Corrosion Behaviour of Bitumen Coated API 5l X65 Steel in Different Concentrations of HCL Environment.

Fatoba O.S. 1, 2*, Popoola A.P.I. 1, Akanji O.L. 1, Bolasodun B.O. 2, Adamson I.O. 2

1Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, P.M.B X680, South Africa 0001.

2Department of Metallurgical and Materials Engineering, University of Lagos, Akoka, Yaba, Lagos, Nigeria.

ABSTRACT

The research work investigates corrosion behaviour of coated X65 steel samples used for oil and gas transportation pipelines in different concentrations of hydrochloric acid medium at 30°C using gravimetric technique. The X65 steel samples were cut to corrosion coupons, and immersed into HCl solutions with pHs of 2, 3, 4, and 7 within a period of twenty one days. The results showed that bitumen coated X65 steel samples had better corrosion resistant compared to uncoated X65 steel samples in the studied medium. From the corrosion rate studied in HCl solutions (pH 2, 3, 4, and 7); uncoated X65 steel samples immersed in HCl solution with pH of 2 showed greater weight loss and recorded the highest corrosion occurrence. While coated samples in solution with pH 7 showed the least corrosion rate. Hence, bitumen coatings have a very successful record for protecting pipelines X65 steels against corrosion. Therefore, the results suggest that bitumen has the potential for future applications as a coating on X65 steels and pipeline steels in general

Keywords: Corrosion rate; environment; X65 steel; Gravimetric method; corrosion; pH.
1.0 INTRODUCTION.

Conveying of liquids and gases over long distances from their sources to final consumers is done by means of pipelines [1]. A significant problem in the transportation system and oil & gas production is corrosion of carbon steel which causes major economic loss [2]. As a result of corrosion, crack of the pipe wall often causes collapse of petroleum and gas pipelines. The collapse is followed by huge losses of the products, environmental pollution and ecological disasters [3].

Corrosion is the greatest source of deterioration and the degradation of materials that are used in engineering structures and components. It accounts for few hundred billion dollars in losses to the global economy [3-5]. There is therefore a need to explore different approaches to the reduction of the economic losses due to corrosion. Similarly, the environments that surround pipelines (soil, oceans and humid environments) can react with the carbon steels that are often used to fabricate pipelines, offshore structures and refineries. The deterioration of material due to corrosion can be caused by a wide variety of environments. Metallic corrosion in aqueous environments with or without dissolved species such as electrolytes and reactants [6]. However, every industry such as the food, pharmaceutical and oil and gas features a variety of applications encompassing a range of corrosive environments. There is therefore a need to develop improved methods for the environmental protection of structures that are used in the oil and gas industry.

X65 steel (low carbon steel) is one of the most commonly used engineering materials in Oil and gas industries. In spite of its fairly limited corrosion resistance, carbon steel is used in large tonnages in chemical processing, marine applications, transportation, chemical processing, metal processing equipment, petroleum production and refining, pipelines, construction and mining. The importance of this material has made different research work to
be carried out by several researchers. A recent study of corrosion behaviour and Stress corrosion cracking (SCC) of low and medium carbon steels in cassava and cocoa extracts was carried out by Afolabi [7]. He found that the medium carbon steel is more prone to corrosion than low carbon steel in both media [7].

Carbon steel corrosion in the atmosphere and in many aqueous environments is best understood from a film formation and breakdown standpoint [8, 9]. Iron in the presence of oxygen and/or water is thermodynamically unstable with respect to its oxides. The corrosion of iron in the atmosphere proceeds by the formation of hydrated oxides. The formation of the rust is observed to be formed at a distance from the surface and attack on metal cannot be stifled. This conclusion was firmly established by Evans [10].

The various oxide and hydroxides of iron form a rather complicated system of compounds. The occurrence of the various oxide species is dependent on pH, oxygen availability, various atmospheric pollutants, and the composition of the steel [11]. Corrosion can be reduced by the use of corrosion resistant materials, chemical treatment, electrochemical protection and protective coatings. The coatings may be organic, inorganic and metallic coatings.

The major purpose of a protective coating is to isolate structural reactive elements from environmental corrosives [12, 13]. A coating must provide a continuous barrier to prevent either chemical compounds or corrosion currents from contacting the substrate, as any imperfection can become the focal point for degradation and corrosion of the substrate [14]. Steel structures, such as underground buried gas pipelines, or over ground pipelines, require the use of protective coatings. Corrosion protections of over-ground and under-ground steel pipes with the help of protective coatings, such as organic coatings is one of the most proven methods. Due to the availability and relatively low cost of bitumen, recent efforts have been made to explore the use of bitumen as a coating material for pipelines in the oil and gas industry.
Bitumens are the residues from the distillation of crude oil. They are non-crystalline viscous materials, possessing adhesive and water proofing qualities and are considerably soluble in carbon disulphide. The stability of bitumen in the environment is thought to be very high. There is no available specific data concerning the transport and distribution of bitumen among environmental transformation, environmental media and degradation, interaction with chemical, physical, biological factors and bioconcentration [15, 16]. Bitumen is a strong and durable adhesive that binds together with a very wide variety of other materials, without affecting their properties. It is insoluble in water and can act as an effective waterproofing sealant. It also resists action by most acids, alkalis and salts. It is a thermoplastic material which softens and becomes liquid, with the application of heat and hardens as it cools.

The abundance reserves of natural bitumen resources in Nigeria is up to the tune of over 14.86 billion barrels located in Ondo, Lagos, Edo, Enugu and Oyo States. The sustained production of some of these bitumens from suitable crudes is done at the Kaduna Refining and Petrochemical Company (KRPC). Rich bitumen deposits can be found in Ondo State around the region of Okitipupa, Foriku and Agbabu [17]. The cutback bitumen is being considered in this work. Cutback bitumen in soils is expected to adsorb to soil particles and be immobilized. It is not considered soluble in water or readily biodegradable [18, 19]. The aim of this study is to investigate corrosion behaviour of bitumen coated and uncoated X65 steel samples used for oil gas transportation pipelines in different concentrations of HCl at a temperature of 30°C by means of gravimetric method.
2.0 MATERIALS AND METHOD

2.1 Material Preparation.

API 5L X65 steel sample used for this research was obtained from SCC (Nigeria) Ltd, Ushafa, Abuja, Nigeria. The reagents used for Corrosion test was HCl with pHs of 2, 3, 4, and 7. The chemical composition of the X65 steel is as shown in Table 1.

Table 1: Chemical composition of API 5L X65 low carbon steel.

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Si</th>
<th>Al</th>
<th>Cu</th>
<th>V</th>
<th>P</th>
<th>S</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition %</td>
<td>0.08</td>
<td>1.6</td>
<td>0.04</td>
<td>0.02</td>
<td>0.01</td>
<td>0.3</td>
<td>0.04</td>
<td>0.02</td>
<td>0.05</td>
<td>0.009</td>
<td>0.0005</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

2.2 Samples Preparation

The X65 steel samples of the composition presented in Table 1 of rectangular dimension 15x15x5 mm with 2mm diameter hole at the centre were used to determine the corrosion rate in a beaker containing the aggressive medium of hydrochloric acid with PHs of 2, 3, 4, and 7. The coupons used were polished, degreased in ethanol, dried in acetone and stored in moisture-free desiccators until used.

2.3 Coating Process

The coated X65 steel samples (with bitumen) were obtained from SCC (Nigeria) Ltd, Ushafa, Abuja, Nigeria.
Bitumen consists of complex mixture of hydrocarbons, the remainder being oxygen, sulphur, nitrogen and traces of various metals. The average bitumen molecular structures are gotten from molecular weight, elemental analysis and nuclear magnetic resonance data. It consists of one or two, 3, 4-ring condensed aromatic systems with several aliphatic side chains and alicyclic systems attached. Bitumen comprises about 25-35% aromatic, 15-30% alicyclic and 35-60% aliphatic carbon [20, 21].

2.3.1 Cutback bitumen grade (MC-1)

The MC-1 Cutback Bitumen used as a corrosion coating was produced from bitumen that was being liquefied by blending a kerosene petroleum solvent. It was blended with 60/70 penetration grade bitumen manufactured by Kaduna Refining and Petrochemical Company Kaduna, Nigeria, to give MC-1 cutback bitumen with standard specification as shown in Table 2. The blend was mixed manually at 80°C with 54% volume of bitumen and 46% volume kerosene. The precise Kerosene concentration was determined by weighing the blend after cooling to allow for evaporative losses during mixing. The sample was stored in an airtight tin container at room temperature (~ 30°C).

Table 2: Composition of Bitumen Cutback

<table>
<thead>
<tr>
<th>Bitumen cutback (BC)</th>
<th>BC</th>
<th>Percent of Total Volume</th>
<th>Percent of Cutter Stock by Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Grade</td>
<td>Penetration Grade</td>
<td>Limits</td>
</tr>
<tr>
<td>MC</td>
<td>1</td>
<td>85 -100</td>
<td>60/70</td>
</tr>
</tbody>
</table>
Table 3: Specifications for Medium Curing Cut Back Bitumen

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>BITUMEN MC-1</th>
<th>STANDARD (ASTM/ AASHTO)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>Viscosity @ 50°C</td>
<td>75</td>
<td>150</td>
</tr>
<tr>
<td>Flash Point (Tag Open-Cup)</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>Residue from distillation to 360°C, % (volume by difference)</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Test on residue from distillation</td>
<td>120</td>
<td>300</td>
</tr>
<tr>
<td>Distillation:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distillate, volume % of total</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distillate to 360°C to 190°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>to 225°C</td>
<td>25</td>
<td>65</td>
</tr>
<tr>
<td>to 316°C</td>
<td>70</td>
<td>90</td>
</tr>
<tr>
<td>Penetration at 25°C, 0.1mm</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Ductility at 25°C, cm</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Solubility in trichloroethylene</td>
<td>99.5%</td>
<td></td>
</tr>
</tbody>
</table>

The different equipment used for spraying of the coatings, pH measurements, temperature increase, weighing and other experimental processes for effective analysis are shown in the figures below.
2.4. Corrosion Rate Measurements

The metal samples were completely immersed in glasses vessel containing 200 ml solutions of HCl with pH of 2, pH of 3, pH of 4, and pH of 7. The pH values of the test solutions were determined using a pH meter [Starter 300C, 4A, 1.5V]. The experiment was carried out within a period of 21 days exposure time at 30°C. The steel samples were weighed, and suspended in the beaker with a hook and thread. After 72 hours (3 days interval), each sample was taken from the solutions of HCl washed in distilled water, dried, and re-weighed. The gravimetric method was used to calculate the corrosion rate (C.R) using the equation used elsewhere [22].
This method involved removing at a regular interval samples immersed in the corrosion media followed by washing, drying and weighing. The samples weight loss was then determined and the corrosion rate calculated.

\[
\text{Corrosion rate (mm yr)} = \frac{87.6W}{DAT} \tag{1}
\]

Where, \(W\) is weight loss of steel samples (mg), \(A\) is the area of the specimen (cm\(^2\)), \(T\) is the exposure time (hr) and \(D\) is the density of steel sample (g cm\(^{-3}\)).

3.0 RESULTS AND DISCUSSION

Figure 1 provides the corrosion rate variations across all the uncoated samples examined in acid medium with different pHs. pH 2 recorded the highest corrosion occurrence. In this group, corrosion is initiated on the same day of exposure in all the samples tested. Samples studied in pH 4 are next to pH 2 samples in corrosion rating. pH 3 and pH 7 samples maintained closer characteristics till the end. The uncoated samples in pH 2 and pH 4 had very related features right from the first day of exposure till the end of the experiment. There is general increase in corrosion rate of the samples in different pH with slight sharp decrease followed by increase again. The increase in corrosion rate can be explained by the dissolution of the metal, where a passive oxide layer is being formed with time at the surface of the steel. This reduces weight loss till around 360\(^{th}\) hour where the presence of chloride ions and moisture breakdown the porous passive oxide layer that is formed resulting in more corrosion of the steel samples.
Figure 1: Variation of corrosion rate of uncoated samples with time in HCl with different pH.

Figure 2 shows the corrosion behaviour of uncoated and bitumen coated X65 steel in pH 2 of HCl solution. The bitumen coated steel showed a sharp increase and sudden decrease in corrosion rate. This could be as a result of destruction or break in the protective oxide film formed which exposes fresh surface of the metal to the environment. The dilution of the environment by the corrosion products could also account for the decline in the corrosion rate of X65 steel.
Figure 2: Variation of corrosion rate with time in HCl (pH 2).

The increase in weight of the coated sample is due to the water absorption of the bitumen coating through pores and micro-cracks as shown in Figure 3. This resulted in gradual coating de-bonding and the formation of blisters at the coating-substrate interface as corrosion could occur in the dis-bondment area leading to subsequent decrease in weight. The small reduction in the weight of the coated steel could be due to formation of iron (II) oxide and the attack of the chloride ion on the sharp edges of the steel samples which could not be properly coated due to the geometry. The comparison of the uncoated (control sample) and the spray coated sample shows though there is high water uptake of the coating.
Figure 3: Variation of corrosion rate with time in HCl (pH 3).

Figure 4: Variation of corrosion rate with time in HCl (pH 4).
Figure 4 shows weight change behaviour for bitumen coated steel samples in HCl medium of pH 4.0. There is increase and decrease in corrosion rate of the samples at pH 4. The decrease is due to a limited supply and reduction rate of oxygen which variably reduced the corrosion rate. The decrease in weight of the coated steel could also be as a result of the sharp edges of the coupons that did not adhere to the coatings. This allows the gradual dissolution of the metal, due to direct attack of the chloride ions on the oxide layer.

![Figure 4: Weight change behaviour for bitumen coated steel samples in HCl medium of pH 4.0.](image1)

In figure 5, the weight percent behaviour of the uncoated (control) and bitumen coated steel in distilled water solution of pH 7 is different from HCl solutions of pH 2, 3 and 4. This is due to different diffusion behaviour as a result of abrupt change in the concentration of the solution. Figure 5 shows decrease in weight in coated samples, after an initial increase in the weight of these coated samples. The comparison of the uncoated and coated samples shows that the coated samples corrode less than the uncoated samples.

![Figure 5: Variation of corrosion rate with time in HCl (pH 7).](image2)
In Figure 6, corrosion initiated the same day of exposure in all the samples tested. Corrosion rate variation across all the coated samples studied in corrosive environment could be found to be more in coated sample exposed to acid medium with pH 3 which also degraded earlier than the other coated samples studied in the acid medium. Coated sample studied in pH 2 has a sinusoidal increase and decrease. Samples in pH 7 showed the least corrosion rate with an increase after 360th hours. Both samples in pH 2 and pH 4 behaved alike with Sinusoidal increase and decrease and pH 4 nearly maintained its values until the last day. Formation of protective oxide film and dilution of the environment by the corrosion products were observed to reduce corrosion rates in the investigated environment.
4.0 CONCLUSIONS

All the results can be concluded as follows:

- Corrosion studied in HCl (pH 2, 3, 4 and 7) showed greater weight loss in the uncoated samples immersed in HCl solution. Uncoated samples in solution with pH 2 recorded the highest corrosion occurrence while coated samples in solution with pH 7 showed the least corrosion rate.
- Corrosion initiated on the same day of exposure in both uncoated and coated samples tested. This is mostly due to the attack of chloride ions on the surface of the steel.
- Blisters formation and coating de-bonding were observed in some of the coated samples after the exposure time of 504 hours (3 weeks). These are attributed to the effects of hydrostatic stresses that can open up micro-pores and micro-cracks following the swelling of bitumen coatings.
- Bitumen coated samples are more resistant to corrosion than uncoated steel samples and showed low corrosion rates than the uncoated samples.

These preliminary results suggest that bitumen may have the potential for future applications as a coating on X65 steels and pipeline steels in general. The results also show that cutback bitumen may be applied using spray deposition techniques.

The use of electrochemical measurement techniques along with the weight measurements method to characterize the organic coatings and analyze the degradation of coated metal surface is a future suggestion work.
5.0 REFERENCES


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