil) of hydrocarbons containing paraffins, naphthenes,(no or very little olefins), aromatics, unsaturated hydrocarbons, sulfur compounds and large varieties of other compounds. There are two major types of base oil depending upon their molecular structure and viscosity index (VI), Paraffinic and Napthenic .Paraffinic base oils have linear chain structure and viscosity index >95 whereas Napthenic base oils have branched chain structure and viscosity index 0-40. Paraffinic base oils are preferable as compared to Napthenic in lubrications due to its better Physico-chemical properties [1 – 2].

It is a matter of fact that the most reliable and effective way to transport oil and gas is to utilize a pipeline system. However, due to the effect of long term wear out and prevailing surrounding environments, the pipeline always be deformed and corroded. This may happen because along with the oil some amount of water and complex compounds such as carbonates, sulphides, etc also flow through the pipeline that may cause degradation and erosion of pipeline material. In other words we may say that erosion-corrosion of pipeline has occurred. During the transportation of Base oil within the refinery through pipeline some amount of water is also carried alongwith it. The compounds present in base oil and water ends up with the start of pipeline corrosion. This degradation of the pipeline material results in the leakage of pipe. Corrosion of pipewalls can either be internal or external. In this research work the internal corrosion of pipe line material has studied .It may occur due to the presence of carbon dioxide, hydrogen sulphide, microorganisms especially bacteria, high flow speed, deposition of solid particles, water hold up etc.

Many research studies have already been carried out on Oil/Gas pipeline corrosion. The principal objective of these studies was how to protect the valuable pipeline material and minimize losses which mainly occur due to the corrosion [3 – 4].

Carbon steels and High Strength Low Alloy (HSLA) steels are particularly susceptible to intense corrosion in CO_2 / H_2S environments [5].

The experimental study undertaken in this research work is "To study the corrosion tendency of API X-70 in Base Oil Environment". The focus of the work was to investigate the corrosion

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tendency of oil / gas pipeline material to corrode in Base oil environments such as extract and emulsion. Rate of corrosion may also be affected by changing the transportation rate of O_2 and reactants from the surface of material [6]. Other factors like time, temperature and pressure are also responsible of higher corrosion rate.

2. Experimental Work

2.1 Chemical Composition

The subject material in this research work is an in-service pipeline steel specimen of API X-70, under API 5L standard, regarding X-70 steel pipes as large diameters steel pipe. It mainly consists of Mn (1.234), P (0.015), Cr (0.027), Si (0.281), V (0.035) and small percentage of Ti, Ni and remaining amount of Fe.

2.2 Surface Preparation

The metallographic examination of API grade x-70 were carried out by cutting the specimens into 1 x 1 cm^2 dimensions and then cold mounted. Each specimen of X-70 was first ground by using emery papers of grit sizes 120, 220, 320, 400, 600 and 1000 respectively and then polished on billiard cloth by utilizing aluminum oxide as an abrasive to produce scratch-free and mirror-like surface.

Two types of surfaces were prepared for electrochemical testing. One type of surface was prepared by grinding the specimen up to 600 grit silicon carbide paper and the second type was prepared by grinding up to 1000 grit silicon carbide paper and polished to a mirror finish using one micrometer Alumina power. The SEM results of ground and polished surfaces are shown in figures 1 – 2.

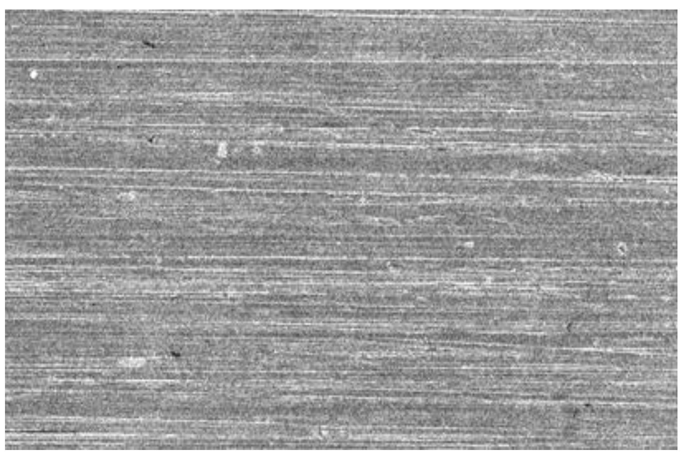

Figure 1: SEM result of rough surface of API X-70

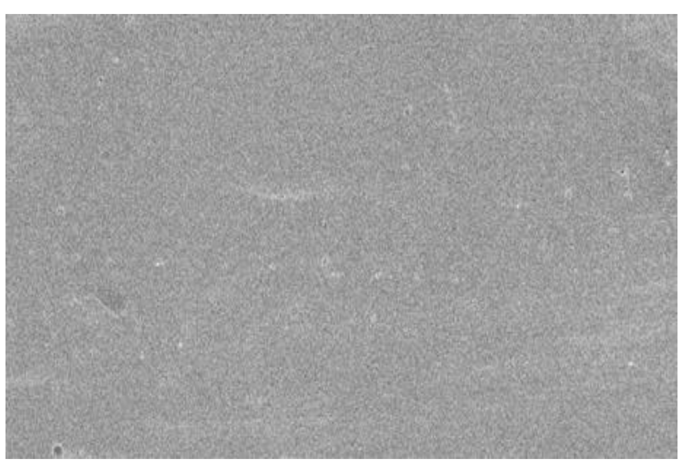

Figure 2: SEM result of polished surface of API X-70

2.3 Base Oil Characterization

The physico-chemical properties of Base oil, such as Kinematic viscosity (ASTM D 7042-04) [7], Density (ASTM 5002-99), and specific gravity (bottom flask method) were determined by standard ASTM methods. The viscosity and density were measured by pouring a sample in to the digital Automatic Analyzer Stabinger SVM 3000 Anton Paar. The subsequent analysis of base oil extract by Potentiometric titration measured NaCl (ASTM D 6470) that is described in (w/w) Percentage [8]. Amount of Sulphur content was measured according to Standard Test method for sulphur in petroleum and petroleum products by X-ray fluorescence spectrometry (Standard D 4294-08)[9]. The base oil characterization has shown in Table-1.

Table 1: Base Oil Characterization

Physical Properties	Result
Density	$0.841 g/cm^3$
Specific Gravity	0.812
Viscosity index	97
Kinematic Viscosity	0.0372 Strokes

2.4 Testing Environments

The test solutions were oil / water emulsion and crude oil extract. For the preparation of oil/water emulsion, a sample of base oil from National Oil Refinery Ltd, Pakistan was collected and used for the studies performed in this paper. The standard practice was followed for all of the procedure using one aliquot of the collected crude oil. The ratio of oil to water phases in oil / water emulsion was (15: 85). One fraction of the same base oil, with BSW equal to 15% V/V, was used to prepare emulsion by adding free water. The oil and water were emulsified in the presence of a surfactant (DSS) 1% (w/v) manually then continuous stirring was carried out so that a stable oil/water emulsion can be obtained. The sample rested for 24h to confirm the stability of the emulsion.

The base oil extract was prepared by mixing of tap water with base oil having ratio 3:1 in a separating funnel. The intermittent mixing of immiscible water-oil mixture for three hours was carried out and allowed to separate for 24 hours at room temperature. Thus, base oil extract was obtained and its chemical analysis is carried out in Laboratory that shows the increased amount of species like Cl, Ca, Mg, pH etc as compared to tap water. The elemental Analysis was also carried out according to standard ASTM methods that show the presence of sulphur, residue carbon and ash content in weight percent.

2.5 Electrochemical Testing

The electrochemical testing was carried out in a three electrode cell. It consists of saturated calomel electrode as reference electrode and graphite rod as counter electrode, whereas the X-70 steel sample acted as a working electrode. Epoxy embedded electrode were made to use as a working electrode. In this electrode electrical connection was made with soldering. A glass tube was used to accommodate the conducting wire. When metal specimen holding with glass tube was positioned, pour the epoxy on to the specimen. Epoxy was used with hardener and both of them were properly mixed before pouring. Approximately give 1- 2 hour for hardening. After the proper hardening of epoxy, grinding and polishing processes were done by following the standard metallurgical procedures. While grinding and polishing made an attempt to prepare flat and smooth surface for accurate corrosion studies. Prior to electrochemical measurements, the electrode was immersed in the test solution for 30 minutes until steady state corrosion potential was achieved. The values of potential and current versus time were measured until a stationary state condition was obtained. The experiments were conducted at 25^0C.

3. Results and Discussion

Potentiodynamic Tafel scan is a direct electrochemical measurement utilized for evaluating the corrosion performance. In this technique, corrosion current density and potential are extrapolated from the polarization profiles scanned across the cathodic and anodic regimes. Cell current is measured during a slow sweep of the potential. The sweep is from -250 to +250 mV relative to E_{oc}. With respect to the selected polarization ranges and potential scan rates, the characteristic performance of the tested API X-70 steel pipeline material is revealed in a typical environmental condition as an electrochemical fingerprint. Potentiodynamic Tafel scan can give a better understanding on the possible multi-step anodic dissolutions, from the variations in the potential / current slopes in the prepassivation ranges. Furthermore, it indicates the importance of the environmental conditions on the passivation from the potential ranges, anodic peaks and from the associated accelerated and/or decelerated current densities.

Complex ions present in base oil, dissolves in the multiphase pipeline flows at different extents, depending on temperature and pressure, producing the corrosive carbon carrying species. These species, besides the conventional salinity, also contain the weak carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), and carbonate (CO_3^{-2}) which drive the corrosion reactions in different fashions depending on their concentrations and on pH levels [Kermani, 2003].

From the variations of the corrosion potentials along with the decelerated corrosion current densities, it was found that oil can act as an anodic or a cathodic inhibitor with respect to temperature, and from the sudden acceleration in the anodic current densities at high overpotentials, important hints on the oil adsorption were revealed accordingly.

The graphical representation of Tafel scan curves for ground specimen of API X-70 both in base oil extract and emulsion, as well as of polished specimen in base oil extract and emulsion are shown in figure 3 – 6.

The results obtained from Tafel scan curve have shown in Table 2 – 3. It is inferred from these results that the corrosion rate of ground surface of X-70 steel is higher than the smooth surface. The reason is that the ground surface have more exposed surface area as compared to polished one .The oxidation tendency of ground surface is also more as compared to polished one .It has also apprehended from results that corrosion rate in base oil extract is also greater than base oil emulsion. The reason for this behavior is that base oil extract is more corrosive for API grade X-70 steel, due to the high concentration of chloride ion, carbonates present in extract and high oxidation potential of oxygen.

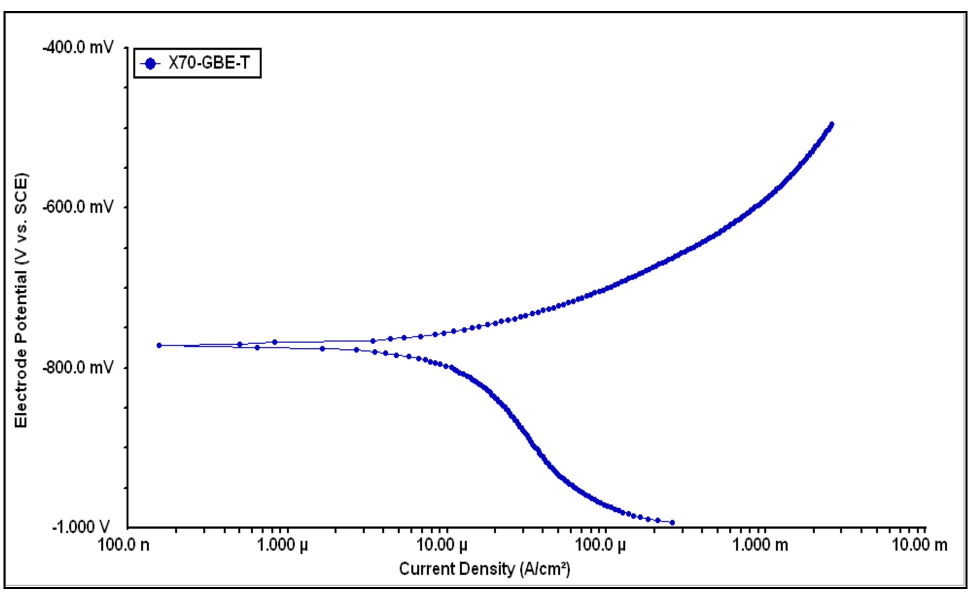

Figure 3 : Tafel Scan of API-X-70 (Ground Surface) in Base Oil Extract

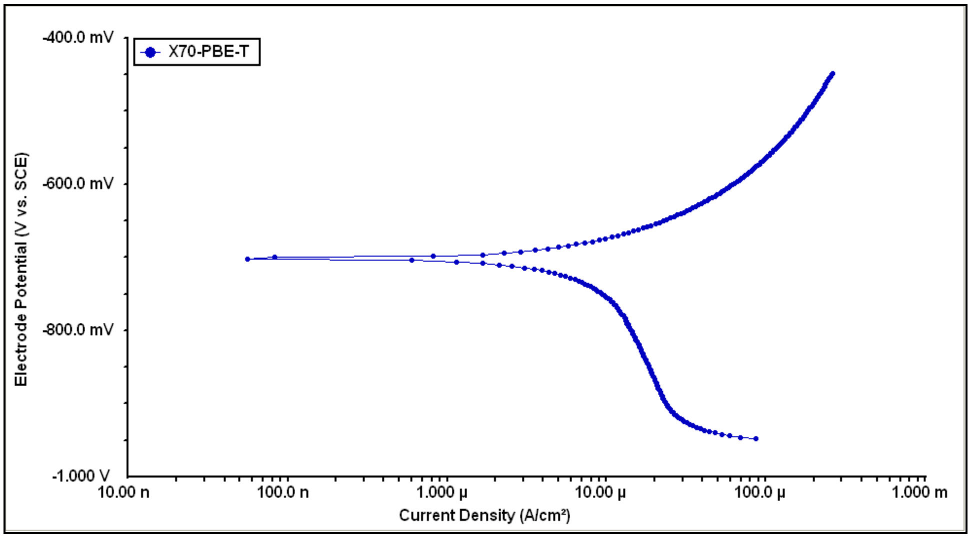

Figure 4: Tafel Scan of API-X-70 (Polished Surface) in Base Oil Extract

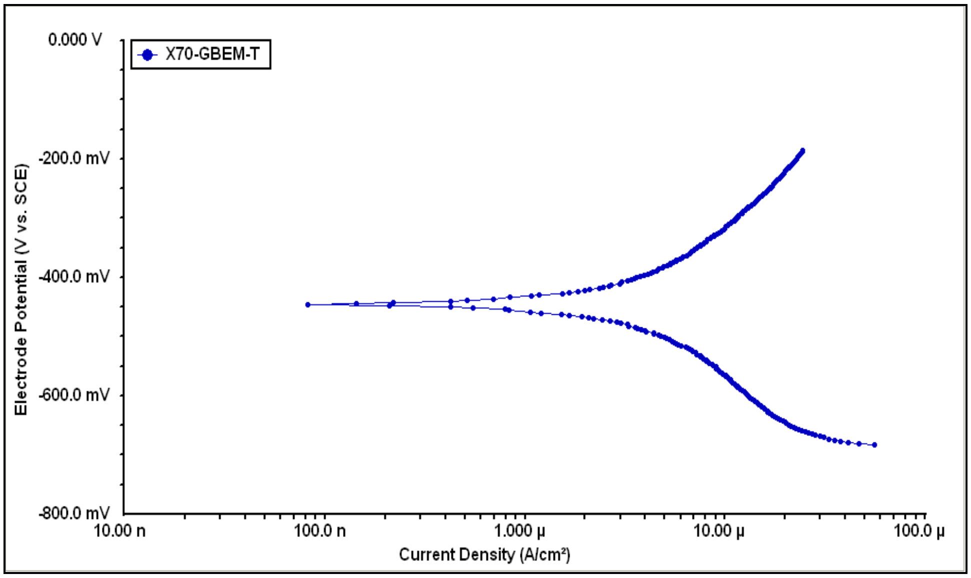

Figure 5: Tafel Scan of API-X-70 (Ground Surface) in Base Oil/Water Emulsion

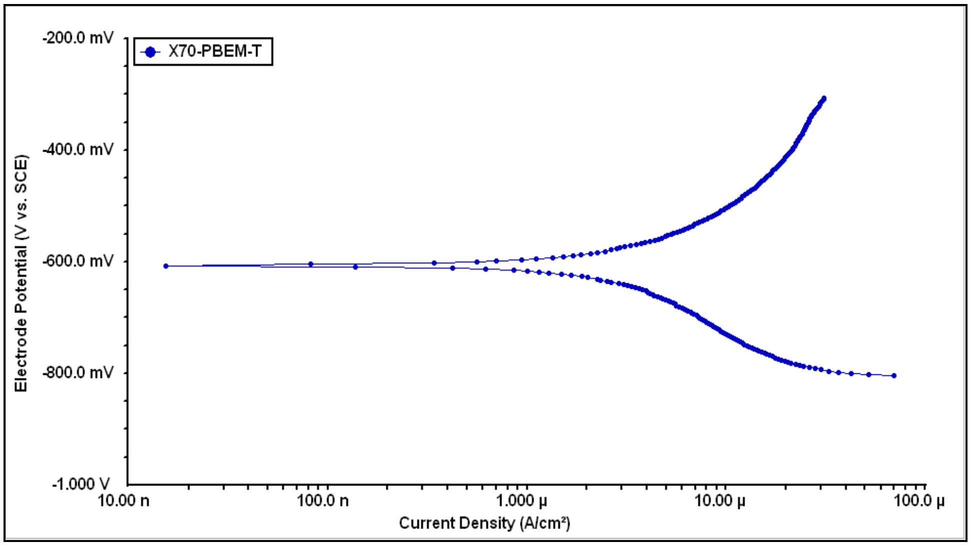

Figure 6: Tafel Scan of API-X70 (Polished Surface) in Base Oil/Water Emulsion

Table 2: Tafel Parameters of API-X-70 in Base Oil Extract

Sample ID	Surface Condition	Electrolyte	Tafel Parameters				
			β_a (V/decade)	β_c (V/decade)	I_{corr} (A/cm^2)	E_{corr} (mV)	Corrosion Rate (mpy)
X70-GBE-T	Ground	Base Oil Extract	75.00E-3	262.3E-3	12.10E-6	-772	5.549
X70-PBE-T	Polished		103.1E-3	578.6E-3	10.50E-6	-701	4.805

Table 3: Tafel Parameters of API-X-70 in Base Oil/Water Emulsion

Sample ID	Surface Condition	Electrolyte	Tafel Parameters				
			β_a (V/decade)	β_c (V/decade)	I_{corr} (A/cm^2)	E_{corr} (mV)	Corrosion Rate (mpy)
X70-GBEM-T	Ground	Base Oil/Water Emulsion	274.3E-3	387.2E-3	7.370E-6	-607	3.374
X70-PBEM-T	Polished		365.1E-3	464.9E-3	5.880E-6	-443	2.693

4. Conclusions

It is inferred from Potentiodynamic Tafel Scan results that the corrosion rate of ground surface of X-70 steel is higher than the smooth surface. The reason is that the ground surface has more exposed surface area as compared to polished one. The oxidation tendency of ground surface is also more as compared to polished one.The Tafel parameters i.e $\beta_{a,}$ $\beta_{c,}$ I_{corr} and E_{corr} also in support of these results.

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