CORROSION CHARACTERISTICS OF MILD STEEL AND DUCTILE CAST IRON EXPOSED TO DIFFERENT MEDIA

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ABSTRACT

The corrosion characteristics and mechanical properties of a low carbon steel and ductile cast iron exposed to selected media have been investigated and compared.

Measurement of the corrosion rates of the materials exposed to seawater, HCl solution,H_2SO_4 solution, and riverine soil were carried out using the weight loss technique. The results of this study show that the environments studied are capable of causing corrosion and mechanical failure of both mild steel and ductile cast iron although at different rates and levels. The corrosion rate is found to be dependent on the nature and concentration of the aggressive ions in the environment.

INTRODUCTION

Corrosion in oil and gas operations should be seen as an economic as well as engineering problem. The cost of corrosion to the industry worldwide is staggering. A figure of 300 billion US dollar in one year was mentioned for U.S.A. alone in a 1998 study. It was estimated that 45 percent of this amount of about 135 billion US dollar was avoidable through existing corrosion control technology (NACE, 2002).

The key economic sector of Nigeria is oil and gas. This oil and gas sector amounts to 85 percent of her total revenue. The products of this petroleum are being transported from one state to the other via pipelines which are made up of metals. These pipelines pass through oceans, rivers, underground or surface of the soil in urban and rural areas to their respective destinations. The deterioration of these pipelines as a result of corrosion causes a lot of havoc to the country by oil leakage which subsequently leads to the bursting of the pipelines thereby contaminating the products being conveyed by the pipelines and consequently reducing their economic value (Jimoh, 2002).

The enormity of the corrosion problem is due to the fact that all metals tend to revert back to one of the forms in which they were originally found in the earth. The beneficiation of an ore yields a metal which is less stable thermodynamically than the original oxide, sulphide, carbonate, or other types of ore. As a result, the decrease in free energy attending the change back to the original form represents the continuous driving force of corrosion (Callister, 1997).

Failure of materials in service can be attributed to poor design, poor material selection, service conditions, operators faults and poorly controlled environment. The main stages in failure investigation are investigation at site of failure (which include taking photos making sketches and collection of samples), assembling of records for office study (to evaluate collapse load, ascertain possible cause of failure and establish material strength), carrying out of laboratory tests and analysis of failure(Fontana, 1987).

Most of the pipeline failures, that have occurred were caused by corrosion, mechanical failures and artificial failure (sabotage). Some pipeline failures which occur in muddy waters (swampy areas) are caused by secretion by microorganisms while others are by chemical attack (Pandey, 1998). The micro-organisms attack the protective coatings on pipes thereby exposing the pipes to chemical attack by the corrosive medium-salt water. Studies have shown that salt water contains chloride ions, which cause corrosion of steel (Askeland, 1989, Jimoh, 2002, Okpala, 1997). It is known that chloride ions are not consumed in the production process in any Industrial process hence, they act as catalysts and their harmful effects, once started, do not diminish with time (Kaminetzky, 1991). Similarly, failure analysis of pipes, which failed in seawater show those failures were due to chemical attack and incorrect appreciation of the service environment (Fontana 1987).

Carbon steel is probably used for at least 80 percent of all refinery equipment and piping. Like cast iron, it is the cheapest and most readily available of common refinery metals (George, 1999). For these reasons, every effort is made to use carbon steel, even if process changes are required to get satisfactory service out of carbon steel. For example, process temperatures can be decreased, hydrocarbon streams dried up (by addition of water settling equipment), or additive can be injected to reduce potential corrosion problems with carbon steel, carbon steel has fairly good resistance to aqueous sulphide corrosion because of protective iron sulphide film found

(Bringham, 1994). In the refinery, most piping, heat exchanger shells, storage tank and all structures are generally fabricated from carbon steel (Colengelo, 1994). The objective of this work is to investigate the effects and rate of corrosion of mild steel and ductile cast iron in sulphuric acid, hydrochloric acid, seawater and marine soil.

MATERIALS AND METHODS

Materials and Preparation

The pipe samples (mild steel and ductile cast iron) were obtained from the NNPC and the average total geometric surface area used was $20cm^2$.

Chemical Composition

This was done at the Quality Control Laboratory, Universal Steel Limited, Ikeja, Lagos, Nigeria.

This was done to determine the elements present and their percentages in the mild steel and ductile cast iron pipes. A 20mm x 30mm piece of standard pipe sample was made. A pin-to-pin spark was impressed on the sample using a solid technique optical emissions spectrograph. The reading was taken from a direct computerized spectrometer. The procedure was repeated four times and the mean value was obtained. The result of the compositional analysis is presented in Table 1.

Test Media

i. $1MH_2SO_4$,
ii. 1MHCl,
iii. Marine soil and
iv. Sea water

Preparation of Test Specimens

The cylindrical mild steel and ductile iron (0.70cm dia) were cut into a number of test specimens of total average geometrical area of $20cm^2$. The two surface ends of each of the specimens were ground with silicon carbide abrasive papers of 240, 320, 400 and 600 grits. They were then polished with $1.0\mu m$ diamond paste, washed with distilled water, rinsed with methyl alcohol, dried and stored in a desiccator for further weight-loss tests.

Weight-loss experiment

The experimental procedure adopted for this study is the total immersion test method. This method was adopted because according to Okpala (1997), it has good reproducibility of result. Weighed test pieces were separately and fully immersed in each of the four test media contained in separate 100ml beakers for a period of 28 days at embient temperatures. Each of the test specimens was taken out every three days, washed with distilled water, rinsed with acetone, dried and re-weighed and the weight recorded was the average of two reading. This procedure was repeated at various intervals over the 648 hours the experiment lasted. Plots of corrosion rate (calculated) versus exposure time (hours) were made (Fig. 1-4).

The respective loss of each of the samples within the immersion periods was then determined and the corresponding corrosion rates in millimeter per year (mm/yr) were calculated according to the relationship suggested by Hucinska and Glowacka (1993) and Callister (1997) :

The corrosion rate (mm/yr) = KW / DAT ...(1)

Where:

K	=	87.6
W	=	weight loss (g)
D	=	Density of specimen (g/cm^3)
A	=	Area of Specimen (cm^2)
T	=	Time of immersion (hours)

The results of the corrosion rate (mm/yr) variation with immersion time are presented in Figs. 1 – 4. The corrosion rate of samples immersed in the various media was found to generally decrease sharply with immersion time in the first nine days after which the rate of decrease became very slow, tending to zero with immersion time. This could be due to the fact that in the first few days, the film formed on the surface of the specimen has not been stabilized while in the later days the presence of corrosion products enhanced the formation of the layer of oxide on the surface of the samples which did not allow diffusion of metal ions and this inhibited the anodic reaction which involves metal dissolution.

The reason for the different behaviour between mild steel and ductile iron could be that within this period (day 0-day10) the passivating oxide formation is being initiated and the complete formation is dependent on the peculiarity of the immediate environment where the sample is immersed. However, as the immersion time proceeds to the eleventh day stabilization of the oxide later goes into completion and hence mild steel with lower chromium content and Nickel content corrode faster than ductile cast iron with higher values respectively.

DISCUSSION

It was found that mild steel has higher weight and density than ductile cast iron of the same volume, this is probably due to the higher percentage of carbon and silicon in ductile iron than mild steel. The difference in weight is about 9.1%.

The experiments revealed that, there are two major corrosion patterns; the adherent and non-adherent corrosion products.

The decreasing trend of corrosion within the first 500 hours (21 days) of exposure can be explained from the standpoint of metallurgy. The corrosion rate was initially high because of stresses built up in the samples during the course of their preparation through cutting, filing and grinding with emery papers. After relieving such stresses, the corrosion is observed to stabilize because at this stage the corrosion process is dependent on the electric potential of the steels and the nature of the environment is the vicinity of the material. This is in agreement with the report of El-sayed, (1986).

Corrosion in 1MHCl Environment

It is evident that the intrusion of Cl^- ions must have been responsible for the corrosion of both mild steel and ductile iron in this environment. What needs to be explained however is the relatively higher corrosion rates of ductile iron in the 1MHCl compared to that obtained in the case of mild steel. It has been reported (Pandey and Banerjee (1998), that the aggressiveness of an environment significantly affects the tendency or otherwise for the passivity to breakdown around a given material. It is known fact that the nature of additives in materials determine their corrosion behaviour in a given environment. (Umoru et al, 2003). Figure 4 shows that mild steel corrosion is lower in HCl environment than that of ductile iron.

Corrosion in Seawater Environment

The corrosion of the specimens in seawater must have been as a result of intrusion of the inherently aggressive chloride ions (Cl^-), which are capable of destroying the passivating film around the steel and ductile iron. (Pandey and Banerjee 1998, and El-Sayed, 1986).

Corrosion in 1MH$_2$SO$_4$ Environment

It has been established that sulphate ions from sulphuric acid play a vital role in facilitating hydrogen sulphide corrosion due to its aggressive nature. The increase in corrosion rate on ductile cast iron is due to accelerated attack on it by the sulphide ions more than that recorded for mild steel in the same environment. Consequently the corrosion resistance of ductile cast iron in H_2SO_4 environment is more than that of a mild steel (figure 1). This is in agreement with the findings of El-Sayed (1986).

Corrosion in Marine Soil Environment

Studies on corrosivity show that the nature of soil determines the corrosion resistance of materials buried in them (Fontana, 1987; Brubaker, 1986 and Brigham, 1994). Marine soil has been reported to have great adverse effect on the metallic pipes buried in them. This is due to the chemical composition of the soil and its corrosivity potential. Ductile cast iron is seen to have higher corrosion rate in marine soil than mild steel, this is due to the fact that ductile cast iron has less corrosion resistance than mild steel in aggressive environment such as marine soil because of the lower pH value of the soil. This result is in agreement to what is reported by Pandey, (1998).

Conclusion

The results of this study has shown that the $1MH_2SO_4$, 1MHCl, Seawater and Marine soil environments are capable of causing corrosion although at different rates and levels on the mild steel and ductile iron investigated. It is also conclusive from the analysis of the results that the breakdown of passivity around steel and ductile iron that eventually leads to their corrosion is dependent on the nature and concentration of aggressive ions in the environment. Finally, it also follows from the results that the ductile iron is more resistance to corrosion than mild steel iron in 1M H_2SO_4 environment and mild steel is more resistant to corrosion than ductile cast iron in the other environments considered. The mechanical properties in table 4 show this fact clearly.

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Table 1: Composition of Test Materials

Element	C	Si	Mn	P	S	Cu	Cr	Ni	Fe
Mild steel	0.22	0.25	0.5	0.65	0.5	0.1	0.1	0.1	Bal.
Ductile cast iron	3.5	2.5	0.8	0.6	0.22	0.1	0.1	0.1	Bal

RESULTS AND DISCUSSION

Table 2: Results of Corrosion Test in Various Media

Medium	**72hr**	**144hr**	**312hrs**	**480hrs**	**648hrs**
			1MH_2SO_4		
Mild steel(c.r)	0.00198	0.001656	0.001524	0.0014986	0.001397
Ductile iron(c.r)	0.0026924	0.0022352	0.001524	0.001372	0.001194
			1MHCl		
mild steel(c.r)	0.009398	0.006096	0.005588	0.005334	0.00508
ductile iron(c.r)	0.0012192	0.007112	0.006858	0.006604	0.005842
			Marine soil		
mild steel(c.r)	0.00127	0.0012192	0.00063	0.0004318	0.0004064
ductile iron(c.r)	0.010668	0.009652	0.007366	0.00365	0.005334
			Seawater		
mild steel(c.r)	0.015494	0.01244	0.00889	0.008382	0.00762
ductile iron(c.r)	0.044064	0.0254	0.0127	0.01168	0.008636

c.r =corrosion rate (mm/yr)

Table 3: Corrosion products

Medium	Adherent corrosion product	Non-adherent corrosion product
Sulphuric acid	$FeSO_4$ (black)	Fe_2O_3 H_2O (reddish brown)
Hydrochloric acid	$FeCl_2$ (black)	"
Seawater	Probably Fe_3O_4 (pale red)	"
Marine soil	Fe_3O_4 (pale red	"

Table 4. MECHANICAL PROPERTIES SPECIMENS

Sample	Hardness (Brinell)	Impact strength Joules	Max strength n/mm^2
As received (Mild Steel)	261	30	450
As received (ductile cast iron)	210	23	236
Mild steel + HCl	251	22	420
Mild steel + H2SO4	252	23	410
Mild steel + sea water	240	26	359
Mild steel + marine soil	248	27	360
Ductile cast iron + HCl	195	19.5	220
Ductile cast iron + H_2 S04	183	19	210
Ductile cast iron + sea water	190	16	190
Ductile cast iron + marine soil	180	17	180

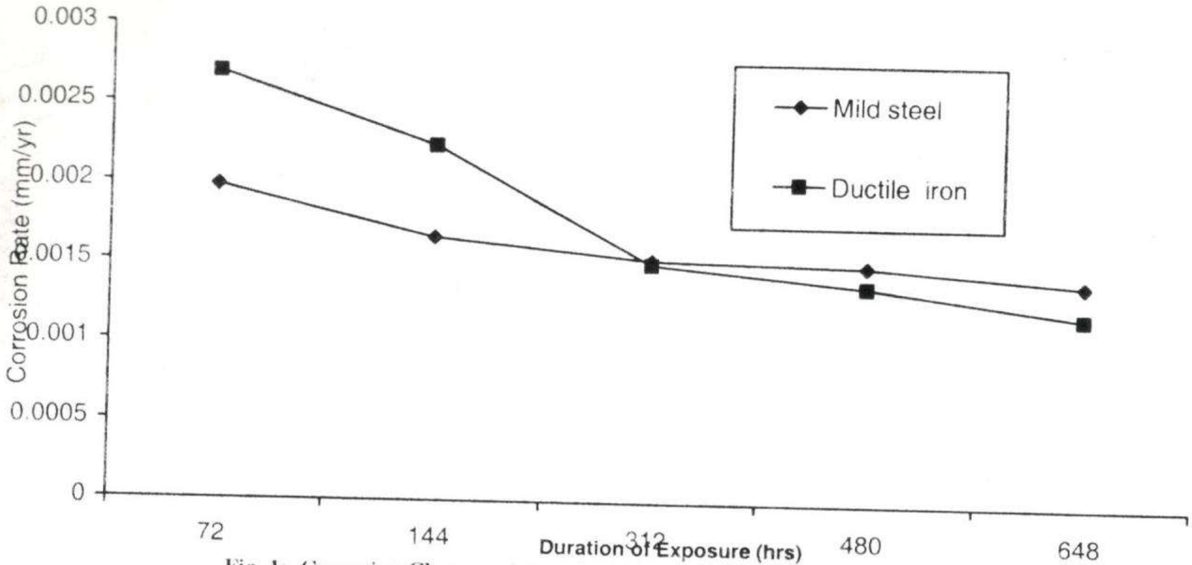

Fig. 1: Corrosion Characteristics of mild steel and ductile iron in 1MH_2SO_4at 30^{0}C

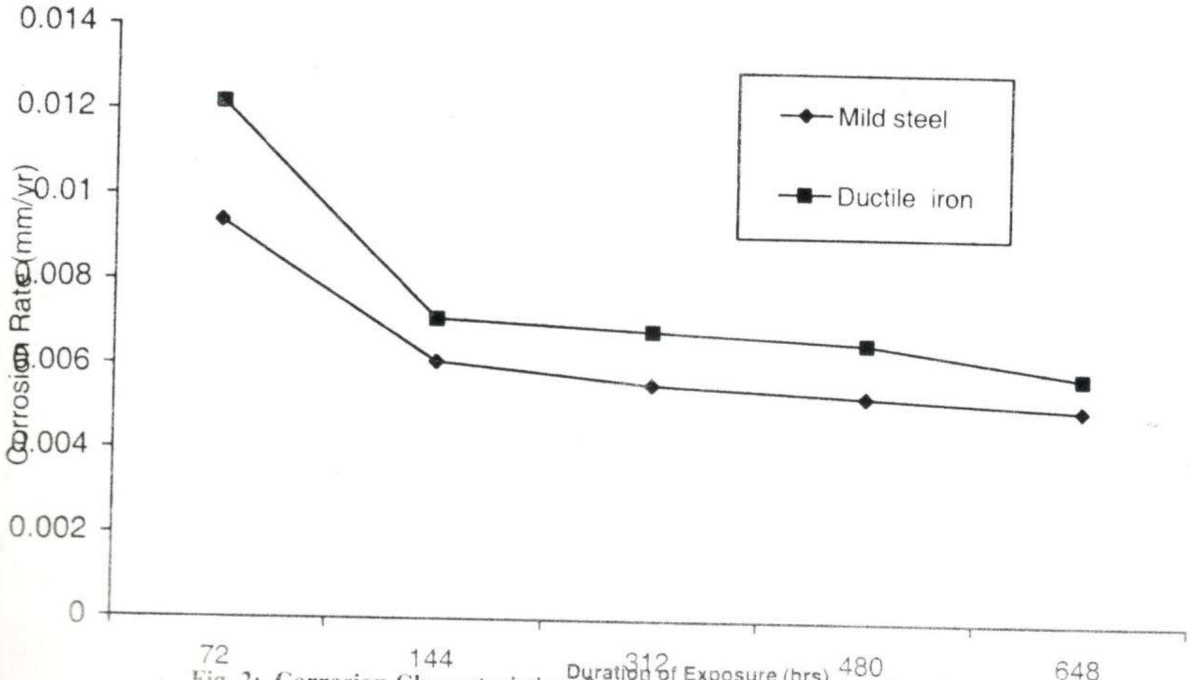

Fig. 2: Corrosion Characteristics of mild steel and ductile iron in 1MHCl at 30^{0}C