Coating Breakdown Mechanism of Epoxy based and Bitumen Coating on Mild Steel in Sea Water and 0.5M HCl

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***Abstract*— A large amount of financial loss is incurred every year due to failure and breakdown of coatings in service on a yearly basis in the industries. The cost of fixing of these breakdowns is often higher than the initial cost of applying such coating due to the complexities and accessibility of the damaged area. Analysis of Ilaje and Lekki sea waters in Nigeria, were done using water auto analyzer. The spectroscopic analysis of the sample were also carried out. The coating breakdown mechanisms of epoxy-based coating and bitumen coating were studied in three different environments using the Electrochemical Impedance Spectroscopy test. The results showed that the two coatings protected the steel, with epoxy-based coating having the best performance of the two in all environments. Lekki seawater had the best corrosion resistance than hydrochloric acid and Ilaje seawater and is likely due to the higher value of total dissolved solids, which has been noted to cause buildup of scales on the surface of the coating, thereby inhibiting corrosion.**

Keywords*— *Corrosion; Coating; Electrochemical Impedance Spectroscopy; Seawater.

I. INTRODUCTION

Most Metals are found in their natural state, before undergoing the process of extraction from their ores. These extracted metals tend to revert back to their natural stable state, that is, their natural oxide form. The fact that corrosion needs to be controlled cannot be overemphasized in view of the colossal amount of money that is expended on it annually [1]. Different variety of measures have been devised to protect metals from corrosion [2]. In some measures, corrosion is avoided by careful selection of material and design of system so that the opportunity for corrosion of a certain specific sort does not arise. In most cases, the occurrence of corrosion is prevented or suppressed by the modification of the environment, modification of the materials properties, and application of protective coatings, cathodic and anodic protection [3]. It must be appreciated that the choice of whether corrosion is to be avoided, suppressed or merely controlled depends on the economics of the processes involved.

The solution proffered by the materials engineer to the severe failure induced by corrosion is the formation of anticorrosion coatings which is expected to have superior chemical and mechanical properties than that exhibited by the parent material [3-9]. This significant improvement of the lifespan and performance of metallic alloys and components through the use of various anti-corrosion coatings are highly advantageous [2]. The coatings provide more efficient metals/components, efficient industrial operations, reduction in costs, scarce material resource conservation and reduction in pollutant emissions. Anti-corrosion coatings most times involve the development of new surface materials which can impart various functional properties unto the surfaces of metals/components [2]

Organic coatings involve a relatively thin barrier between substrate material and the environment. Paints, varnishes, lacquers, and similar coatings doubtless protect more metal on a tonnage basis than any other method for combating corrosion [4, 9-12]. Aside from proper application, the three main factors to consider for organic coatings are listed in order of importance as surface preparation, type of primer or priming coat and the selection of topcoat or coats.

Combating metal corrosion in marine environment (seawater) is a serious environmental problem, especially in the oil industry. Sea water is a very complex and heterogeneous solution. It contains a huge amount and diversity of dissolved solid material, dissolved gases, and various species of biological matter. Reaction equilibria and the mechanisms by which materials corrode in sea water are under study [10-11]. The most important sea water parameters, from the viewpoint of corrosion in seawater, are salinity, pH, dissolved oxygen concentration, temperature, velocity and types of biological species. The type of biological species varies with geographical location, and tend to be of higher concentration near the water surface than at great depths, which is the reason for the use of two seawater samples from Lekki (Lagos state) and Ilaje (Ondo state) both in Nigeria in this study..

II. METHODOLOGY

A. Seawater

Natural sea water was collected from the sea at Lekki, Lagos state and from Ilaje, Ondo state, Nigeria. Upon collection the samples of the seawater were then stored in closed light-coloured containers to reduce the deterioration of the water. It has been discovered that stored sea water could display different behavior as a corrosive medium than that of the main water body from which it was collected. This is partly because the minor constituents, including the living organisms and their dissolved organic nutrients, which are in delicate balance in the natural environment. This delicate balance undergoes changes as soon as a natural seawater sample is isolated from the parent water mass [13]. The seawater samples collected were analysed to check for pH, conductivity, dissolved oxygen, total dissolved solids, amount of chlorides and sulphides. The composition of the two sea water samples is shown in Table I.

Table I. Sea Water Composition

	Total Dissolved Solids (TDS) mg/L	Conductivity µs/cm	Dissolved Oxygen (DO) mg/L	Chloride (Cl^-) mg/L	Sulphate (SO_4^-) mg/L	pH
Lekki	25000	14,997.00	9.4	198622.5	4217.48	3.53
Ilaje	20600	12,357.53	5.6	97447.5	3931.60	3.66

B. *Material*

Low carbon steel was used as the metal substrate for the experiments. The steel sample was cut into plates of sizes 20mm x 20mm x 10mm. The selected steel samples were grinded using a series of emery paper with different grit sizes from 60 down to 1200 grade (coarser to finer), to remove rust and other impurities which are gathered on the substrate surface. The metal was also analysed by means of optical microscopy and spectrometry analysis to get the elemental composition of the metal. The chemical composition of the steel is given in Table II.

Table II. Composition of Mild Carbon steel

Element	C	Mn	S	Cr	Ni	Cu	As	Fe
Composition (%)	0.0766	0.2980	0.0239	0.0226	0.0167	0.0235	0.0142	Bal.

C. *Application of coatings on substrate*

The coatings that were applied are Epoxy resin coating and Bituminous coating. The coatings were carefully applied onto the substrate surface. The epoxy resin was applied by means of spray gun with the aid of air compressor, and was then left to cure naturally for a period of 24-36 hours. The bitumen paint was heated (raising the temperature of the metal above room temperature to aid easy application) and then spread on the metal by means of brush. This was done due to the lack of flow in the bitumen coating when at room temperature, and hence the application allowed the coating to flow enough for it to be applied unto the metal substrate.

D. *Electrochemical tests*

Electrochemical measurements were conducted in an unconventional three electrode Pyrex cell. A saturated calomel electrode (SCE) and a platinum electrode were used as the reference and the counter electrodes, respectively. Potentiodynamic polarization measurements were performed using an instrument potentiostat to perform all polarization and EIS measurements. The potential scan rate was $5mVs{-}1$. The impedance measurements were carried out in the frequency range of 100,000 KHz to 0.01 KHz with a signal amplitude perturbation of 10 mV. Data were collected and analyzed using EC-Lab software.

0.5 M HCl was also prepared with analytical grade chemicals as the third environment for the experiment.

Table III. Solution resistances values, capacitance, and charge transfer resistance values of selected coatings in different environment

	R_s (Ohm)	C (F)	R_{ct} (Ohm)
EPOXY COATED MILD STEEL			
HCl	0.4317e-276	0.621e-9	7656
LEKKI SEA WATER	22063	9.751e-6	661263
ILAJE SEA WATER	1657	45.12e-6	242124
BITUMEN COATED MILD STEEL			
HCl	8.413	0.2404e-6	57.42
LEKKI SEA WATER	0.177 9e-12	19.24e27	0.8395e39
ILAJE SEA WATER	133.3	10.4e-6	2143

III. RESULTS AND DISCUSSION

A. *Electrochemical measurements*

From the electrochemical impedance spectroscopy tests, Nyquist plots are derived. The Nyquist plots show the imaginary part as a function of the real part of the impedance and helps to determine the properties including electrode & electrolyte resistance, charge transfer resistance and capacitance of the half-cell. The curve-fitting was done with the EC-Lab software to get the values for the charge transfer resistance (Rct) indicating the coating effectiveness in a

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particular environment, solution resistance (Rs) which indicates the rate at which the coating diffuses into the solution and capacitance C which indicates the ability of the coating to remain intact during exposure as shown in Table III. Figure 1- 6 showed the Nyquist plots of mild steel in Ilaje sea water, Lekki sea water and 0.5M HCl environments.

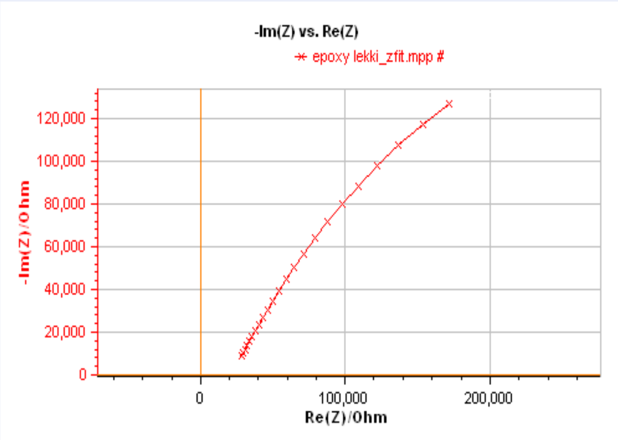

Fig. 1. Nyquist diagram of epoxy coated mild steel in Lekki sea water.

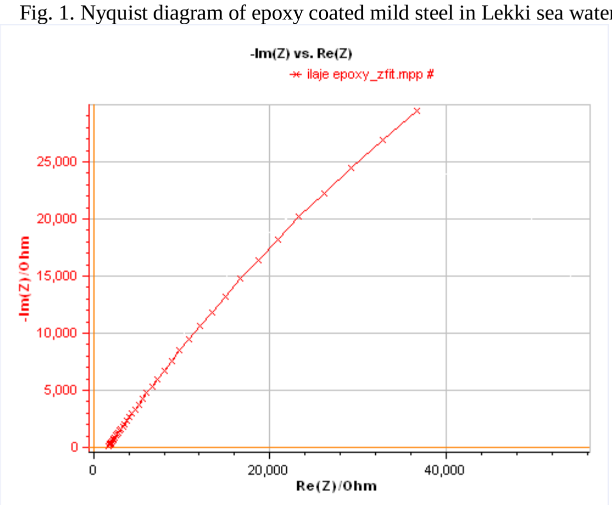

Fig. 2. Nyquist diagram of epoxy coated mild steel in Ilaje sea water.

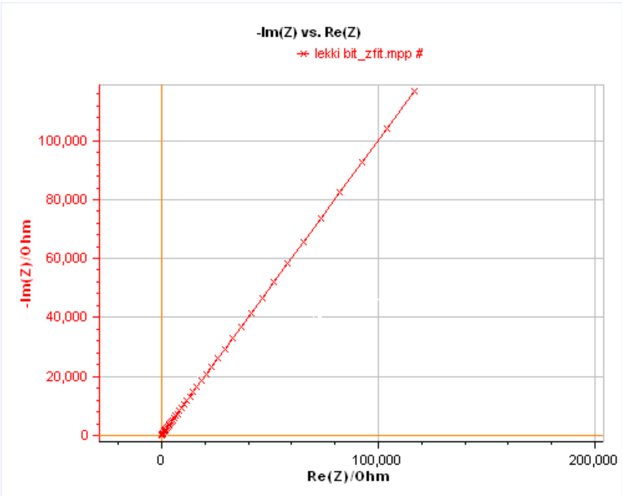

Fig. 3. Nyquist diagram of bitumen coated mild steel in Lekki sea water.

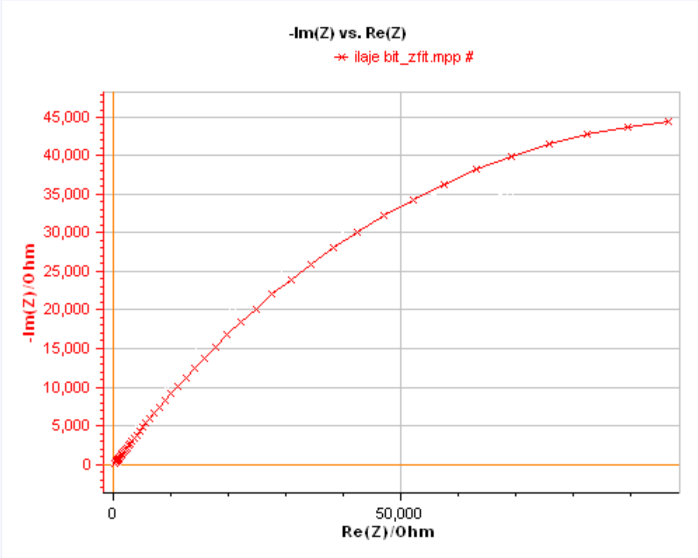

Fig. 4. Nyquist diagram of bitumen coated mild steel in Ilaje sea water.

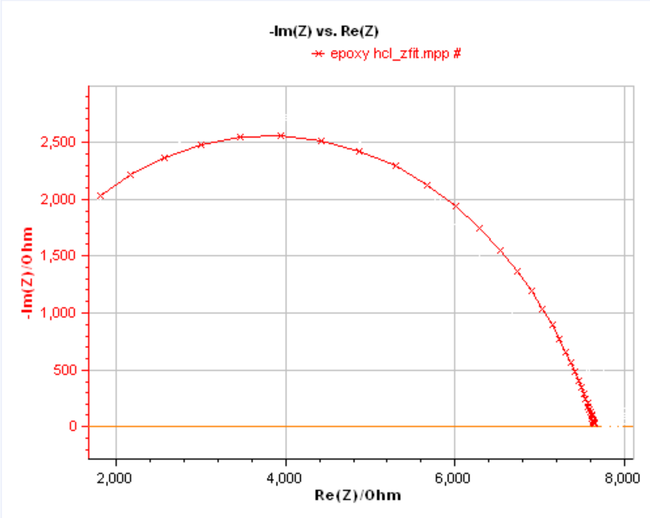

Fig. 5. Nyquist diagram of epoxy coated mild steel in 0.5M HCl.

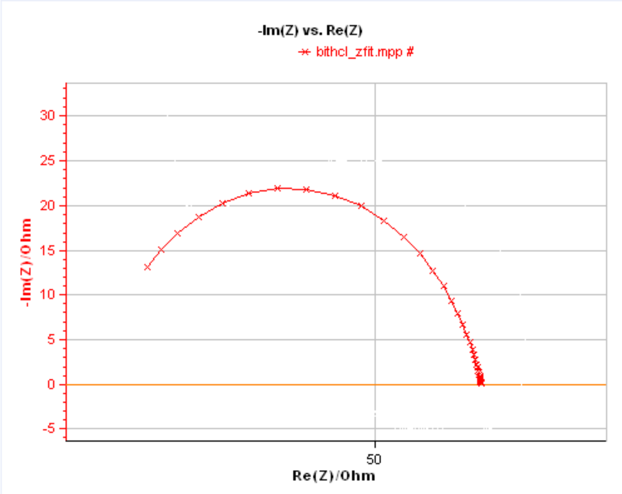

Fig. 6. Nyquist diagram of bitumen coated mild steel in 0.5M HCl.

B. Epoxy Coated Mild Steel

It was observed from Table III that HCl had the lowest value of Rs at 0.4317e-276 ohms, Ilaje seawater had a Rs value of 1657 ohms and Lekki seawater had the highest value at 22064 ohms. HCl was the most aggressive environment for the epoxy coating indicating that the epoxy coating diffuses into 0.5M HCl environment faster than in any other environment under study. The Ilaje seawater which has a value of 1657 Ohms, is the second most aggressive environment and the Lekki seawater with the highest solution resistance indicating less diffusion of the coating into the environment than Ilaje and 0.5M HCl.

HCl has a pH value of 0.3 which is more acidic than 3.53 of Ilaje seawater and 3.66 of Lekki seawater and is one of the environment variables responsible for the low value of Rs gotten from the 0.5M HCl environment. Corrosion rates increases rapidly with hydrogen evolution when below pH value of 4.

Also noted from Table III, Lekki sea water had the highest value of Rct and it infers that epoxy-based coating performed most effectively in Lekki sea water, while in Ilaje seawater and 0.5 M HCl coating effectiveness is less. The smaller the value of Rct, the less effective the coating will be. Although it is expected that epoxy-based coating will perform better in Ilaje sea water than in Lekki seawater because of the values gotten from the water analysis, but the dissolved solids are likely to have formed scales on the surface of the coating, thereby increasing the resistance to corrosion.

For C (capacitance) which is a property which indicates the ability of the coating film to remain intact during entire exposure, the epoxy-based coating in Ilaje seawater had the highest value of capacitance at 45.12E-06 F and in this environment the ability to remain intact is greatly reduced. An increase in the film capacitance is usually attributed to water uptake, in view that the increase in the water uptake of the coating during service is reflected in increasing value of capacitance.

C. Bitumen Coated Mild Steel

From the portion of bitumen coated mild steel in Table III, it can be deduced that bitumen coating will have its highest effectiveness in Lekki seawater. The Rct value of Lekki seawater gotten as 0.8395E39 Ohms is indicative of the fact that bitumen coating performed best in Lekki sea water, while in 0.5M HCl (57.42 Ohms) and Ilaje seawater (2143 Ohms) the effectiveness of the bitumen coating is lower. High values of total dissolved solids (TDS) have been noted to cause buildup of scales in valves and pipes[] It is likely for TDS to have formed scales on the surface of the coatings, thereby increasing the charge resistance of Lekki seawater, despite the fact that it had higher values of conductivity, dissolved oxygen, chlorides, sulphates and being the more acidic medium.

From the solution resistance values gotten from Table III for bitumen coated mild steel, we are provided evidence that bitumen coating will diffuse fastest in Ilaje seawater (133.3 Ohms) and more slowly in 0.5 M HCl (8.413 Ohms). The bitumen coating diffuses slowly in Lekki seawater (0.1779E-12). it supports the higher Rct values (showing coating effectiveness) noted for bitumen coated mild steel in Lekki sea water.

Among the three environments the bitumen coated mild steel was exposed to, Lekki seawater had the highest capacitance value at 19.24e27 F which shows that the bitumen coating will have the highest water uptake. The other environments 0.5M HCl and Ilaje seawater having lower capacitance values will cause the coating to have less water uptake, and in these environments the coating will remain more intact.

Factors that causes coating breakdown such as water uptake, ion transport are seen to be of greater effect in the bitumen coating. This can partly be attributed to the fact that epoxy resin cure to form three dimensional cross-linked thermoset structures with ionic bonding compared to covalent bonding that is in bitumen.

CONCLUSION

The results gotten showed that the coatings used (epoxy and bitumen) served as protective barriers for the steel substrate. This research also showed that, various constituents of sea water aid the breakdown of coatings applied on the metal especially the properties like total dissolved solids (TDS), amount of chlorides and sulphides, pH, amongst others.

From the analysis of the results gotten from the Electrochemical Impedance Spectrometry, epoxy based coating offered better protection to the mild steel than the bitumen coating in all environments used.

.Lekki seawater had the best corrosion resistance than 0.5M HCl and Ilaje seawater. This is probably due to the high value of total dissolved solids (TDS), which has been stated to cause buildup of scale on the surface of the coating, thereby inhibiting corrosion.

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