

Research article

Corrosion Performance and Application Limits of Materials in Oil Field

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Abstract

In recent years, atmospheric corrosion of materials have attracted materials community, for it accounts for more failures on both a tonnage basis and cost basis than any other type of environmental corrosion. Tremendous amounts of materials in industries are exposed to the atmosphere and attacked by pollutant and water. In this project research attention is paid to the atmospheric corrosion of zinc, mild steel and carbon steel in 0.1M, 0.2M and 0.3M medium concentration of H_2SO_4 for three (3) months and empirical expression relating corrosion rate, weight loss, period of exposure were deduced for the various coupons. Graph showing corrosion rate against period of exposure were established for the various coupons at different concentrations which depicts that as concentration of H_2SO_4 medium increases there is a corresponding increase in corrosion rate. The corrosion behavior of material in sour environment was investigated using mild steel, carbon steel and zinc as a representative. Changes in corrosion morphologies resulting from changes in environmental aggressiveness were elucidated. The application limits of materials were shown to be determined by whether corrosion occurred thus, determining the application limits of the material. The validity of prediction by the experimental results was confirmed by good agreement with results from long-term immersion tests. Since this theory was based on the corrosion mechanism, it showed many advantages: the prediction was accurate, the results for one environment could be extended to other environments, and the prediction was conducted very quickly. **Copyright © IJACSR, all rights reserved.**

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1. Introduction

Corrosion has wide ranging implications on the integrity of Materials used in the Petroleum Production industry. It manifests itself in several forms amongst which CO_2 corrosion (sweet corrosion) and H_2S corrosion (sour corrosion) are by far the most prevalent form of attack encountered in oil and gas production. The implication of these types of

attack can be viewed in terms of their effects on both capital and operational expenditures and health, safety and the environment (HSE) (Almeida et al., 2000; Anderson, 1956; Alves and Ferreira; 1992; Barton, 1976, 1972; Brierly, 1965; Black 1968; Briggs, 1968; Caruthers, 1986; Chawla and Payer, (1990). Increasing water production gives rise to these types of attack and potential corrosion of carbon and low alloy steels in the presence of acidic gases. i.e means of corrosion control is through the use of effective inhibitor packages. Subject to continuous and sufficient availability, corrosion inhibitors can offer adequate corrosion mitigation against the risk of CO₂ corrosion for the safe and trouble free application of carbon and low alloy production tubulars Naeemi and Albercht, 1984; Morcillo et al., 1999; Hatch and John, 1984; Grossman, 1987; Graedel et al., 1986; Horng et al., 1987; Roberge, 1999).

Corrosion is a prevailing destructive phenomenon in science and technology. In industries such as pulp and paper industry, power ration, underground structures, chemical and oil industries, metals used in over 90% of construction process (Osarolube et al, 2004; Pourbaix and Purbaix 1989; Nriagu, 1978; Natesan, 1995; Naixin et al., 2002).

Iron and steel are the most commonly used materials in the fabrication and manufacturing of oil field operating platforms because of their availability, low cost, ease of fabrication, and high strength (Umezurike, 1998; Nwoko and Umoru, 1998). Most industrial media are usually rich in elemental gases, inorganic salts, and acidic solutions most of which influence corrosion rates, and mechanisms (Abu and Owate, 2003; Abiola and Oforka, 2005). Metals are usually exposed to the action of bases or acids in the industries. Processes in which acids play a very important role are acid pickling, industrial acid cleaning, cleaning of oil refinery equipment, oil well acidizing and acid descaling (Farina et al., 2004; Stiles and Edney, 1989; Spence et al., 1992; Thomas and Alderson, 1968; Trimgham, 1958; Uhlig, 1985). The exposures can be severe to the properties of the metals and thus lead to sudden failure of materials in service. There is therefore the need to study the corrosion behaviour of metals when exposed to various environments, as this is an important factor in material selection that determines the service life of the material.

The application limits of materials and Changes in corrosion morphologies resulting from changes in environmental aggressiveness has been an issue in oil field. The study covered both H₂S and CO₂ corrosion performance and application limits of materials in oil field conditions. The results have led to the determination of effective means of corrosion mitigation to enable wider uses of materials for oil field and downhole applications (Schweitzer and Philip, 1991; Sinclair and Psota-Kelty, 1984; Rice et al., 1981; Evans, 1981, 1972, 1932; Flinn et al., 1986; Fontana, 1987).

This research project deals with the evaluation of corrosion performance and application limits of material in oil field.

The aim and objectives of this research project is to examine, investigate and carry out experimental analysis to establish the suitability and corrosion performance and application limits of material in oil field. This project work considers the corrosion risks that may arise downhole, summarizes the options available for corrosion control, and describes some field experience with materials that have been used in various corrosive conditions.

In particular it focuses on the increasingly aggressive (i.e. deep, high pressure/high temperature (HP/HT), H₂S containing) downhole environments provide a framework for assessing the severity of an environment with respect to corrosion and for establishing likely candidate materials for specific applications. Corrosion issues occur across various industries. Modeling of the various aspects of the corrosion behavior of materials is in its early stages. At the

heart of the approach of this research work was the development of correlations between corrosion performance and application limits of material with respect to changes in environment. These correlations will be used to predict the occurrence of corrosion and damage in base materials as it concerns oil field application.

The word corrosion is derived from the Latin *corrosus* which means eaten away or consumed by degrees; an unpleasant word for an unpleasant process (Trimingham T.C.E., 1958; Donchenko and Saenko, 1979; Divers and Mellor 1952; Cuesta, 1993; Godard et al., 1967; Galloway, 1987). Corrosion is defined as the destruction of materials caused by chemical or electrochemical action of the surrounding environment. This phenomenon is experienced in day to day living. The most common examples of corrosion include rusting, discoloration and tarnishing (Speller F.N., 1951; Johanasson, 1981, Lobnig, 1996; Mardar, 1997; Haynie, 1980, 1988) Corrosion is an ever occurring material disease. It can only be reduced it cannot be prevented because thermodynamically it is a spontaneous phenomena. In fact, economy of any country would be drastically changed if there were no corrosion. For example automobiles, ships, underground pipelines and house-hold appliances would not require coatings. The stainless steel industry would disappear and copper would be used for electrical applications.

Although corrosion is inevitable, its cost could be reduced. Corrosion can be fast or slow. In the oil & gas industry the use of Corrosion Resistant Alloys (CRAs) has been common practice since the mid 70's, when oil companies started to exploit deeper and deeper natural gas reservoirs and CO₂ injection technique was introduced to facilitate oil recovery. These events led to extremely aggressive environments for the use of carbon or low alloyed steels due to the presence of high CO₂ partial pressures and H₂S as a pollutant. In the 70's, the choice of 9Cr-IMo became cost effective with respect to carbon steels plus inhibitor in a large number of situations (s). 9Cr-IMo steel was mainly utilized as tubing or casing in the completion of gas wells with no H₂S or in environments where the concentration of this corrosive compound was a few part per million (ppm). Nowadays 9Cr-IMo steels are used in many other applications such as down hole and well head equipment, including packers, tubing hangers and safety valves.

Although field data on the down hole equipment are quite encouraging, the lack of information in some cases and contrasting laboratory data, has lead to an increasingly use of more alloyed materials with respect to 9Cr- IMo. Concerning the corrosion behavior in the so called 'sweet' environment, although tested in very aggressive conditions, 16 MPa CO₂ and 80°C, 9Cr-IMo steel is immune to general corrosion. The corrosion rate is high at the initial step but after a few hours it is strongly reduced due to surface enrichment with chromium in the form of an amorphous oxide Ikeda et al. (10) studied the influence of high temperatures in 0.1 MPa CO₂ environment: 9Cr-iMo and 13Cr withstand general corrosion at temperature lower than 150°C and 200°C, respectively. If the pressure of CO₂ is as high as 3.0 MPa, the temperature threshold limit is 100°C for 9Cr-iMo and 150°C for 13Cr. Further Ikeda et al studied the effect of a little amount of H₂S on the corrosion rate of steels with an increasing amount of chromium is a function of temperature at 3.0 MPa of CO₂. 9Cr IMo alloy shows an anomalous behaviour with respect to higher chromium containing alloys.

The oil and gas industries - mainly concerning the exploration, production operations> the field operators normally would like to have uninterrupted supply of oil and gas to the export or processing points. The lines and the component fittings of the lines would undergo material degradations with the varying conditions of the well due to

changes in fluid compositions, so ring of wells over the period, changes in operating conditions of the pressures and temperatures. This material degradation results in the loss of mechanical properties like strength, ductility, impact strength etc; leads to loss of materials, reduction in thickness and at times ultimate failure. Hence it is imperative for the field operators, pipeline engineers, designers to have “Corrosion Awareness” concerning the oil and gas industries in their day to day activities to combat and mitigate corrosion and to ensure smooth and uninterrupted &w of oil and gas to the end users.

2. Materials and Methods

2.1 Apparatus and Reagents Used

The following apparatus and reagents were used for the experiment.

Digital weighing balance, Vanier Caliper, Pyrex beaker, Smoothing file, Sand paper, Iron and smooth brush, Rope (copper), Distilled water, Acidic solution (H_2SO_4), Ethanol, Toluene, Zinc powder, NaOH (Boiling Solution) and Supporting rod

2.2 Source of Experimental Specimen

The Various materials such as carbon steel, mild steel and zinc used in this work were obtained from a steel mill industry. Carbon steel specimen of size 9cm x 3.2cm x1.3cm Mild steel specimens of size 10cm x 1.7cm x0.5cm Zinc specimens of size .5cm x 4.6cm x 0.02cm

2.3 Experimental Procedure

Before the weight loss measurements of all the samples or specimens were tested and polished using sand paper. They were thoroughly washed in distilled water using clean iron brush; a smoothing file and sand paper were used to dress the edges of the specimens to remove rough fillings to avoid accelerated corrosion at the edges. A hole is made at the center of each of the specimen for the insertion of rope. They were degreased in Ethanol, dried in Toluene. They are weighed and stored in plastic bags.

2.4 Initial Weighing of Specimen

The various specimens, tested, washed and dried were taken and each weighed carefully using Digital weighing balance. The readings were taken to decimal places. The weight of each of the specimen were recorded, marked and kept separated to avoid mix up.

2.5 Specimen Arrangement for Corrosion Test

A Total of fifty four Pyrex beakers were used as containers for the corrosion media.

The first set of the eighteen (18) containers contains 0.1 M of H_2SO_4 . Among these containers, the first six (6) were inserted with a sample of the specimen (zinc). Another six (6) containers each were inserted with a sample of specimen carbon steel). The last six (6) containers also inserted with a sample of the specimen mild steel). The second set of the eighteen (18) containers contains 0.2M of H_2SO_4 and the first six (6) of these containers were inserted each with a sample of the specimen (zinc).

Another set of six (6) containers were inserted with a sample of the specimen (carbon steel) Likewise the last set of the Six (6) inserted each with a sample of the specimen (mild steel).

The same to the last set of the eighteen (18) containers containing 0.3M of H_2SO_4 the same procedures were used, the first six (6) were inserted each with zinc, the second sets of the six (6) inserted with carbon steel and the last sets of the six (6) inserted with mild steel. The containers were distinguished by label and the coupons (specimens) were suspended with a supporting rod as shown below for easy immersion removal.

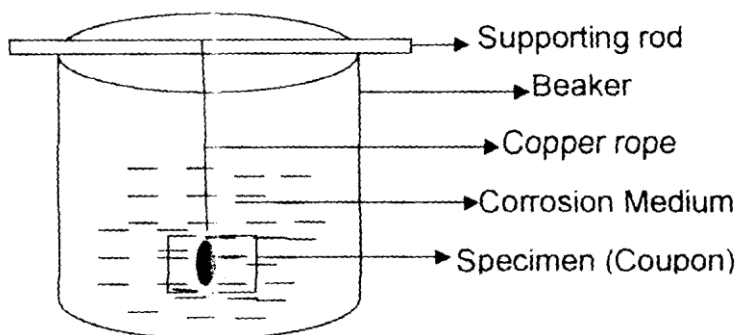


Figure.1 Pyrex beaker used as corrosion medium

The fifty four specimens (coupons) immersed in different concentration of H_2SO_4 were exposed at the Rivers State University of Science and Technology, chemical / petrochemical Engineering laboratory were used for a total of three months 90 days). All the specimens (coupons) were uniformly prepared and exposed on the same day (June, 2011). For every 15 days interval after setting the experiment, the corrosion product were removed by scrubbing the metal surface with a soft brush used boiling solution of 20% NaOH/200g/L of Zinc powder. After the removal of the rust, the coupons were degreased and rinsed with Ethanol, dried with acetone and weighed to determine their weight losses. The weight losses were recorded. Thus, this process is repeated for six times, that is on the 15th day, 30th day, 45th day, 6th day, 75th day and 90th day respectively.

3. Results and Discussion

The results obtained from the research work are presented in Tables and Figures as shown below

Table 1: Corrosion rate of zinc in 0.1M OF H_2SO_4

Sample	Period or (day)	Length (CM)	Width (CM)	Thickness (CM)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (CM/day)
1	15	5.50	4.60	0.02	5.253	5.2529	0.00010	0.0073
2	30	5.50	4.60	0.02	5.256	5.2552	0.00080	0.0291
3	45	5.50	4.60	0.02	5.253	5.2510	0.00200	0.0485
4	60	5.50	4.60	0.02	5.253	5.2340	0.00400	0.0727
5	75	5.50	4.60	0.02	5.253	5.2349	0.0190	0.276
6	90	5.50	4.60	0.02	5.463	5.4349	0.0232	0.281

Table 2: Corrosion rate of zinc in 0.2M OF H₂SO₄

Sample	Period or (day)	Length (CM)	Width (CM)	Thickness (CM)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (CM/day)
1	15	5.50	4.60	0.02	5.253	5.2528	0.00020	0.015
2	30	5.50	4.60	0.02	5.253	5.244	0.00090	0.327
3	45	5.50	4.60	0.02	5.254	5.2325	0.020	0.0485
4	60	5.50	4.60	0.02	5.252	5.222	0.030	0.545
5	75	5.50	4.60	0.02	5.253	5.208	0.045	0.655
6	90	5.50	4.60	0.02	5.252	5.192	0.060	0727

Table 3: Corrosion rate of zinc in 0.3M OF H₂SO₄

Sample	Period or (day)	Length (CM)	Width (CM)	Thickness (CM)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (CM/day)
1	15	5.50	4.60	0.02	5.254	5.2537	0.00030	0.022
2	30	5.50	4.60	0.02	5.253	5.235	0.018	0.655
3	45	5.50	4.60	0.02	5.254	5.207	0.047	1.139
4	60	5.50	4.60	0.02	5.252	5.177	0.075	1.364
5	75	5.50	4.60	0.02	5.253	5.153	0.10	1.457
6	90	5.50	4.60	0.02	5.254	5.124	0.130	1.576

Table 4: Corrosion rate of zinc in 0.4M OF H₂SO₄

Sample	Period or (day)	Length (CM)	Width (CM)	Thickness (CM)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (CM/day)
1	15	9.00	3.2	1.3	83.6	83.5988	0.0012	0.0394
2	30	9.00	3.2	1.3	83.5	83.497	0.003	0.0492
3	45	9.00	3.2	1.3	83.6	83.5895	0.0105	0.1148
4	60	9.00	3.2	1.3	83.6	83.5772	0.0228	0.1869
5	75	9.00	3.2	1.3	83.4	83.3685	0.0315	0.2066
6	90	9.00	3.2	1.3	83.5	83.4514	0.0486	0.2657

Table 5: Corrosion rate of zinc in 0.2M OF H₂SO₄

Sample	Period or (day)	Length (CM)	Width (CM)	Thickness (CM)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (CM/day)
1	15	9.00	3.2	1.3	83.6	83.5476	0.0024	0.0787
2	30	9.00	3.2	1.3	83.5	83.5907	0.0093	0.1525
3	45	9.00	3.2	1.3	83.6	83.449	0.051	0.5578
4	60	9.00	3.2	1.3	83.6	83.510	0.09	0.7381

5	75	9.00	3.2	1.3	83.4	83.334	0.246	1.6139
6	90	9.00	3.2	1.3	83.5	83.282	0.318	1.7276

Table 6: Corrosion rate of zinc in 0.3M OF H₂SO₄

Sample	Period or (day)	Length (CM)	Width (CM)	Thickness (CM)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (CM/day)
1	15	9.00	3.2	1.3	83.6	83.5952	0.0048	0.1575
2	30	9.00	3.2	1.3	83.5	83.6721	0.0279	0.4576
3	45	9.00	3.2	1.3	83.6	83.447	0.153	1.6727
4	60	9.00	3.2	1.3	83.6	83.28	0.27	2.2142
5	75	9.00	3.2	1.3	83.4	83.032	0.468	3.0703
6	90	9.00	3.2	1.3	83.5	82.724	0.876	4.7892

Table 7: Corrosion rate of zinc in 0.1M OF H₂SO₄

Sample	Period or (day)	Length (CM)	Width (CM)	Thickness (CM)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (CM/day)
1	15	10.00	1.7	0.5	45.20	45.1996	0.0004	0.0256
2	30	10.00	1.7	0.5	45.15	45.149	0.001	0.0321
3	45	10.00	1.7	0.5	45.20	45.1965	0.001	0.0748
4	60	10.00	1.7	0.5	45.21	45.2024	0.0035	0.1278
5	75	10.00	1.7	0.5	45.22	45.2095	0.0076	0.1346
6	90	10.00	1.7	0.5	45.20	45.1838	0.0162	0.1731

Table 8: Corrosion rate of zinc in 0.2M OF H₂SO₄

Sample	Period or (day)	Length (CM)	Width (CM)	Thickness (CM)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (CM/day)
1	15	10.00	1.7	0.5	45.21	45.2092	0.0008	0.0513
2	30	10.00	1.7	0.5	45.22	45.2169	0.0031	0.0994
3	45	10.00	1.7	0.5	45.22	45.203	0.0017	0.3633
4	60	10.00	1.7	0.5	45.20	45.17	0.030	0.4808
5	75	10.00	1.7	0.5	45.21	45.128	0.082	1.0414
6	90	10.00	1.7	0.5	45.21	45.104	0.106	1.1327

Table 9: Corrosion rate of zinc in 0.3M OF H₂SO₄

Sample	Period or (day)	Length (CM)	Width (CM)	Thickness (CM)	Initial weight	Final weight	Weight loss (g)	Corrosion rate
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					(g)	(g)		(CM/day)
1	15	10.00	1.7	0.5	45.20	45.1984	0.0016	0.1026
2	30	10.00	1.7	0.5	45.21	45.2007	0.0093	0.02981
3	45	10.00	1.7	0.5	45.20	45.149	0.051	1.0899
4	60	10.00	1.7	0.5	45.20	45.11	0.09	1.4425
5	75	10.00	1.7	0.5	45.22	45.064	0.156	2.0003
6	90	10.00	1.7	0.5	45.21	45.918	0.292	3.1201

Table 10: Showing various C_R of zinc in various H_2SO_4 concentration

Period of exposure	Corrosion rate of 0.1M H_2SO_4	Corrosion rate of 0.2M H_2SO_4	Corrosion rate of 0.3M H_2SO_4
15	0.0073	0.015	0.022
30	0.0291	0.327	0.655
45	0.0485	0.485	1.139
60	0.0727	0.545	1.364
75	0.276	0.655	1.457
90	0.281	0.727	1.576

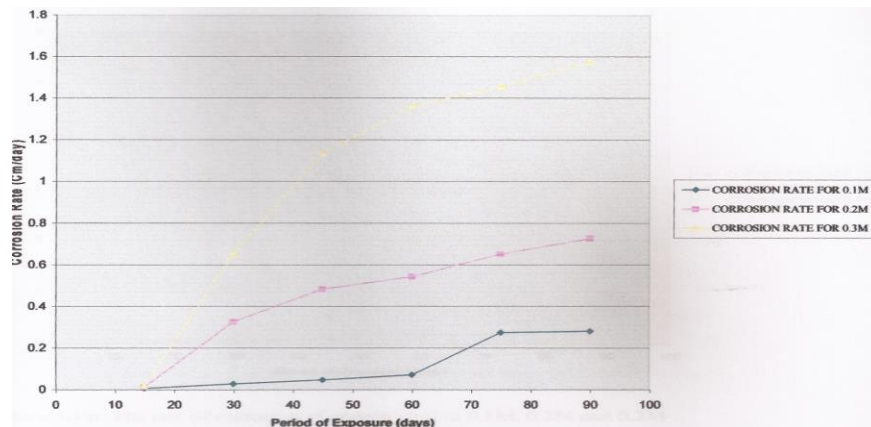


Figure 2: The rate of corrosion of zinc in 0.1M, 0.2M and 0.3M

Table 11: Showing various C_R of carbon steel in various H_2SO_4 concentration

Period of exposure	Corrosion rate of 0.1M H_2SO_4	Corrosion rate of 0.2M H_2SO_4	Corrosion rate of 0.3M H_2SO_4
15	0.0394	0.0787	0.1575
30	0.0492	0.1525	0.4576
45	0.1148	0.5576	1.6727
60	0.1869	0.7381	2.2142

75	0.2066	1.6139	3.0703
90	0.2657	1.7276	4.7892

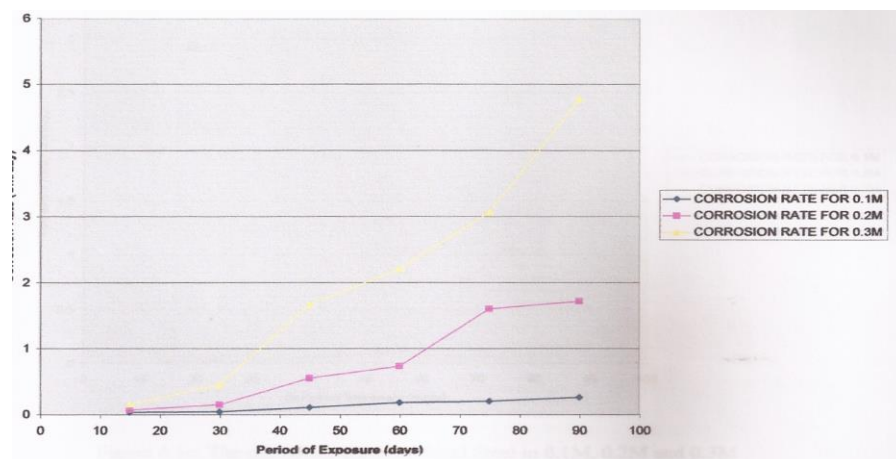


Figure 3: The rate of corrosion of carbon steel in 0.1M, 0.2M and 0.3M

Table 12: Showing various C_R of mild steel in various H_2SO_4 concentration

Period of exposure	Corrosion rate of 0.1M H_2SO_4	Corrosion rate of 0.2M H_2SO_4	Corrosion rate of 0.3M H_2SO_4
15	0.0256	0.0513	0.1026
30	0.0321	0.0994	0.2981
45	0.0748	0.3633	1.0899
60	0.1278	0.4808	1.4425
75	0.1346	1.0514	2.0003
90	0.1731	1.1327	3.1201

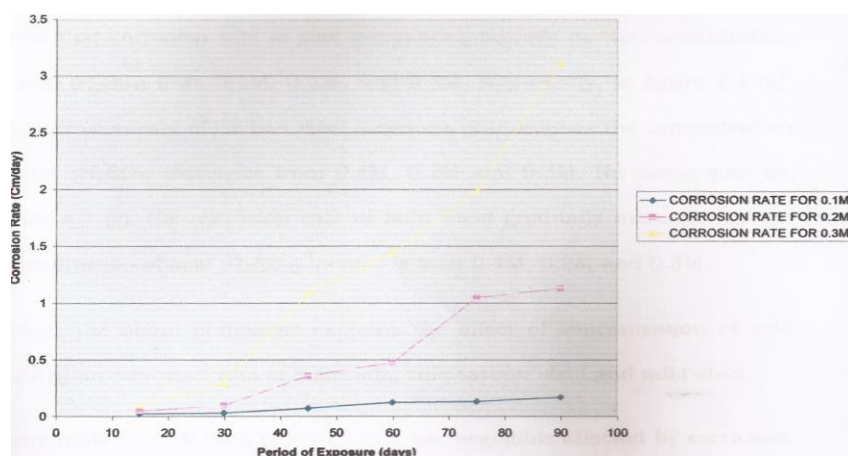


Figure 4: The rate of corrosion of mild steel in 0.1M, 0.2M and 0.3M

From the plot of the graph that was obtained showing corrosion rate against period of exposure in Figure 2, 3 and 4 for the various coupon in my experimental analysis it can be deduced that as the rate of corrosion increases, the period of exposure and concentration of the medium also increases, this explain the effect of concentration of acid (H_2SO_4) on the corrosion rate. Following the graph of figure 2 it is noted that corrosion rate of zinc increases gradually as the concentration of acid (H_2SO_4) from 0. 1M, 0.2M, and 0.3M. Apparently, in Figure 3 the corrosion rate of carbon steel increases gradually as the concentration of acid (H_2SO_4) increase from 0.1M, 0.2M and 0.3M the same goes for figure 4, the corrosion rate of Mild Steel gradually increases as the concentration of acid (H_2SO_4) increases from 0.1M, 0.2M and 0.3M. Hence, the above statement explains the effect of concentration of acid (H_2SO_4) on corrosion rate of materials, zinc carbon steel and mild steel.

Many materials exhibits passivity and are negligible affected by corrosion. The graph obtained above shows characteristic up to a point where there is an increase in corrosion rate as the concentration increases because the concentration has surpassed the passivity. It is noted that, there is a high significant increases in the corrosion rate. Addition of more concentration is required to have a significant effect on corrosion rate due to the increase in cathodic reaction. According to the experimental results, it appears that a high concentration significantly increase the overall general corrosion reaction rate of zinc, mild steel and carbon steel in the presence of H_2SO_4 Figure 2 to Figure 4 depicts the comparison of general corrosion rates with different concentration such as 0.1M, 0.2M and 0.3M of H_2SO_4 for 90 days.

4. Conclusion

This research project provides a comprehensive review of the corrosion performance and application limits of zinc, mild steel and carbon steel in various medium. It also provides basics theory of corrosion, influence of exposure parameters and other atmospheric contaminant and airborne particles. The result of the study of this work has shown that the corrosion rate of the coupons increases as concentration of the medium increases. However, the corrosion of metals caused by acid deposition is mainly a local problem restricted to areas close to pollution sources. Therefore, material scientists have an important role to play in selection of materials because of corrosion accounts for more failures on both a tonnage basis and cost basis than any other type of environmental corrosion.

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