Effects of pH Variation on Corrosion of Mild Steel in Bore-hole Water using 1M Sodium Hydroxide Solution

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ABSTRACT

Corrosion of metals is a major industrial problem that has attracted a lot of investigators in recent years and huge financial losses are always incurred by the replacement of corroded parts. The corrosion of mild steel in bore-hole water of different pH values of 7.20, 8.20, 9.20, 10.20 and 11.20 using 1M sodium hydroxide (NaOH) solution at room temperature was investigated by chemical technique. The specimen in bore-hole water of pH value 11.20 has the least corrosion rate of 8.650 mpy while the one in bore-hole water of pH 7.20 has the highest value of 12.974mpy. It is shown that there is a progressive decrease in both conductivity and rate of corrosion product formation on the test specimens from the solutions as the pH increases from 7.20 to 11.20. This is due to that fact that sodium hydroxide supplies hydroxyl ions OH^- which possibly absorb to the surface of the specimen by acting as an anodic inhibitor which increases anodic polarisation by helping to form a protective film and keeps it repaired thereby retarding or reducing the rate of corrosion as the pH increases.

Keywords: *Mild Steel, Bore-hole water, NaOH, Corrosion, pH, Conductivity, Optical Emission Spectrometer.*

1. INTRODUCTION

Corrosion of industrial metals is one of the oldest problems that have ever challenged the industrial world and is defined variously [1, 2, 3]. Corrosion is the destruction of a solid body through an unintentional chemical or electrochemical action with the environment starting at its surface. All but a few metals are corroded more or less by water and atmosphere. Furthermore, the attack on a metal occurs mostly by electrochemical action because of the characteristics structure of metals, which accounts for phenomenon such as the free movement of electrons through their lattices. Corrosion is the gradual physiochemical destruction of materials by the action of environment. It is also known as the deterioration of materials or its properties because of reaction with its environment. Most metals exist in nature in combined forms such as oxides, hydroxides, carbonates, sulphides, sulphates and silicates. The extraction of metals from their ores requires a considerable amount of energy. The isolated metals therefore can be regarded as being in a much higher energy state than in their corresponding ores, and they will show a natural tendency to return to their lower energy or combined state. Thus corrosion of metals can be regarded as the reverse process of that of reducing from their ores [4].

Metallic material constitutes a great part of construction material elements in industries, agricultural equipment, oil and gas and petrochemical, medical services, process and allied industries. In these industries, the metallic material as a result of interaction with its environment loses its integrity over a period of time [5]. Problems of corrosion are more pronounced in processing industry. A typical reference is agro-processing industries. The production of bio-compatible and bio-degradable industrial raw-material from purely agricultural sources has increased in recent years. For instance, ethanol is

being produced from cassava tubers through multi processing stages. The factory processing of cassava produces the toxic compound hydrogen cyanide. The cyanide is very corrosive and is responsible for the corrosion of agro-processing equipment which is usually made of plain carbon steel. The corrosiveness of the cassava fluid is due to the cyanide ion in the cyanogenic glycosides whose concentrations vary widely as a result of genetic and environmental factors, location, seasons and soil types [6] and [7].

The composition and physical integrity of a solid material are altered in a corrosive environment. In chemical corrosion, the material is dissolved by a corrosive liquid while in electrochemical corrosion; metal atoms are removed from the solid material as the result of an electric circuit that is produced. Metals and certain ceramics react with a gaseous environment usually at elevated temperatures and the material may be destroyed by formation of oxides or other compounds. Polymers degrade when exposed to oxygen at elevated temperatures. Materials may be altered when exposed to radiation or even bacteria and a variety of wear and wear-corrosion mechanisms alter the shape of materials. Billions of dollars are required to repair the damage done by corrosion each year [8]. Corrosive environments include the atmosphere, aqueous solutions, soils, acids, bases, inorganic solvents, molten salts, liquid metals, and last but not the least, the human body. On a tonnage basis, atmospheric corrosion accounts for the greatest losses [9].

In light of the thermodynamic basis for corrosion, it is not surprising that costs associated with corrosion are high. Several studies over the past 30 years have shown that the annual direct cost of corrosion to an industrial economy is approximately 3.1% of the country's Gross National Product (GNP). In the United States, this amounts to over $276 billion per year. The

highest segments of the cost of corrosion are associated with utilities, transportation, and infrastructure. The Department of Defence alone has corrosion costs of $20 billion annually [10]. Traditionally, corrosion is classified into eight categories based on the morphology of the attack, as well as the type of environment to which the material is exposed [11].

Corrosion control is an important activity of technical, economical, environmental and aesthetical importance. Thus, the search for efficient corrosion inhibitors has become a necessity to secure metallic materials against unmitigated

degradation. Corrosion of mild steel is of great practical interest because mild steel is widely used in the oil, gas and offshore environments for pipelines, flow-lines, platforms, down-hole tubular equipments, well heads, industrial vessels etc. Corrosion inhibition is being extensively employed in minimising metallic wastage of engineering materials in service [12]. In this research, the effect of pH variation on the corrosion rate of mild steel in borehole water using 1M of sodium hydroxide solution (NaOH) is experimentally investigated and presented.

2. EXPERIMENTAL DETAILS

Table 1. Chemical composition of mild steel specimens (%)

Specimen	C	Si	Mn	P	S	Cr	Mo	V	Ni	Cu	Al	Fe
A	0.178	0.210	0.770	0.030	0.040	0.118	0.018	0.008	0.079	0.084	0.003	98.480
B	0.167	0.190	0.640	0.035	0.040	0.134	0.018	0.008	0.070	0.073	0.012	98.613
C	0.168	0.192	0.641	0.036	0.032	0.112	0.020	0.007	0.086	0.066	0.004	98.640
D	0.181	0.230	0.693	0.030	0.040	0.110	0.018	0.004	0.078	0.072	0.010	98.552
E	0.151	0.170	0.746	0.032	0.040	0.100	0.019	0.006	0.102	0.081	0.006	98.547
F	0.167	0.250	0.761	0.039	0.033	0.120	0.016	0.003	0.073	0.061	0.004	98.473

The mild steel used in this study has a carbon content of approximately 0.2%. Six mild steel test specimens (coupons) of dimensions 3 x 1 x 0.15cm were cut from mild steel sheet of 0.15cm in thickness and were labelled A, B, C, D, E and F. The composition analysis of the specimens was determined using an optical emission spectrometer (OES) ARL 3460B model. On each specimen, a hole of 1mm diameter was drilled near one of the ends to allow for easy hanging of the specimen into the corrosive media using a thread. The specimens' surfaces were prepared with 220 grit paper which gave good reactive surfaces. The specimens were degreased in ethanol, air dried and etched in 5% concentrated hydrochloric acid (HCl) for 30 seconds and weighed before immersion in the test environment. Specimen A was suspended in room air environment while B, C, D, E and F were immersed in five separate 250 ml open beakers containing 200 ml of bore-hole water of different pH values. Different volumes of 1M NaOH solution were added to the five beakers in order to vary their pH values. The pH and conductivity of the solutions before and after the experiment were measured and recorded. Initial pH values of 7.20, 8.20, 9.20, 10.20 and 11.20 were used for specimens B, C, D, E and F respectively. The variation of weight loss was monitored after 240 hours immersion per specimen/coupon at room temperature. After 240 hours, the specimens were taken out, immersed in dilute H_2SO_4 (Sulphuric

acid of specific gravity 1.84) at room temperature, scrubbed with a bristle brush, rinsed in distilled water, rinsed in ethanol, air-dried and re-weighed. The weight loss was calculated in gramme (g) as the difference between the initial weight and the final weight after removal of the corrosion products. The reduction of the thickness as a function of time was calculated. The experimental readings were recorded to the nearest 0.0001g on a Mettler digital analytical balance (digital analytical balance with sensitivity of ± 1mg). Corrosion rate in mil/yr was determined using the equation [13]:

$$R = \frac{K(W_1 - W_2)}{\delta At} \qquad (1)$$

Where: R = corrosion rate (mil/yr)

K = constant and its value is 534 for (mil/yr)

W_1 = initial weight of specimen before corrosion in milligrams (mg)

W_2 = final weight of specimen after corrosion in milligrams (mg)

δ = density of specimen in g/mm^3 = 7.86 x 10^{-3} g/mm^3

A = total surface area of specimen exposed (mm^2)

t   = time of exposure (hr)

3.   RESULTS AND DISCUSSION

The spectrochemical analysis shown in table 1 reveals that the mild steel specimens used in this study have an iron content of approximately 99% with other trace elements residued from metal extraction process. The levels of these trace elements are insignificant to influence the chemistry of the behaviour of the steel samples in the corrodant and medium.

Table 2: Corrosion of specimen suspended in air at room temperature for 240 hrs

| Specimen	Initial Weight (W_1) x 10^3(mg)	Final Weight (W_2) x 10^3(mg)	Weight Gain (Wg) x 10^3(mg)	Exposure Time t (hrs)	Corrosion Rate (R) (mpy)
A	3.088	3.448	0.360	240	141.539

Area of the test specimen = 2(L x B) + 2(L x T) + 2(B x T)   (2)

Where: L = length of test specimen = 3cm, B = breadth of test specimen = 1cm, T = thickness of test specimen = 0.15cm. Using equation (2), Area of the specimen = $7.20cm^2$ = 7.20 x $10^2 mm^2$. The mild steel used in this study has a carbon content of approximately 0.2% and the density (δ) is 7.86 x $10^{-3}g/mm^3$. Using equation (1), the corrosion rate (R) of the specimen suspended in air at room temperature in the laboratory is 141.539mpy.

Table 3: Corrosion in bore-hole water of different pH using 1M NaOH solution at room temperature for 240 hrs

Specimen	pH_1	pH_2	C_1(μs) x 10^2	C_2(μs) x 10^2	W_1x 10^3 (mg)	W_2x 10^3 (mg)	W_Lx10^3 (mg)	Exposure t (hrs)	Corrosion Rate (mpy)
B	7.20	7.90	1.32	1.34	3.012	2.979	0.033	240	12.974
C	8.20	8.40	1.31	1.32	3.050	3.020	0.030	240	11.795
D	9.20	8.50	1.29	1.30	3.070	3.042	0.028	240	11.009
E	10.20	9.00	1.27	1.29	3.075	3.050	0.025	240	9.829
F	11.20	9.90	1.26	1.27	3.093	3.071	0.022	240	8.650

pH_1 and pH_2 represent the pH of the various solutions before and after the experiment.
C_1 and C_2 represent the conductivity of the various solutions before and after the experiment.
W_1 and W_2 represent the weight of the various specimens before and after the experiment.
W_L represents the weight loss of the various specimens after the experiment.
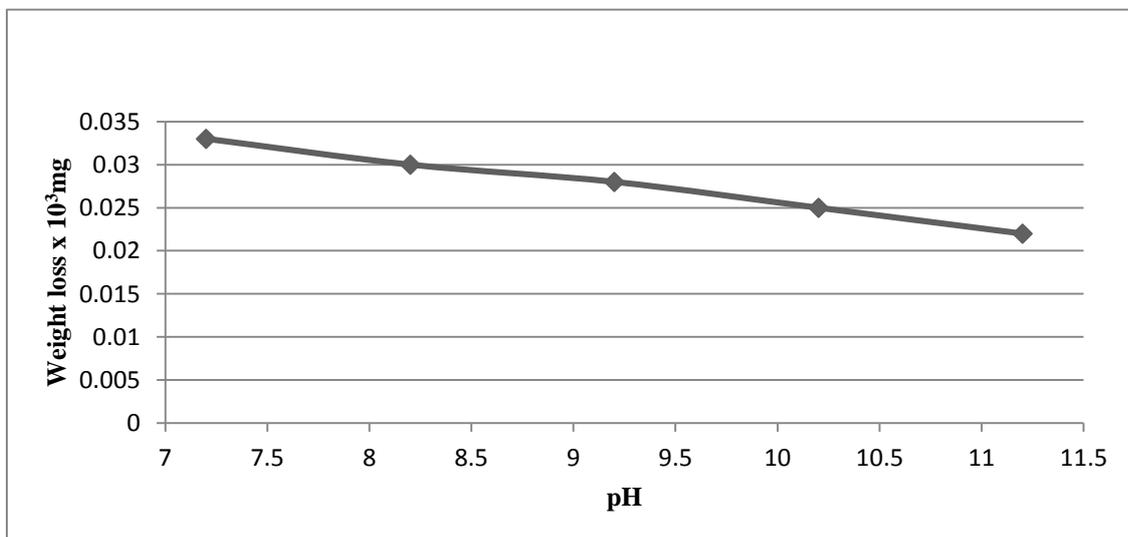
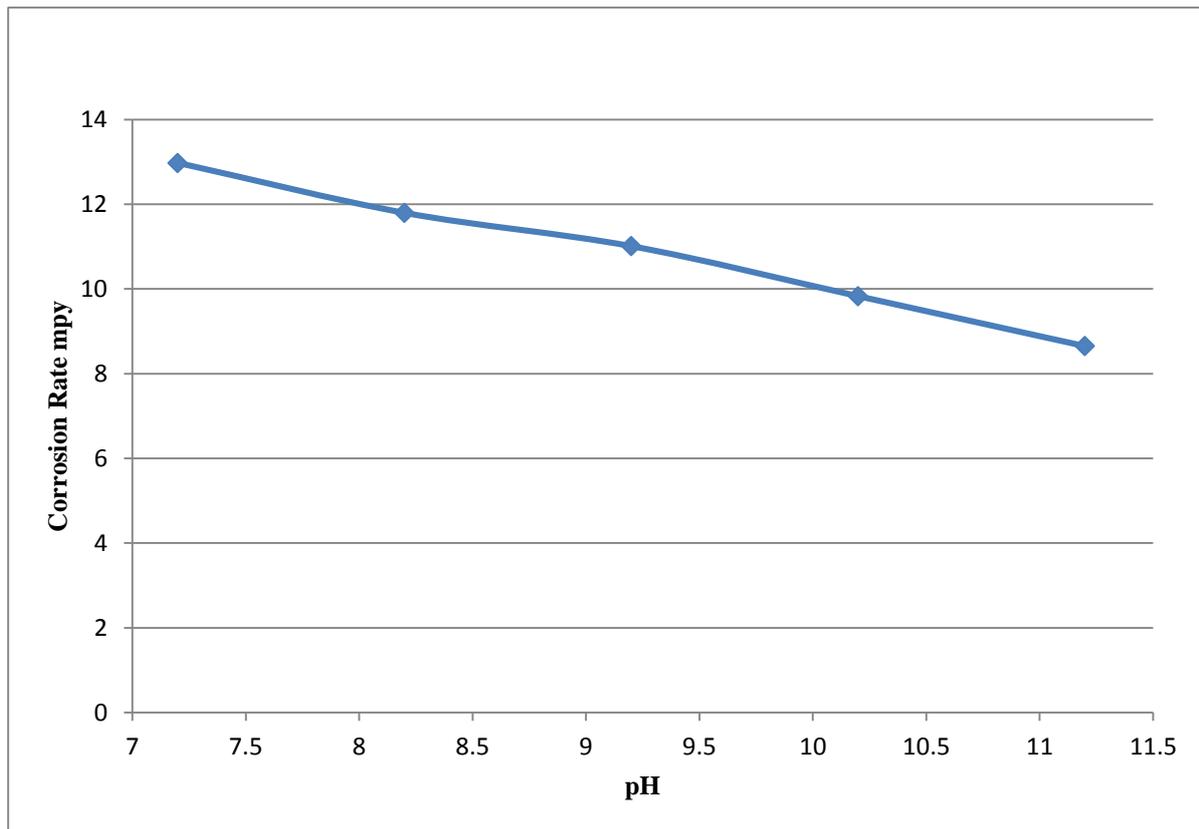**Figure 1: Weight loss against pH of specimens in bore-hole water at room temperature using 1M NaOH solution.**

Figure 2: Corrosion rate against pH of specimens in bore-hole water at room temperature using 1M NaOH solution.

Table 1 shows the composition analysis of the specimens.

Table 2 shows the corrosion rate of specimen suspended in air at room temperature for 240 hrs.

Table 3 shows the weight loss and corrosion rate of the specimens in bore-hole water of different pH using 1M NaOH solution at room temperature for 240 hrs.

Figure 1 shows the plot of the weight loss against the pH of the specimens in bore-hole water of different pH using 1M NaOH solution at room temperature.

Figure 2 shows the plot of the corrosion rate against the pH of the specimens in bore-hole water of different pH using 1M NaOH solution at room temperature.

As indicated in table 2, the specimen that was exposed to the room air in the laboratory had an initial weight of 3.088(g) and a final weight of 3.448(g). An increase in weight of 0.360(g) in the test specimen was observed with a corrosion rate value of 141.539 mpy after 240 hrs of exposure. This is due to the corrosion product that adhered to the surface possibly due to the acidic environment in the laboratory. After about an hour of exposure to the room atmospheric air, the metallic bright gray colour had changed to yellowish-brown. Changes of the specimen surface seemed to have reached its climax by the 10th day (240 hrs) with a light-brown deposit (rust) which must have been due to its reaction with air and moisture. The mild steel specimen was exposed to moist air and reacted with oxygen in the air to form $Fe(OH)_3$. This is due to the fact that the electrons produced as a result of oxidation of iron (Fe) is conducted through the metal and the iron ions diffused through the moist layer to another point on the specimen's surface where oxygen is available. This process results into an electrochemical cell in which iron serves as the anode, oxygen as the cathode and the aqueous solution of ions as a salt bridge.

The specimen corroded in the solution by an electrochemical mechanism involving its oxidation as ions according to:
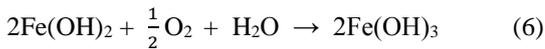
$$Fe \rightarrow Fe^{2+} + 2e^-. \quad (3)$$
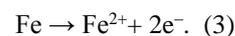
The excess electrons generated in the aqueous solution created hydroxyl ions $[OH^-]$ by the reduction of dissolved oxygen according to:

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

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad (5)$$
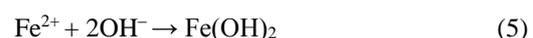
The reaction continues as the $Fe(OH)_2$ reacts with more oxygen and moisture lead

Fe_3^+ as $Fe(OH)_3$ according to:

$$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O \rightarrow 2Fe(OH)_3 \qquad (6)$$

The compound $Fe(OH)_3$ is a light-brown deposit, an insoluble compound known as rust which is formed as a consequence of oxidation [13, 14]. This shows that even in the laboratory, corrosion of mild steel specimen is possible. The other specimens that were completely immersed in the corrosive solutions also manifested similar corrosion behaviour. As indicated in table 3, the weight loss of the specimen in bore-hole water at pH value of 7.20 is 0.033(g) while it decreased to 0.030(g) at pH value of 8.20. The highest weight loss of 0.033(g) was recorded at pH value of 7.20 while the lowest weight loss of 0.022(g) was recorded at pH value of 11.20. Corrosion rate of 12.974mpy was recorded in specimen B in solution with pH value of 7.20 while corrosion rate of 8.650mpy was recorded in specimen F in solution with pH value of 11.20. It is obvious that weight loss and corrosion rate decreased with increase in pH values from 7.20 to 11.20. This shows that weight loss is directly proportional to corrosion rate. The results also show that the specimens have reacted with their corrosive medium as:

In the first stage, Fe in the specimens is oxidised to Fe^{2+} as $Fe(OH)_2$ according to:

$$Fe + \frac{1}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2OH^- \rightarrow 2Fe(OH)_2$$

$$(7)$$
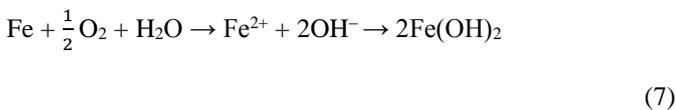
The reaction continues in the second stage as the $Fe(OH)_2$ reacts with more oxygen and water resulting into oxidation to Fe^{3+} as $Fe(OH)_3$ according to:

$$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O \rightarrow 2Fe(OH)_3$$

$$(8)$$

The compound $Fe(OH)_3$ is an insoluble compound known as rust which is formed as a consequence of the dissolution of the specimens' (iron) ions by oxidation [13, 14].

The specimens corroded in the solution by an electrochemical mechanism involving their dissolution as ions at the anodic site due to oxidation:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (9)$$
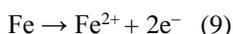
The excess electrons generated in the solution created hydroxyl ions $[OH^-]$ by the reduction of dissolved oxygen which enhances uniform corrosion at the cathodic site according to:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (10)$$
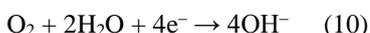
The corrosion rate of the specimens is associated with the flow of electrons with the two reactions involving oxidation (in which the specimens ionised) and reduction occurring at the anodic and cathodic sites respectively, on the surfaces of the specimens. Generally, the specimens' surfaces consist of both anodic and cathodic sites, depending on segregation, microstructure, stress, etc [15]. The graphical representations of weight loss and corrosion rate of the mild steel specimens with increase in the pH of the solutions are shown in figures 1 and 2 respectively. The graph lines decrease as the pH values increase. This is due to increase in volume of sodium hydroxide solution which enhances the supply of hydroxyl ions OH^- which possibly absorbed to the surface of the specimens. These ions act as anodic inhibitors which increased anodic polarisation by helping to form a protective film and keep it repaired thereby retarding or reducing the rate of corrosion.

$$NaOH\ (aq) \leftrightarrow Na^+\ (aq) + OH^-\ (aq).$$

$$(11)$$

4. CONCLUSION

There is a progressive decrease in conductivity, weight loss and the rate of corrosion product formation on the test specimens as the pH value increases from pH 7.20 to 11.20 using 1M NaOH in bore-hole water. The test specimen B of pH 7.20 had the highest corrosion rate while specimen F had the lowest. Increase in the pH of the bore-hole water is due to increased volume of sodium hydroxide solution which enhances the supply of hydroxyl ions $[OH^-]$. The ions got absorbed to the surface of the specimens by acting as an anodic inhibitor which increased anodic polarisation thereby helping to form a protective film and keeps it repaired by retarding or reducing the rate of corrosion which is also a good corrosion control method that can be adopted.

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