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CORROSION OF STEELS IN WATER AND HYDROGEN SULPHIDE

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ABSTRACT

The importance of carbon steel in the petroleum industries cannot be over emphasized. The carbon steel is susceptible to internal corrosion due to H2S/CO2 environment. The two gasses, in combination with water, defines most of the corrosion problems in the oil and gas production. This research paper is aimed at investigating the corrosion rate of steels in water and H_2S. Eight steel samples (AISI 301, AISI 302, AISI 304, AISI 304L, AISI 308, AISI 309, St 35 and St 37) were used for the experiment. The results obtained showed that the corrosion rate in water saturated H_2S was higher as compared to wet and dry H_2S gases. This was attributed to the aqueous state of water saturated H_2S, which increases the rate of ion dissociation. The high rate of ion dissociation increases the rate of ion penetration into the steel (diffusion rate) and thus the corrosion rate.

Keywords: Hydrogen sulphide, Corrosion rate, Stainless steel. Nickel, Water, Environment.

Contribution/ Originality

The paper primary contribution is the findings that corrosion rate is higher in water saturated hydrogen sulphide as a result of its aqueous state which increases the rate of ion dissociation. Also, stainless steels are more resistance to corrosion than carbon steels.

1. INTRODUCTION

The importance of carbon steels in the petroleum industry cannot be over-emphasized. They are generally used for the transportation of crude oils and gases from offshore to different refining platforms and from there to different destination of their applications. The corrosion of metallic materials especially ferrous alloys in water saturated with H_2S is a complex phenomenon which implies a general attack as well as localised attack [1]. H_2S impacts an acid reaction to water and in many of its chemical properties behaves like a weak dibasic acid from which series of sulphide were derived[4].The carbon steel is susceptible to internal corrosion due to H_2S/CO_2 environment. The two gases, in combination with water, define most of the corrosion problems in oil and gas production. The corrosion of carbon steels in CO_2 environment has received a lot of attention and its mechanisms are generally well defined. Corrosion of carbon steels in H_2S environment on the other hand has not

received much attention, some mechanisms have been proposed but have not been validated [2]. Over the last decades, some researchers [1, 3-5] have carried out rigorous studies on the effects of sulphides on the corrosion behaviour of various steels under different conditions. In the above studies, dissolved free sulphide has been proved to be a very aggressive species for the corrosion of many metals such as iron, steel and copper. However, sulphide can also exhibits strong inhibitor to the iron corrosion under some special conditions due to the formation of protective iron sulphide layer. Ma, et al. [6] It is generally known that sulphides enhances the susceptibility of various steel to corrode in several ways [4] : (i) causing the cathodic hydrogen reduction, (ii) changing the local pH upon oxidation and initiating pitting, (iii) promoting active dissolution, (iv) mediating electron transfer due to their good conductivity and (v) rendering the passive film less proactive. In general, iron sulphides have good conductivity, noble electric potential and low overvoltage for hydrogen evolution with respect to the underlying steel. It has been proposed that the corrosion proceeds through the depolarisation of the cathodic area by adsorption of the polarising H_2 into the crystal lattice of the iron sulphide species or the establishment of an aggressive galvanic cell of iron/iron sulphide Kittel, et al. [1], both of which the result in acceleration of corrosion. There is need for further investigation into the corrosion of carbon steel in H_2S environment [8]. A research study has been carried out to establish a mechanistic model of uniform H_2S corrosion of mild steel, which is able to predict the rate of corrosion with time. Frankel [8] Research work on the theoretical investigation of H_2S corrosion of mild steel has also been carried out [4]. This present study is focused on investigation of the corrosion rate and mechanism of steels in water and H_2S environment.

2. MATERIALS AND METHODS

The study was conducted using eight steel samples. The eight steel samples used were AISI 301, AISI 302, AISI 304, AISI 304L, AISI 308, AISI 309, St 35 and St 37 with chemical composition shown in Table 1.1 was used.

Table-1.1. Chemical composition of the steel (wt%) (www.lincornelectric.com)

Class of Steel	Chemical composition (%)									
	C	Si	Mn	P	Cr	Ni	Mo	S	Ti	Fe
AISI 301	0.014	0.47	1.50	0.036	17.30	12.60	2.75	-	-	65.3
AISI 302	0.017	0.58	1.01	0.026	18.38	10.05	-	0.009	-	69.9
AISI 304	0.019	0.26	1.66	0.028	17.78	9.53	-	0.005	-	70.7
AISI 304L	0.090	0.50	1.25	0.031	17.24	10.45	-	0.015	0.59	69.8
AISI 308	0.045	0.62	1.86	0.040	17.30	10.65	2.15	0.024	0.25	67.1
AISI 309	0.390	0.29	0.61	0.019	17.03	0.14	0.18	0.009	-	81.3
St 35	0.160	0.35	0.40	0.040	-	-	-	0.045	-	99.0
St 37	0.200	0.40	0.26	0.025	-	-	-	0.055	-	99.1

However, the aim of this work is to study id to investigate the corrosion rate of steels in water and H_2S. In achieving this aim, a systematic experimental approach was used in this investigation. In achieving the aim, the steel samples were polished with abrasive papers to remove atmospheric impurities, then cleaned in boiling benzene and further with acetone for five minutes. The sample were

then chemically activated for two minutes in boiling nitro fluoric solution. The samples were then exposed to dry H_2S gas, wet H_2S gas, and water saturated with H_2S. All the tests were conducted under a constant temperature of 25°C so as to remove varying temperature having an effect on the results. Linear polarization method was used in measuring and determining the rate of corrosion on the exposed steel samples. The microscopic examination focuses on the zone of maximum stress of polished samples from the transversal section of the samples.

3. RESULTS AND DISCUSSION

Figure 1.1a and b illustrates the corrosion rate in dry hydrogen sulphide. This shows an increase in the corrosion rate for all the sample. The corrosion rate was slower in AISI 301 and AISI 308 as shown in Figure 1.1a and Figure 1.1a respectively. However, the corrosion rate were higher in in some of the samples as shown in figure 1.1b. Corrosion is also a function of time.
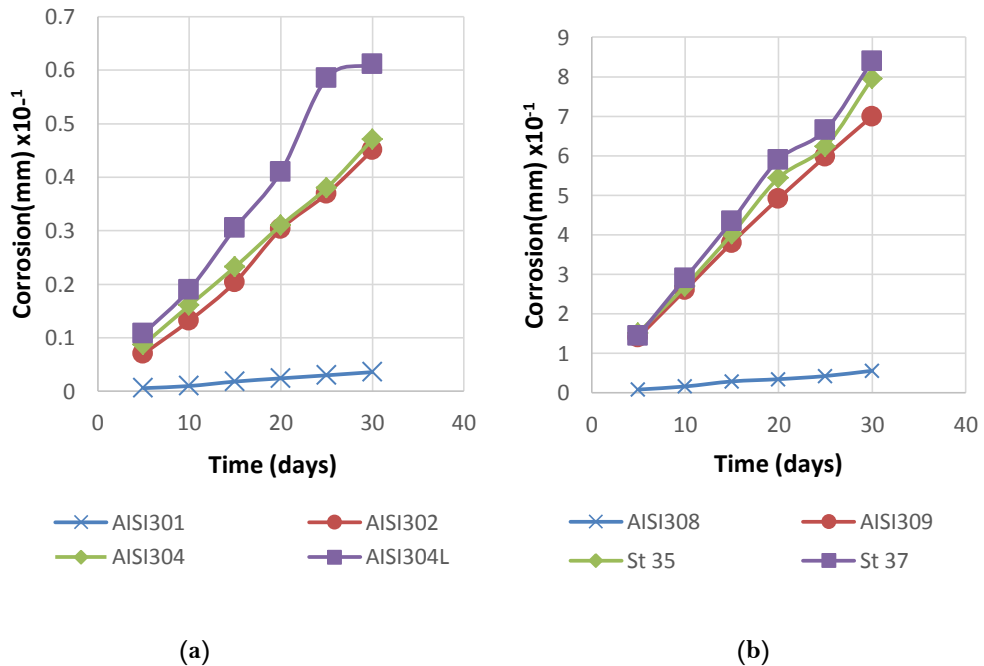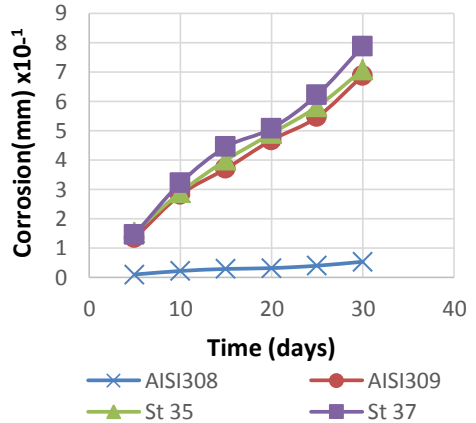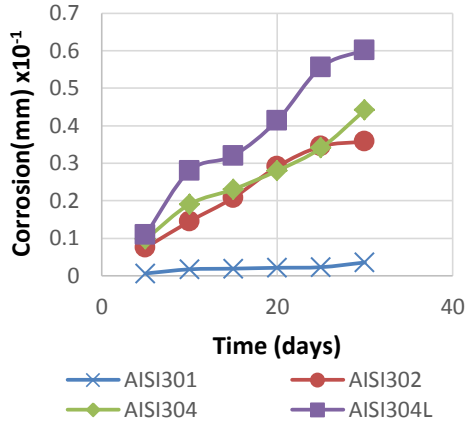

(a)   (b)

Figure-1.1. Corrosion of steel in dry hydrogen Sulphide

The Corrosion of the samples in wet hydrogen Sulphide were shown in Figure 1.2 which shows a similar trend when compared with corrosion in dry hydrogen sulphide.
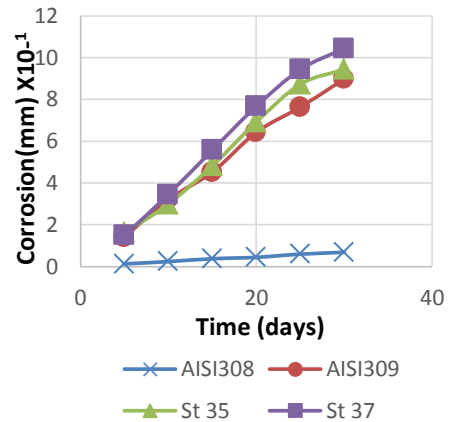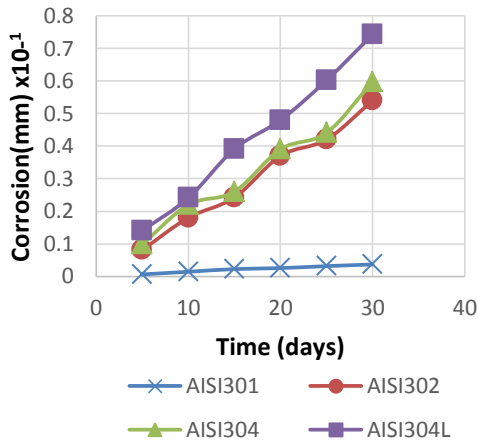
(a)　　　　　　　　　　　　　　　　(b)

Fig-1.2. Corrosion of steel in wet hydrogen Sulphide

Figure-1.3. Illustrates the results of the samples in saturated hydrogen sulphide. This also follows the same trend with a much higher corrosion rate in some of the samples as shown in Figure 1.2b.

(a)　　　　　　　　　　　　　　　　(b)

Fig-1.3. Corrosion of steel in water saturated hydrogen Sulphide

4. DISCUSSION

4.1. Analysis of AISI 301

The corrosion rate increases in each sample for the days. In comparison, the corrosion in wet H S had values higher than that of dry hydrogen sulphide for 5-15 days of testing but dry hydrogen sulphide corrosion rate superseded that of wet H_2S for the next 20-30 days. The initial increase in wet hydrogen sulphide is due to the release of sulphide ions when dissolved in water.
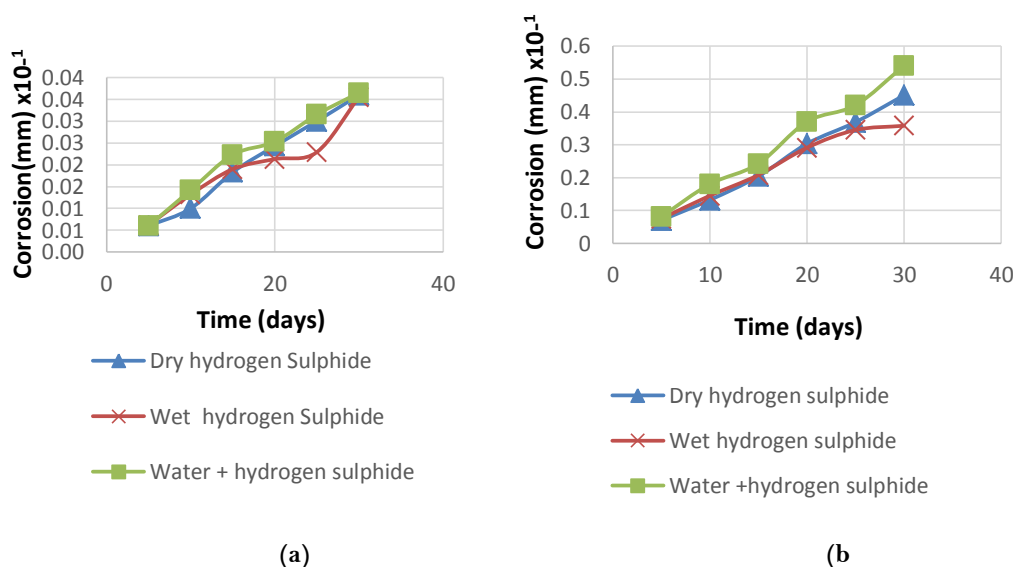
83

(a)   **(b**

Fig-1.4. Corrosion rate in (a) AISI 301 (b) AISI 302

This sulphide ions are reducing agents but since the wet H_2S is not aqueous, the H_2S gas tends to use up the available moisture over the period thereby leading to the decreasing rate over the 2-30 days period. Comparing the conditions of dry hydrogen sulphide, wet H_2S and water –saturated H_2S, the significant increase in corrosion by water-saturated H_2S can be attributed to the aqueous state of the medium thereby increasing the sulphide ion dissociation and effective diffusion of the ions into the steel. The overall increasing rate of corrosion is due to the reducing resistance action of the chromium and nickel elements. This result is in agreement with the findings of Shaojun, et al. [4].

4.2. Analysis of AISI 302

From Figure1.4b above, it can be observed that there is an increase in corrosion rate over the preceding sample. This can be attributed to the reduction in the manganese, nickel and molybdenum content. These act as anti-corrosive agents due to their oxidizing properties Shaojun, et al. [4]. The significant increase in the chromium content accounted for the major resistance to corrosion comparing the data from the dry and wet H_2S medium. The significant increase of the former over the 20-30 days period can be attributed to the kinetic energy of the dry gas. The bombardment in fairly constant thereby allowing for higher corrosion rates. Though the sulphide ions dissociated in wet hydrogen sulphide were more effective within the 5-15 days period, but due to the reduction in the dissociation rate, the reducing ions available were considerably reduced. Though the corrosion rate increased within the days, it can be due to the cumulative effect of previous actions. Comparing the corrosion rate in dry hydrogen sulphide, wet and water-saturated hydrogen sulphide medium; in the latter, the rate of dissociation into ions is considerably increased due to its aqueous state and with considerable reduction in the content of anti-corrosive of the steel. This increase the concentration and

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aids rapid penetration. It increases the energy available to overcome the barriers at the corrosive medium- steel interphase. This allows for effective microstructural and chemical reactions to take place.

4.3. Analysis of AISI 304

Figures 1.5a and b represents the Corrosion rate in (a) AISI 304 (b) AISI 304L. Taking a closer look at the above data in comparism with Figure 1.4b (AISI 302) above, the corrosion rate is higher for AISI 304. Considering the composition of the specimen, AISI 304 has a higher carbon content, a lower chromium and nickel content and a higher manganese content as compared to AISI 302. This above factors account for the higher corrosion rate obtained.
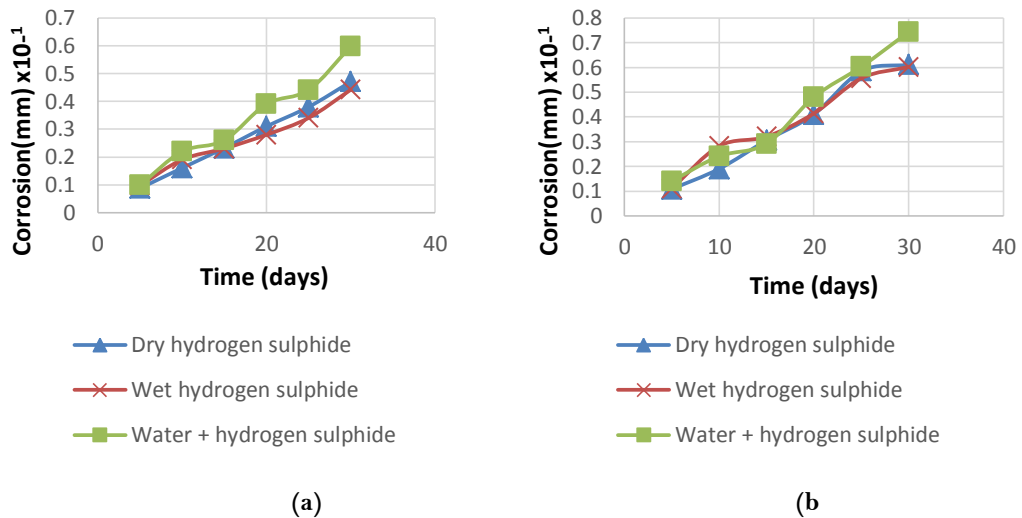

(a)   **(b**

Fig-1.5. Corrosion rate in (a) AISI 304 (b) AISI 304L

The corrosion rate is wet H_2S was higher during the first 10 days and lower for the next 20 days as compared to dry hydrogen sulphide. This can be due to the declining rate of sulphide ions produced and hence the reduction process. The corrosion rate increases for water-saturated hydrogen sulphide. The aqueous state allows for the adsorption of the medium into the steel. This allows for effective diffusion into the macrostructure of the steel. The rate of sulphide ion dissociation is considerably higher. This is supported by other researchers.[1, 3]

4.4. Analysis for AISI 304L

Comparing the data in Figure 1.5b above with Figures 1.4b and 1.5a, a higher corrosion rate is observed. The higher carbon content (Table 1.1), increased silicon and nickel content and reduced chromium content contributed to the higher values. The rate of corrosion increased significantly in wet hydrogen sulphide over dry H_2S for the first 20 days with a corresponding decrease for the

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remaining 10 days. These can be attributed to the increasing resistance to corrosion after reduction in sulphide ion penetration with time in wet H_2S. The gaseous H_2S maintain a regular bombardment of the specimen surface giving a fairly constant increment. The moisture content in wet $-H_2S$ is a determining factor in the quantity of sulphide ions produced. All the medium displayed an increase in corrosion over the days. The rate of corrosion in water saturated H_2S is higher compared to wet H_2S and dry H_2S. The saturation state which allows for increased penetration must have increased the corrosion rate. There is an increase of about 20% and 23% for water-saturated H_2S compared to dry H_2S and wet H_2S respectively.

4.5. Analysis of AISI 308 Steel

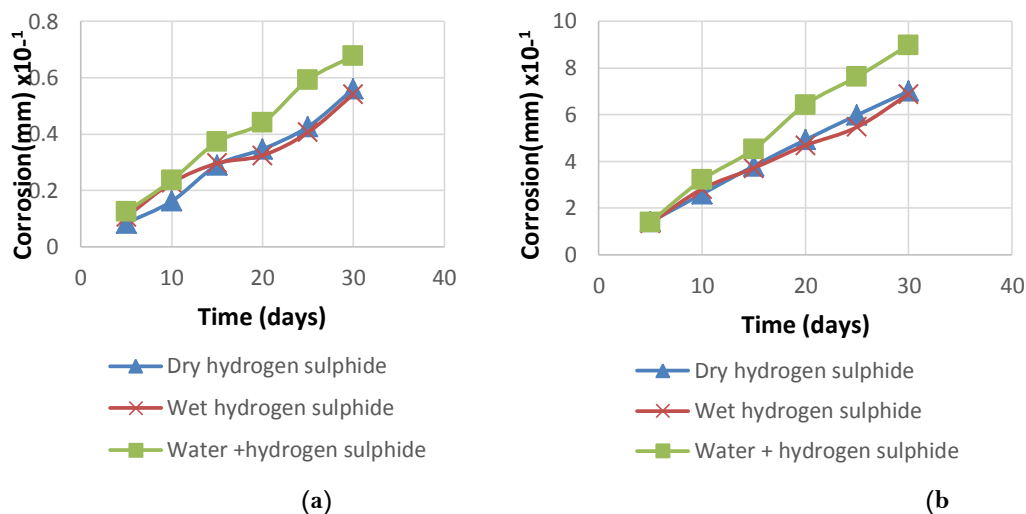There was a gradual increase in corrosion rate for each medium as shown in Figure 1.6a.

Fig-1.6. Corrosion rate in (a) AISI 308 (b) AISI 309

When compares with AISI 304L, the composition of the steel showed that the nickel, chromium, manganese and molybdenum content were increased. The lower corrosion rate obtained can be ascribed to the anti-corrosive properties of these elements. The elements acted as inhibitors to the penetration of corrosive materials into the structure of the steel which can lead to metal disintegration. During the first 10 days, the corrosion rate was higher in wet H_2S, slightly different for the 15th day and lower for the remaining days. The reducing action of the limited sulphide ions in wet H_2S is further hampered by the resistance of the anti-corrosive elements over the increasing period of time. The higher values in water saturated H_2S is due to the continuous dissociation of hydrogen and sulphide ions which aid gradual and consistent penetration over the time. [5,9]

4.6. Analysis of AISI 309 Steel

Comparing Figure 1.6b with previous values, there were really significant increases in the corrosion rate. Considering the composition of the steel, chromium and nickel content were 1.03% and

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0.14% respectively. These elements from the main anti-corrosive in the metal composition. Their reduction in quantity is an indication of reducing resistance to corrosion by the steel. Kittel, et al. [1] The corrosion increases over the days due to the rapid penetration and diffusion by the hydrogen and sulphide ions. The energy barrier to be overcome at the interface is lower. The increased carbon content of the steel also contributes to the corrosion process. The corrosion rate was rapid for each medium showing the weak protective action on the surface. The corrosion rate is observed to be higher in water-saturated H_2S as compared to dry and wet hydrogen sulphide. This can be due to its aqueous and its faster diffusion rate. [1]

4.7. Analysis for the Carbon Steel St 35
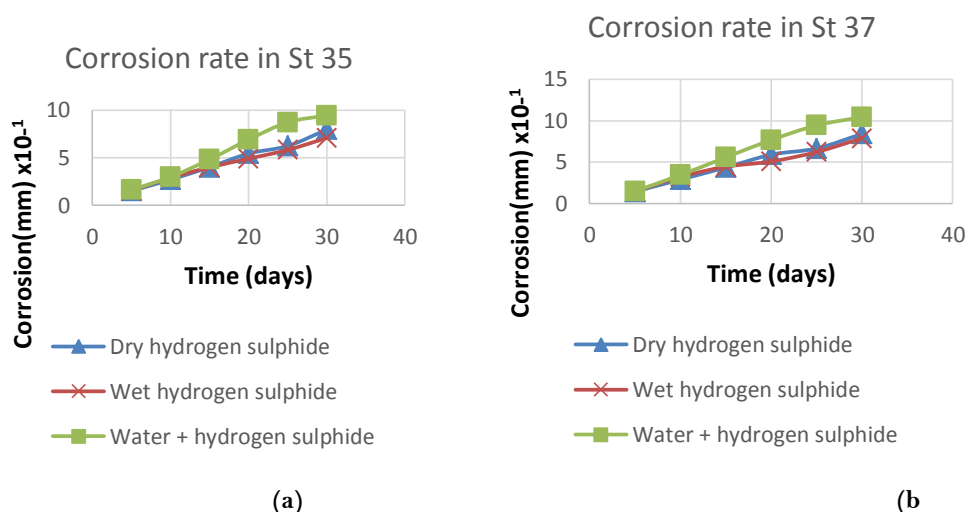

(a) **(b**

Fig-1.7. Corrosion rate in (a) St 35 (b) St 37

Considering Figure 1.7a and with reference to the composition of the steel, the major anti corrosive agents (nickel and chromium) are absent. The absence of these elements can be adduced as the reason for the higher corrosion rate although the manganese content could have offered only a little resistance to the corrosion. These allowed for the reduction in the energy barrier to be overcome at the interphase. Comparing with stainless steels, it can be observed that stainless steels are more resistance to corrosion than carbon steel due to the protective film by nickel and chromium elements. There was an increase of about 34% in water- saturated hydrogen sulphide over wet-H2S. Overall, the corrosion rate increased steadily over the days in each medium.

4.8. Analysis for the Carbon Steel St 37

The corrosion rate over the days in each case as shown in the water saturated H_2S which were on the increase over the wet H_2S and dry H_2S respectively. In the composition, there was a significant increase in the carbon content and decrease in the molybdenum content. Chromium and nickel elements were absent which really shows the underlying resistance of the carbon steel to corrosive

action. The action of the anticorrosive serves to emphasize their action in corrosion control as evidenced by the protective film which they form on stainless steels.

5. CONCLUSION

The outcome of this study provides an understanding into the corrosion rate of steels in water and H_2S. From the results and analysis, it can be inferred that:

1) The corrosion rate is higher in water saturated hydrogen sulphide as a result of its aqueous state which increases the rate of ion dissociation. These increase in ion dissociation increased the quantity of ion penetrating into the steel and the rate of diffusion and hence the corrosion rate.

2) Stainless steels are more resistance to corrosion than carbon steels. The lower corrosion rate is as a result of the protective action of chromium and nickel elements in their composition.

3) The action of reducing agents i.e. sulphide ions was responsible for the steel corrosion. The energy required to overcome the barrier at the interface varied with the metallurgical composition of the steel and this had an overbearing effect on the corrosion rate.

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